FIRE AND MATERIALS, VOL. 11, 55–70 (1987)

A Literature Review of the Chemical Nature and Toxicity of the Decomposition Products of Polyethylenes

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The literature on polyethylenes has been reviewed with an emphasis on the identification of gaseous products generated under various thermal decomposition conditions and the toxicity of those products. This review is limited to publications in English through 1984. The analytical chemical studies of the thermal decomposition products generated under vacuum, inert and oxidative experimental conditions are described. In oxidative atmospheres, which most closely simulate real fire conditions, carbon monoxide (CO) was found to be the predominant toxicant. Acrolein was another toxicant often noted in these reviewed studies. More acrolein was generated under non-flaming than under flaming conditions. Results from seven different test procedures were considered in assessing the acute inhalation toxicity of combustion products from various polyethylene formulations. The combustion products generated from the polyethylenes studied in the non-flaming mode appeared to be slightly more toxic than those produced in the flaming mode. In the non-flaming mode the LC_{50} values ranged from 5 to 75 mg l^{-1}. In the flaming mode the LC_{50} values ranged from 31 to 51 mg l^{-1}. The toxicity of the degradation products of polyethylenes appears to be similar to that found for other common materials designed for the same end uses.

Keywords: Combustion products, literature reviews, polyethylenes, thermal decomposition, toxicity.

INTRODUCTION

Polyethylene has been in commercial production for over forty years. With sales of about 6.25×10^6 metric tons in 1983, polyethylenes compose the largest fraction of plastic materials produced.[1] Typical uses of polyethylenes include household goods (bottles, dishes and toys), packaging materials and coatings for tubing and cables in the building and electrical industries. This report reviews the literature on polyethylene published in English through 1984 with special emphasis on the gaseous products generated under various thermal decomposition conditions and the toxicity of those products.

Polyethylenes are thermoplastic materials that are produced primarily by the catalytic polymerization of ethylene gas (C_2H_4) at elevated temperatures (T) and pressures (P),

$$\underset{\text{ethylene}}{n(CH_2=CH_2)} \xrightarrow[T,P]{\text{catalyst}} \underset{\text{polyethylene}}{+CH_2-CH_2+_n} \quad (1)$$

The polyethylene molecules usually contain branches of various lengths. Of all the hydrocarbon polymers, polyethylene has the simplest structure and the highest ratio of hydrogen to carbon in its backbone. Most commercial polyethylene formulations also contain additives, such as stabilizers, antioxidants, crosslinking agents, slip and antiblock agents, and fire retardants.

The molecular structure, molecular weight distribution and density will differ in various polyethylenes depending on the manufacturing process conditions. Low-density polyethylene (LDPE) is of low crystallinity ($<60\%$) and has a density in the range of 0.91–0.94 g cm^{-3} and a molecular weight of about 4×10^5 g mol^{-1}. High-density polyethylene (HDPE) is of high crystallinity ($\sim 90\%$) and has a density in the range of 0.94–0.95 g cm^{-3} and a molecular weight up to about 3×10^6 g mol^{-1}. LDPE molecules are highly branched in structure and may contain up to 30 branches with as many as 10 carbon atoms each. HDPE molecules are almost linear in structure with only few short branches. HDPE is more thermostable than LDPE since secondary carbon–hydrogen bonds are stronger than tertiary carbon–hydrogen bonds.[2,3]

THERMAL DECOMPOSITION

The combustion of polyethylenes can produce many gaseous products, the nature of which depends mainly on the external conditions such as temperature and oxygen availability. The final products formed during complete combustion of polyethylenes are carbon dioxide (CO_2) and water (H_2O). Under incomplete flaming or non-flaming combustion conditions many other low-molecular weight hydrocarbons and oxygenated compounds (e.g. carbon monoxide (CO), alcohols, aldehydes, ketones and esters) are also generated. The combustion products that have been identified in the literature reviewed for this report are presented in Table 1.

As all the C–C bonds in polyethylenes are of the same strength (except those in the terminal positions or at the sites where branching occurs), polyethylenes decompose mostly by a random-chain scission type mechanism

Received 1 February 1986
Accepted 20 October 1986

Table 1. **Thermal degradation products produced from polyethylenes**

Compound	Atmosphere	Reference
Acetaldehyde	O	10, 19
Acetic acid	O	10, 18, 19
Acetone	O	10, 19
Acetylene	O, I	8
Acrolein	O	10, 18, 19, 24, 26
Acrylic acid	O	6, 10
Anthracene	O	20, 21
Benzene	O, I	6, 8, 9, 10, 16
Benzoanthracene	O	20, 21
2, 13-Benzofluoranthene	O	21
1, 2-Benzofluorene	O	21
2, 3-Benzofluorene	O	21
Benzo(a)pyrene	O, I	11, 20
Benzo(c)pyrene	O	20
Butadiene	O, I	6, 7
Butanal	O	6, 10
Butane	O, I, V	4, 5, 6, 7, 10, 17
Butene	O, I	4, 6, 10
1-Butene	O, I, V	5, 7, 9, 10, 17
2-Butene, cis	O, V	5, 17
2-Butene, trans	O, V	5, 17
Butyric acid	O	10
Butyrolactone	O	10
Caproic acid	O	10
Carbon dioxide	O, I	6, 8, 9, 10, 14, 15, 17, 24, 26, 30, 32, 33, 34, 47, 53, 54, 55
Carbon monoxide	O, I	8, 9, 13, 14, 15, 17, 24, 26, 30, 32, 33, 34, 39, 40, 44, 45, 47, 51, 52, 53, 54, 55, 56, 57, 58
Chrysene	O	21
Crotonic acid	O	10
Cyclohexane	O, I	6, 9
Cyclohexene	O	6
Cyclopropane	O	10
Decanal	O	6
Decane	O, I	6, 7
1-Decene	O, I	6, 7, 10
2, 2-Dimethylbutane	I	9
2, 2-Dimethyl-cis-3-hexene	I	9
3, 3-Dimethylheptane	I	10
2, 4-Dimethylhexane	I	9, 10
2, 3-Dimethyl-l-hexene	I	9
2, 3-Dimethylpentane	I	9
Dodecanal	O	6
Dodecane	O, I	6
1-Dodecene	O, I	6, 10
Epoxide	O	6
Ethane	O, I, V	4, 5, 7, 9, 10, 16, 17, 19, 47, 53, 55
Ethanol	O	10
Ethyl benzene	O, I	6
Ethyl cyclopentene	I	6
Ethylene	O, I, V	4, 5, 7, 8, 9, 10, 16, 17 19, 47, 53, 55
2-Ethyl-l-hexene	I	10
Fluoranthene	O	20, 21
Formaldehyde	O	10, 18
Formic acid	O	10, 18
Furan	O	10
Heptadecane	I	6
1-Heptadecene	O, I	6
1, 3-Heptadiene	I	9
1, 6-Heptadiene	I	9
Heptanal	O	6
Heptane	O, I	4, 6, 7, 9, 10
2-Heptanone	O	10
Heptene	O, I	4, 20
1-Heptene	O, I	6, 7, 9, 10
Hexadecane	O, I	6
1-Hexadecene	O, I	6
Hexadiene	I	4
1, 3-Hexadiene	I	9
1, 5-Hexadiene	I	9
Hexanal	O	6
Hexane	O, I, V	4, 5, 6, 7, 9, 10
2-Hexanone	O	10
Hexene	O, I	4, 10
1-Hexene	O, I, V	5, 6, 7, 9, 10, 17
2-Hexene	O	17
3-Hexene	I	9
Hydrogen chloride	O	16
Hydroperoxide	O	10
Hydroxyvaleric acid	O	10
Isobutene	I	7
Isobutanal	O	10
Isobutylene	V	5
Isodecane	I	7
Isononane	I	7
Isooctane	I	7
Isovaleric acid	O	10
Methane	O, I, V	5, 7, 8, 9, 16, 17, 39, 40, 44, 45, 47, 53, 55, 56, 58
Methanol	O	10
2-Methylbutane	V	5
2-Methyl-1-butene	V	5
3-Methyl-1-butene	I, V	5, 9
Methylcyclohexane	I	9
Methylcyclohexene	I	10
Methylcyclopentene	O	6
4, 5-Methylene phenanthrene	O	21
2-Methyl-4-ethylhexane	I	10
Methyl ethyl ketone	O	10, 19
2-Methyl-3-ethylpentane	I	9
2-Methyl-3-ethyl-2-pentene	I	9
2-Methylheptane	I	9
2-Methyl-1-heptene	I	9
2-Methyl-3-heptene	I	9
3-Methyl-1-heptene	I	10
2-Methyl-1-hexene	I	9
3-Methyl-1-hexene	I	9
4-Methyl-2-hexene	I	9
Methyl-4, 5-methylene phenanthrene	O	21
2-Methylpentane	V	5
2-Methyl-1-pentene	V	5
2-Methyl-2-pentene	I	9
4-Methyl-1-pentene	I, V	5, 9
Methyl-phenanthrene	O	21
2-Methylpropane	V	5
2-Methyl-2-propenal	O	10
2-Methylpropene	V	5
Methylpyrene	O	21
Methyl vinyl ketone	O	10
1, 3-Nonadiene	I	9
Nonanal	O	6
Nonane	O, I	6, 7, 9, 10
1-Nonene	O, I	6, 7, 9, 10

Table 1. (*Contd.*)

Compound	Atmosphere	Reference
Octadecane	I	6
1-Octadecene	O, I	6
1, 3-Octadiene	O	9
Octanal	O	6
Octane	O, I	6, 7, 9, 10
Octene	O	20
1-Octene	O, I	6, 7, 9, 10
Pentadecanal	O	6
Pentadecane	O, I	6
1-Pentadecene	O, I	6
Pentadiene	I	4
1, 3-Pentadiene	I, V	5, 9
1, 4-Pentadiene	I, V	5, 9
Pentanal	O	6, 10
Pentane	O, I, V	4, 5, 6, 7, 9, 10, 17
2-Pentanone	O	10
Pentene	O, I	4, 6, 9
1-Pentene	O, I, V	5, 7, 10, 17
2-Pentene	V	5
Phenanthrene	O	22
Propadiene	I	4
Propane	O, I, V	4, 5, 7, 9, 10, 17, 19
Propanol	O	10
Propionaldehyde	O, I	6, 10, 14, 19
Propionic acid	O	10, 18
Propylene	O, I, V	4, 5, 6, 7, 9, 10, 16, 17, 19
Pyrene	O	20, 21
Tetradecanal	O	6
Tetradecane	O, I	6
1-Tetradecene	O, I	6
Tetrahydrofuran	O	10
Toluene	O, I	6, 19
Tridecanal	O	6
Tridecane	O, I	6
1-Tridecene	O, I	6
2, 3, 3-Trimethyl-1-butene	I	9
2, 2, 3-Trimethyl-1-pentane	I	9
Trimethylcyclopentane	I	10
2, 2, 5-Trimethylhexane	I	9
2, 3, 4-Trimethylpentane	I	9
Triphenylene	O	21
Undecanal	O	6
Undecane	O, I	6
1-Undecene	O, I	6, 10
Valerolactone	O	10
Water	O	9, 10

O: oxidative atmosphere
I: inert atmosphere
V: vacuum

involving free-radical ($\dot{R}$) reactions. The suggested decomposition mechanisms include free radical formation by breakdown (Eqn (2)), free radical transfer within (Eqn (3)) or between molecules (Eqn (4)) with subsequent decompositions, and free radical termination by disproportionation (Eqn (5)) or by combination (Eqn (6)):[4–6]

$$R-R\rightarrow 2\dot{R} \tag{2}$$

$$2\dot{R}\rightarrow R-\dot{C}H-CH_2-CH_2-R \tag{3}$$
$$\hookrightarrow \dot{R}+CH_2=CH-CH_2-R$$

$$\dot{R}+R-CH_2-R\rightarrow R-\dot{C}H-R+RH \tag{4}$$
$$\hookrightarrow R-CH=CH_2+\dot{R}$$

$$\dot{R}+\dot{R}\rightarrow R-CH=CH_2+RH \tag{5}$$

$$\dot{R}+\dot{R}\rightarrow R-R \tag{6}$$

Under oxidative conditions additional reactions may occur. Oxygenated free radicals are involved in these reactions, as for example:

$$\dot{R}O+H_3C-R\rightarrow R-CH_2OH+\dot{R} \tag{7}$$

$$RO\dot{O}+R-CH_2OH\rightarrow RCOOH+R-\dot{C}HOH \tag{8}$$

$$\dot{R}O+\dot{R}\rightarrow R-O-R \tag{9}$$

Fundamental studies of polyethylene degradation under various conditions have been reviewed by Madorsky,[4] Schwartz[7] and Cullis and Hirschler.[3]

Thermal degradation in the absence of oxygen

When polyethylenes are exposed to elevated temperatures under inert atmospheric conditions saturated and unsaturated hydrocarbons of various chain lengths are generated. Since polyethylenes do not contain any oxygen in their molecular structure, no CO, CO_2 or oxygen-containing organic compounds are produced. The composition of the volatile compounds which are formed from polyethylene products will reflect the presence of any additives present in the formulation.

Vacuum pyrolysis Identification of the volatile compounds generated from polyethylenes thermally decomposed under vacuum has been used in determining these degradation mechanisms. For example, a systematic mass spectrometric (MS) investigation by Madorsky *et al.*[4] found that a polyethylene (m.w. 20 000) pyrolyzed in vacuum at temperatures up to 450°C yielded 15 alkane and alkene type compounds, each containing 2–7 carbon atoms (Table 1). Only a small portion (4.3 mole %) of the fraction volatile at − 80°C appeared as the monomer, indicating the absence of a zip mechanism, in which the polymer degrades into a monomer one unit at a time. Increasing the temperature increased the percentage of the monomer found in the degradation products. In particular, when a high-molecular-weight grade unbranched polyethylene (polymethylene) was pyrolyzed at 500°C, 800°C and 1200°C, the weight per cent of the monomer, ethylene, in the total volatiles increased from 0% to 5.5% and to 26.4%, respectively. Based on the amount of ethylene formed, Madorsky proposed that two competing reactions occur when polyethylene decomposes. Below 800°C the thermal degradation proceeds by a fragmentation process. At higher temperatures, degradation proceeds by formation of free radicals which unzip producing the ethylene monomer.

Tsuchiya and Sumi also proposed that the main volatile degradation products from a polyethylene were formed by a mechanism involving the intra-molecular migration of free radicals.[5] When samples of a commercially available HDPE were decomposed at fixed temperatures ranging from 375°C to 425°C, twenty-six compounds consisting mainly of normal alkanes and normal 1-

alkenes containing one to six carbon atoms were identified by gas chromatography (GC) (Table 1). As expected from Eqn (3), the concentrations of these two classes of compounds were similar. The concentrations of ethylene and other hydrocarbons increased with increasing temperature. At 425°C, the monomer yield was 11 mole % in the fraction which was volatile at room temperature. These results agree reasonably with those of Madorsky[4] and other degradation studies cited by Tsuchiya and Sumi.[5] Free radical transfer involving local coiling was considered responsible for the relatively large amounts of propane and 1-hexene found in the degradation products. The predominant decomposition product, propylene, as well as isobutylene and 2-butene, were all considered produced by a cleavage of the relatively weak C–C bond in the β-position to the terminal double bond.

Inert atmospheres The thermal degradation products of polyethylenes decomposed in inert atmospheres are very similar to those generated under vacuum conditions. In a study using infrared spectrometry (IR) to characterize the pyrolysis and combustion products of various polymers, Morimoto detected methane, ethylene, acetylene and benzene when a commercially available polyethylene was decomposed at 700°C in a nitrogen atmosphere.[8]

Michal *et al.* studied the decomposition products of polyethylenes under three different conditions: pyrolysis in inert atmospheres, thermo-oxidation and combustion in air.[6] When the pyrolysis products generated from a sample of a commercial polyethylene heated at 400°C under a flow of helium were analyzed by gas chromatography/mass spectrometry (GC/MS), forty-four different hydrocarbons were identified (Table 2). These compounds contained three to 18 carbon atoms and consisted mainly of alkanes and 1-alkenes. In addition, three aromatic compounds, benzene, toluene and ethyl benzene, were also detected.

A similar detailed study of the volatile products of an industrial high-pressure type polyethylene decomposed at 510°C in an inert atmosphere was conducted by Pacakova *et al.* using pyrolysis gas chromatography.[9] The 48 compounds identified were mainly unsaturated hydrocarbons, consisting of 1-alkenes containing five to nine carbons, corresponding n-alkanes and 1, 3-alkadienes (Table 1).

The composition of the thermal degradation products of polyethylenes was demonstrated to be partially dependent on the molecular structure of the starting material by Hoff *et al.*[10] They examined two samples of commercial polyethylenes: an LDPE without any additives and a HDPE containing an antioxidant and carbon black. The materials were decomposed in a Pyrex tube with a movable furnace at 360°C under a helium atmosphere, and the gases were analyzed by GC and GC/MS techniques. Among the 25 products identified, the C_4 hydrocarbons were dominant in both cases (Table 1). During the initial stages of thermal degradation the degree of formation of C_2 to C_7 linear hydrocarbons was about the same for both samples. However, in final products, short-chain branched hydrocarbons were relatively more abundant in the combustion products generated from the LDPE sample than from the HDPE sample, which formed mostly linear hydrocarbons.

Table 2. Degradation products generated from a polyethylene during pyrolysis, thermooxidation and combustion[6]

Product	Pyrolysis (%)[a]	Thermo-oxidation (%)	Combustion (%)
Carbon dioxide	0.1	0.4	N
Propylene	0.1	0.35	0.5
Butylene	1.5	3.7	2.7
Butane	1.5	—	2.3
1, 3 Butadiene	0.75	4.1	1.1
Pentene + Propanal	6.5	7.5	6.7
	—	7.4	—
n-Pentane	—	6.2	3.9
Butyraldehyde	—	14.5	5.8
Cyclohexane	—	4.5	3.3
Hexene-1	9.9	—	10.8
n-Hexane	4.8	—	4.9
Cyclohexene	—	0.27	2.2
Benzene	2.6	0.65	5.9
Methylcyclopentene	—	2.5	0.8
Valeraldehyde	—	11.5	5.6
Heptene-1	5.6	1.4	3.0
n-Heptane	6.2	1.3	1.6
Toluene	0.8	0.9	3.3
Ethylcyclopentene	0.5	—	—
Methyl isobutyl ketone (or allyl acetate)	—	2.2	1.7
Hexanal	—	5.6	2.7
Octen-1	5.7	—	3.9
n-Octane	4.6	—	2.0
Acrylic acid	—	0.9	0.8
Ethyl benzene	1.3	0.89	2.5
Heptanal	—	3.1	3.1
Nonene-1	5.4	0.7	2.7
n-Nonane	3.5	1.4	1.2
Epoxide	—	0.3	0.2
Keto-aldehyde	—	0.6	0.3
Octanal	—	2.5	0.2
Decene-1	5.8	—	0.7
n-Decane	3.0	0.6	0.3
Undecene-1	4.3	—	0.9
n-Undecane	3.0	—	0.3
Nonanal	—	1.9	—
Decanal	—	0.8	—
Tridecene-1	1.9	—	0.2
n-Tridecane	1.5	—	0.4
Undecanal	—	0.4	—
Silicone	—	0.1	—
Tetradecene-1	2.0	—	0.15
n-Tetradecane	1.2	—	0.2
Dodecanal	—	0.2	—
Pentadecene-1	1.8	—	0.15
n-Pentadecane	0.7	—	0.15
Tridecanal	—	0.1	—
Hexadecene-1	1.3	—	0.07
n-Hexadecane	0.9	—	0.07
Tetradecanal	—	0.1	—
Heptadecene-1	0.5	—	0.15
+ n-Heptadecane	0.4	—	—
Pentadecanal	—	0.1	—
Octadecene-1	0.6	—	0.15
+ n-Octadecane	0.5	—	—

Pyrolysis: thermal degradation in inert atmospheres.
Thermooxidation: thermal degradation in oxidative atmosphere.
Combustion: flaming degradation.
[a]: Percentage calculated from the total chromatogram area.
N: Not determined.

In addition to the usual decomposition products observed, polycyclic aromatic hydrocarbons (PAHs) have also been detected among the degradation products of polyethylenes.[11] Morikawa pyrolyzed a commercial grade of polyethylene in a quartz furnace under a nitrogen atmosphere. Benzo(a)pyrene (BaP), which was used as an indicator for PAHs, was determined by high-pressure liquid chromatography (HPLC). Evolution of BaP was found to increase at 900°C and higher temperatures. At 1000°C, BaP was detected at a concentration of 1 mg g^{-1} of polyethylene; this amount is equivalent to that detected in an air-flowing atmosphere (see below).

Since pure polyethylenes contain no oxygen, no oxygen-containing compounds would be expected to be generated during their pyrolysis in inert atmospheres. However, CO and CO_2 have been detected in some studies.[6,8] (Michal, who specifically set out to measure the CO produced during the pyrolysis and thermooxidation of polymeric materials, detected no CO when a high-pressure type polyethylene was decomposed in helium at 500°C.[12]) The CO and CO_2 reported by others must have originated from additives, air trapped in the polyethylene formulation or the inadvertent introduction of air or water vapor into the inert experimental environment. The production of CO can occur by the following reactions:

$$C + H_2O \rightarrow CO + H_2 \qquad (10)$$

$$C_nH_{2n+2} + m'H_2O \rightarrow C_mH_{2m+2} + m'CO + 2m'H_2 \qquad (11)$$

where $m + m' = n$.

Morikawa examined this last possibility and found that when a polyethylene was decomposed in nitrogen the evolution of CO due to the presence of added water vapor was small.[13] At 1000°C, the amount of CO generated from a 500 mg sample of polyethylene was about 0.05 g g^{-1}, which was an order of magnitude less than that found for materials containing oxygen in their structure. No CO generation was observed below 900°C.

Small-scale tests in oxidative atmospheres

In order to evaluate the toxic atmospheres produced by polyethylenes decomposed in real fire situations the thermal degradation of polyethylenes has been studied under a wide range of oxidative conditions and temperatures. Although large-scale tests can more closely simulate actual fire conditions, almost all the experiments included in this review have been conducted as small-scale laboratory tests. Non-flaming conditions, when used in small-scale tests, are considered to represent an early fire stage when a material may be pyrolyzed some distance away from the combustion zone without being ignited.

In both flaming and non-flaming tests performed under oxidative conditions a complex mixture of oxygen-containing organic compounds is formed in addition to the saturated and unsaturated hydrocarbons that were noted above to be generated in the absence of oxygen. CO and CO_2 are the principal decomposition products generated. Certain oxygen-containing organic compounds, such as acrolein, formaldehyde and volatile carboxylic acids (formic acid, acetic acid and propionic acid), are also detected and may be of toxicological importance, since these compounds are considered to be irritants.

Generation of CO and CO_2 Concentrations of CO and CO_2 have been measured in most of the combustion studies of polyethylenes. The results of these studies have shown that the evolution of CO and CO_2 is dependent on the air supply rate, the temperature of decomposition and residence time of fuel vapor in the combustion zone.

In order to simulate different real-fire conditions Michal[12,14,15] used different combustion systems for pyrolysis in helium, oxidative non-flaming and flaming tests. During combustion in air with depleted oxygen content the CO content in the thermal degradation products of a commercial polyethylene increased with increasing temperature. Under ventilated conditions greater amounts of CO were detected in the non-flaming mode than in the flaming one. When the O_2 supply was limited the concentration of CO was greater in the flaming mode than in the non-flaming mode. As expected, the CO_2 content was found to be greatest during well-ventilated flaming combustion and was not temperature dependent.

In one study Michal decomposed a high-pressure type polyethylene (Bralen RB 03–23) in a quartz combustion tube at 550°C in various gas mixtures of helium and oxygen.[12] Gas chromatography was used for determination of CO in the thermal degradation products. The pyrolysis results in pure helium atmospheres, described above, showed no CO production; whereas under thermooxidative conditions with unspecified O_2 concentrations the CO yield was found to be 29.7 mg g^{-1}.

The same polyethylene was also decomposed under depleted O_2 atmospheres in a 4.2 l combustion chamber (CAB 4.2) containing a crucible furnace under the combustion chamber. The chamber was designed to simulate combustion in air with depleted oxygen. As the atmospheric O_2 was decreased under restricted flaming conditions the CO concentration increased. The average CO yield under limited flame combustion in five tests was 100.2 mg g^{-1}. Under these conditions the CO concentration increased as the temperature of the crucible was raised from 500°C to 800°C.[12]

In a second study Michal decomposed the same high-pressure type polyethylene in another combustion chamber (CAB 4.5) and the gaseous products were measured in an adjoining chamber.[14] This two-chamber system was designed in an attempt to model the natural flow of toxic combustion products. The total volume of the system was 4.5 l, and samples (less than one gram) were combusted in a crucible furnace under both non-flaming and flaming

Table 3. CO and CO_2 concentrations in the combustion products from a Polyethylene[14]

Combustion mode	Temperature (°C)	Sample weight (mg)	CO (%)*	CO_2 (%)
NF	500	100	0.238	1.24
		200	0.472	1.95
		300	0.738	2.71
F	600	100	0.126	2.60
		200	0.297	3.72
		300	0.513	3.66

*Percentage volume as measured in the animal test chamber.
NF: Non-flaming.
F: Flaming.

conditions. Table 3 indicates that more CO was formed in the non-flaming mode (500°C) than in the flaming one (600°C). By contrast, the CO_2 concentration was considerably higher when the polyethylene was decomposed during flaming combustion than in non-flaming combustion. When compared with other polymeric materials (polypropylene, polystyrene, and polyamide) investigated under non-flaming conditions the polyethylene was found to produce the most CO and therefore was considered by the author to be the most dangerous of these materials.[14]

In a third study by Michal a sample of a low-density polyethylene (Bralen 03-23) was decomposed in a 650 l combustion chamber (CAB 650) designed to accommodate larger amounts of material (up to several grams) and provide more variable conditions for thermal degradation.[15] This combustion chamber was intended to simulate well-developed fires. Carbon monoxide and carbon dioxide determinations were made after complete combustion of the sample.

There were several differences between the CAB 650 and CAB 4.5 systems. In the former a fan was used for mixing the thermal degradation products and for providing more air to the crucible furnace, whereas in the latter, since there was no forced air supply the gases moved by natural convection. The ratio of sample weight to the chamber size in CAB 650 was about an order of magnitude lower than that in CAB 4.5.

Under the experimental conditions in CAB 650 polyethylene flamed at 500°C. In the presence of the increased amount of air supplied to the furnace in this test the CO production was relatively low, i.e. less than 0.5 mg g^{-1} for all samples tested. However, more CO_2 was generated in CAB 650 than that observed under the restricted flame combustion in CAB 4.5, an indication that more thorough thermooxidation occurs in the presence of the greater air supply. Generation of CO_2 under these flaming conditions was not found to be temperature dependent since approximately the same amount was measured at 600°C, 800°C and 1000°C.[15]

Morikawa studied the effect of oxygen and water vapor on the generation of CO from polymeric materials including a polyethylene.[13] The results in nitrogen were discussed above. In air, the thermal decomposition of this polyethylene in the presence of water vapor was examined in a tube furnace at three temperatures—500°C, 600°C and 700°C. The effluent gases were analyzed by GC. The evolution of CO was generally greater in the presence of water vapor and depended upon the air flow rate. The highest concentration of CO was observed at 500°C at an air flow of 1 l min^{-1} and water vapor flow of 1 g min^{-1}. In this case the CO production in the presence of water vapor and air was five times greater than in the absence of water vapor, namely, 500 mg g^{-1} and 100 mg g^{-1}, respectively. When the CO generation in air (500 mg g^{-1} at 500°C) was compared with that in nitrogen (0 mg g^{-1} at 900°C and 50 mg g^{-1} at 1000°C) it was concluded that the evolution of CO seems to be a function of the atmospheric oxygen content, temperature and water vapor.

The presence of CO and CO_2 has been also determined in several other studies on the oxidative degradation of polyethylenes.[6,8,10,16,17] For example, during studies of hazards generated in underground mines Paciorek *et al.* measured the amount of CO and CO_2 that was produced when a polyethylene wire insulation (crosslinked, pigmented and containing about 0.5% amine antioxidant) was decomposed in a test designed to simulate the oxidative overheating and combustion that can occur in mines.[16] Gaseous products were analyzed by MS. The major fraction (about one third) of the volatiles detected was CO_2. Only small amounts of CO were observed.

Morimoto *et al.* measured the toxic gaseous products generated by a series of polymers and cellulosics decomposed under flaming conditions.[8] When a polyethylene sample was burned in a tube furnace at 700°C under an air flow of 100 l h^{-1}, both CO_2 (738 mg g^{-1}) and CO (210 mg g^{-1}) were detected.[8] The concentration of CO_2, but not CO, was found to depend on the air supply rate. When the air flow rate was reduced by 50%, the CO_2 levels decreased to 502 mg g^{-1}, whereas the CO level remained about the same (195 mg g^{-1}).

Boettner *et al.* studied the products of incomplete combustion of polyethylenes and other plastics which may be produced during waste incineration and could be toxic in real fire situations.[17] Three polyethylene samples were studied: LDPE and HDPE powders and a HDPE in pellet form. Samples were decomposed in a tube furnace under various controlled heating rates and air and oxygen supplies. The major combustion products were identified by IR, minor ones by MS. Although the concentrations of CO and CO_2 depended again upon the heating rates and air flow rates, CO_2 and CO were the major volatile products formed from all three polyethylene samples. For example, at a heating rate of $5°\text{C min}^{-1}$ and air flow rate of 100 ml min^{-1} the CO and CO_2 concentrations ranged from $255–312 \text{ mg g}^{-1}$ and $88–213 \text{ mg g}^{-1}$, respectively. As the heating rate was increased tenfold to $50°\text{C min}^{-1}$, the concentration of CO decreased to $110–208 \text{ mg g}^{-1}$ and that of CO_2 increased somewhat to $178–388 \text{ mg g}^{-1}$. When oxygen ($40 \text{ ml min}^{-1}$) was added to the air flow during the $5°\text{C min}^{-1}$ experiments the CO concentration decreased slightly to $171–179 \text{ mg g}^{-1}$ and the CO_2 concentrations considerably increased to $753–1842 \text{ mg g}^{-1}$.

Organic combustion products. ***Irritants*** When polyethylenes are thermally degraded under oxidative experimental or real fire conditions complex volatile organic chemical species are produced. The reaction to form these organic volatiles occurs partially within the heated polyethylene material, which has a restricted oxygen supply, and partially in the gas phase, which has a rich oxygen supply. Short-chain compounds, such as aldehydes and ketones, are generated predominantly by the gas-phase oxidation of the volatilized hydrocarbons.

In an attempt to identify the volatile breakdown products of toxicological concern several studies have been performed to detect irritants, such as acrolein, formaldehyde and low-molecular-weight carboxylic acids. Morikawa studied the irritant components of smoke from various polymeric and cellulosic materials and found that the evolution of irritants from a polyethylene was relatively large.[18] Polyethylene samples were thermally decomposed in a quartz tube furnace in air. The concentrations of carboxylic acids and acrolein in impinger samples were determined by a GC technique. Formaldehyde was measured by a colorimetric technique using a spectrophotometer.

Under non-flaming conditions the amount of irritants from this polyethylene sample increased with oxygen concentration, whereas under flaming conditions the concentration of irritants decreased (presumably due to further oxidation and/or decomposition). Maximum evolution of acrolein ($350\,\mu mol\,g^{-1}$), formaldehyde ($2600\,\mu mol\,g^{-1}$) and the volatile carboxylic acids ($380\,\mu mol\,g^{-1}$) was obtained when the samples of polyethylene were subjected to smoldering combustion at 300–400°C. Formic acid and acetic acid accounted for the greatest fraction of the detected carboxylic acids.

A limited comparison of the above results to those from a few other non-oxygenated polymers studied by Morikawa showed that this polyethylene appears to generate significant amounts of irritant gases. When compared with wood, several times more acrolein and formaldehyde were generated from polyethylene. Only the evolution of carboxylic acids from polyethylene was equivalent to that generated from wood under similar smoldering conditions.[18]

Hodgkin *et al.* also detected irritant volatile gases in the combustion products of polyethylenes.[19] Four commercial polyethylene samples, LDPE and HDPE pellets, and two LDPE foams, were decomposed in a muffle furnace under a wide range of air flows at temperatures ranging from 500°C to 800°C. The volatile products were analyzed by IR, nuclear magnetic resonance (NMR), GC/MS and wet chemical techniques. The list of products identified included acrolein, formaldehyde, acetaldehyde and acetic acid (Table 1). These results differed somewhat from those of Morikawa[18] in that the only carboxylic acid detected by Hodgkin *et al.* was acetic acid and only trace amounts of acrolein were found. These differences may be attributed to the higher experimental temperatures used by Hodgkin *et al.* and the different chemical sample collection and analysis methods.

Whereas Morikawa and Hodgkins *et al.* investigated the generation of irritant gaseous products from polyethylenes exposed to elevated temperatures (to simulate real fire conditions),[18,19] Hoff *et al.* studied the decomposition of polyethylenes at lower temperatures (to simulate industrial processing conditions).[10] Three different commercial LDPE and HDPE samples were decomposed in a tube furnace at 280°C. Volatile products were detected by GC and MS/GC techniques. At this temperature the predominant products were the carboxylic acids, formic and acetic, followed by the aldehydes, acrolein, formaldehyde and acetaldehyde.

The study of Hoff *et al.* also showed that processing polyethylenes under real manufacturing conditions gives rise to the same volatile irritants as those generated in the laboratory tests. For industrial hygiene purposes, atmospheric measurements were made near machinery processing polyethylenes at temperatures ranging from 140°C to 250°C. The average concentrations of formaldehyde, acetaldehyde, acrolein, formic acid and acetic acid, however, were very low ($< 1\,mg\,m^{-3}$) and not considered hazardous.[10]

Non-irritant organic compounds To assess the toxic hazards associated with the combustion of polyethylenes in fires many laboratories have looked for volatile organic compounds other than CO, CO_2 and irritant gases in the smoke evolved during thermal decomposition.[6,8,14,16,17,19] Both hydrocarbons and oxygen-containing compounds have been identified. Under non-flaming conditions a variety of aldehydes and ketones are produced, whereas under flaming conditions hydrocarbons predominate and the evolution of aromatic compounds is increased.

Michal *et al.* examined the thermal degradation products from a polyethylene decomposed under three conditions: pyrolysis in helium, non-flaming thermooxidation and flaming combustion in air.[6] In addition to the hydrocarbons observed during pyrolysis in helium (see above), many oxygen-containing compounds were identified in the studies conducted in air (Table 2). In these studies, samples of a commercial polyethylene (Bralen Z 1907–601) were thermally decomposed in a flow quartz micro-reactor at 350°C (non-flaming thermooxidative mode). The volatile products were identified by GC/MS. Under the thermooxidative conditions, the main products were 3–15 carbon aldehydes (48%). Other minor oxygen-containing products included ketones, acetic acid, ethanol and epoxide. In addition to the oxygen-containing compounds, the volatile products included 25% olefins and 12% paraffins. Under flaming conditions conducted under a glass funnel, hydrocarbons represented the most substantial fraction (~65%) of the identified volatile products. The yield of aromatic compounds was also greater under flaming than under non-flaming thermooxidative conditions. Among the numerous organic products generated, acrylic acid was considered the most toxic compound identified.[6]

Hydrocarbons were found also to represent a substantial portion of the combustion products when samples of a high-pressure type polyethylene (Bralen RB 03–23) were decomposed under flaming combustion conditions in a two-chamber combustion system (CAB 4.5) [14]. Propionaldehyde constituted only a minor percentage of the total volatiles and no ketones were detected at all (see Table 2).

Hodgkins *et al.* identified many combustion products of polyethylenes decomposed under both flaming and non-flaming oxidative conditions.[19] The organic products from the oxidative flaming experiments included saturated and unsaturated hydrocarbons with a chain length ranging from two to 23 carbons. Only a few of the low molecular weight hydrocarbons were actually identified (Table 1). Most of the products identified were in the higher molecular weight range and consisted of aldehydes, ketones and aromatic compounds. Basically, the same product pattern was observed for four different samples of polyethylene decomposed under similar conditions. The composition of the hydrocarbons varied with changes in temperature but not with changes in air flow rates. The major changes noted as the temperature increased were the increase in the aromatic hydrocarbons, benzene and toluene, and the large decrease in acetone production.

Boettner *et al.* also noted that the composition of the organic volatile products was similar for different polyethylenes.[17] When three different polyethylene samples (LDPE pellets, HDPE powder and HDPE pellets) were heated in a tube furnace under various combustion conditions the organic compounds identified included mostly straight-chain saturated and unsaturated hydrocarbons containing one to six carbon atoms (Table 1). Unsaturated hydrocarbons predominated over saturated products. The only oxygen-containing compounds detected were methanol and acetaldehyde.

The presence of low-molecular-weight hydrocarbons in the combustion products of a polyethylene wire insulation was also observed by Paciorek *et al.*[16] Methane, ethylene, ethane, propane and benzene were detected as minor components of the smoke produced when a commercial polyethylene wire insulation was decomposed in a 'stagnation' burner arrangement in which preheated air was passed over the test specimen.

Morimoto *et al.*[8] performed a detailed study on the low-molecular-weight hydrocarbons generated from polyethylene decomposed under different ventilation conditions at a constant temperature of 700°C. In air, the main products detected by IR were methane, ethylene and acetylene. At an air flow rate of 50 l h^{-1} the concentrations for methane, ethylene and acetylene were 65 mg g^{-1}, 187 mg g^{-1} and 10 mg g^{-1}, respectively. Only the concentration of acetylene was found to be dependent on oxygen availability. When the air flow through the combustion chamber was doubled from 50 l h^{-1} to 100 l h^{-1}, the acetylene concentration increased from 10 mg g^{-1} to 34 mg g^{-1}, respectively.

In industrial processing, polyethylenes are subjected to temperatures significantly lower than those used in the studies described above. During tests to examine industrial processing hazards Hoff *et al.* studied the decomposition of LDPE and HDPE type polyethylenes over a temperature range of 265–290°C using a tube furnace.[10] The volatile organics were analyzed by GC and MS techniques. Hoff *et al.* identified a total of 44 products representing hydrocarbons, alcohols, aldehydes, ketones, acids, lactones, cyclic ethers and cyclic esters. Essentially the same products were formed for both types of polyethylene tested. This agrees with results of Hodgkin *et al.*[19] and Paciorek *et al.*[16] Contrary to the non-flaming and flaming studies conducted at higher temperatures,[6,14,19] the oxygen-containing organic compounds constituted the majority and hydrocarbons the minority of compounds detected.

Polycyclic aromatic hydrocarbons Polycyclic aromatic hydrocarbons (PAHs) are not considered acute toxicants; however, some have been shown to be carcinogens. Since generation of PAHs is generally associated with smoke and soot particulates, PAHs may be of importance in long-term or repetitive exposures to fire gases (e.g. in the case of fire fighters). The presence of PAHs in the smoke of polyethylenes has been demonstrated in a number of studies.[11,20,21] Morikawa studied the evolution of PAHs, especially benzo(a)pyrene during pyrolysis under inert conditions (see above for details) and oxidative combustion of polyethylene and other materials.[11,20] Samples of a polyethylene were decomposed in a tube furnace at several temperatures ranging from 600° to 900°C under varying airflow rates.[20] PAHs were determined by GC analysis of the extracts of the collected soot and solid products. Evolution of condensed matter from this polyethylene was highest at 600° and 900°C and lower at 700° and 800°C. The corresponding yields of benzo(a)pyrene increased with increasing temperatures (from 0.1 mg g^{-1} at 600°C to 1.3 mg g^{-1} at 900°C). In addition to benzo(a)pyrene, five other PAHs—anthracene, fluoranthene, pyrene, benzo(a)anthrathene and benzo(c)pyrene—were detected in the soot and solid products from this polyethylene.

The evolution of PAHs is normally associated with soot formation during fires. However, Morikawa found that formation of benzo(a)pyrene is not always accompanied by the formation of soot and solid products as the consistency of the condensed matter may vary over the temperature range. More benzo(a)pyrene was observed to evolve from a polyethylene than from a polystyrene, even though the polystyrene produced three to four times more soot than the polyethylene.[20] In addition, when the polyethylene was decomposed at 900°C (a non-sooting temperature) in nitrogen, benzo(a)pyrene was also produced.[11]

PAHs in the smoke from samples of a polyethylene (containing additives 5% by weight) exposed to radiant thermal fluxes of 4.3 W cm^{-2} (non-flaming) and 5.0 W cm^{-2} (flaming) were also detected by Zinn *et al.*[21] Chemical characterization of the smoke particulates was performed by HPLC, GC and MS/GC. The PAH yields were 0.045 mg g^{-1} in the non-flaming tests and 0.025 mg g^{-1} in the flaming ones. The principal compounds detected in the non-flaming combustion of this polyethylene were anthracene and/or phenanthrene and pyrene; in the flaming mode the major product was pyrene (Table 4).

Compared with other polymers (polystyrene, polymethylmethacrylate and polypropylene) studied by Zinn, and decomposed under similar conditions, the polyethylene generated the greatest quantities of PAHs. Again, the generation of PAHs did not correlate with soot formation as polystyrene generated the most soot but only traces of PAHs.[21] These results agree well with those of Morikawa.[11,20]

Free radicals When polyethylenes are decomposed in a fire or processed at elevated temperatures in air the heated polymer undergoes an oxidative thermal degradation which proceeds partly through alkyl, peroxy and alkoxy radical formations. Free radicals from the combustion of polymers have been observed to cause injuries to cells in tissue cultures[22] and are of toxicological concern due to their high reactivity.

Two research groups have detected free radicals by electron spin resonance (ESR) spectroscopy from the

Table 4. Concentrations of polycyclic aromatic hydrocarbons in smoke particulates from a polyethylene[21]

PAH Species	NF	F
Phenanthrene, anthracene	48.16[a]	12.47
4, 5-Methylene phenanthrene		2.45
Methyl-phenanthrene		0.64
Fluoranthene		18.98
Pyrene	51.84	46.38
Methyl-4, 5-methylene phenanthrene		0.61
1, 2-Benzofluorene		1.77
2, 3-Benzofluorene		1.33
Methyl-pyrene		1.14
2, 13-Benzofluoranthene		5.64
Chrysene, Benzoanthracene, triphenylene		8.59

[a] Mole %.
PAH: Polynuclear aromatic hydrocarbon.
NF: Non-flaming.
F: Flaming.

industrial processing of polyethylenes.[10,23] These studies indicated that the detected species were alkoxy and peroxy radicals formed by decomposing polyethylenes in oxygen. In addition to free radicals, one of these groups also detected the presence of hydroperoxides.[10] The concentration of free radicals and peroxides in the environment were estimated roughly to be about the same as that found for the total aldehydes ($\sim 2.2\,\mathrm{mg\,m^{-3}}$).[10] Even though both these studies demonstrated that processing of polyethylenes gives rise to free radicals, free radicals are normally very short-lived species, and there is no clear evidence that the free radicals constitute a hazard when polyethylenes are involved in real fires.

TOXICOLOGY

Several bioassay methods have been used to assess the acute toxicity of fire gases. In these tests animals are exposed to smoke and toxic gases and either death or incapacitation serves as the biological endpoint. Most test procedures include some chemical analysis of specific toxicants of interest. The various toxicity test methods have been described in detail by Kaplan *et al.*[28]

In the reviewed literature, seven different toxicity test procedures were utilized to assess the toxicity of combustion products from polyethylenes. A brief summary of the five main methods used and the biological endpoints that have been evaluated is given in Table 5.

DIN toxicity test method

The toxicity of the combustion products from various materials, including polyethylenes, has been evaluated by two groups of workers using several variations of the DIN method. Briefly, the DIN Draft 53436 test method uses a dynamic flow system in which materials of equal volume or equal weight per unit length are decomposed in a quartz tube. The tube is heated by an externally moving ($1\,\mathrm{cm\,min^{-1}}$) furnace at fixed temperatures between 200° and 600°C. The decomposition products are diluted with air at chosen flow rates. Chambers of various designs have been used to expose animals in the head-only or whole-body mode. These exposures usually last for 30 min and lethality is the usual biological endpoint.

An early version of the DIN method was used by Hoffmann and Oettel to compare the toxicity of the thermal decomposition products of building materials.[29] They demonstrated that ranking materials based solely on the chemical analyses of a few of the decomposition products may be misleading and does not correspond with results from toxicological experiments on animals.

Table 5. Biological endpoints

Method	Lethality			Incapacitation	
	LC_{50}	No. animals affected	Time to death	IC_{50}	Time to incapacitation
DIN[a]		×			
USF[b]		×	×		×
FAA/CAMI[c]			×		×
Dow[d]	×	×			
CMIR[e]	×			×	×

[a] Method developed in response to the German Commission of Standards.
[b] University of San Francisco.
[c] Federal Aviation Administration.
[d] Dow Chemical Company.
[e] Carnegie–Mellon Institute of Research.

Table 6. Toxicological effects on rats exposed to the pyrolysis products from a polyethylene[a] decomposed by the DIN method[29]

Temperature (°C)	COHb (%)	Number of deaths / Number of exposed animals
200	<15	0/12
300	<15	0/12
400	79	12/12
500	85	12/12
600	82	12/12

[a] Sample weight = 5 g.

In these experiments a polyethylene (without a filler) was decomposed at 100° increments between 200° and 600°C with an air flow rate of $100\,\mathrm{l\,h^{-1}}$. The pyrolysis products were further diluted with an $100\,\mathrm{l\,h^{-1}}$ air supply. Rats were exposed in the whole-body mode for 30 min. The blood carboxyhemoglobin (COHb) levels in the experimental animals were determined immediately after the exposure. The results of these experiments showed that when 5-g samples of a polyethylene were pyrolyzed, 100% mortality occurred at temperatures of 400°C and greater, whereas no deaths were observed at lower temperatures (Table 6). Since COHb concentrations in the dead animals ranged from 79 to 85%, the lethalities were attributed by Hoffmann and Oettel to CO.[29]

Hoffmann and Oettel also compared the toxicity produced by the thermal degradation of the same polyethylene to that of other conventional building materials tested at the same sample weight under similar conditions. The toxicity of these materials, cellulose, rigid poly(vinyl chloride) (PVC) and pine, were classified 1, 2 and 3, respectively, according to a Swiss classification (where 1 indicates the most toxic case). The polyethylene that was tested was assigned a toxicity classification of 4. Based on animal test results, temperatures above 400°C generated decomposition products with the same toxicity from all four materials. However, at 300°C the decomposition products from the polyethylene were less toxic than those from the other three materials. At 200°C cellulose was the only material to produce toxic combustion products.[29]

In another study Hoffmann and Sand investigated the toxicity of the decomposition products from two types of polyethylene (HDPE and LDPE) and compared the results with those from pine wood.[30] Conditions were set such that sublethal concentrations of CO were generated. In these experiments 10 g of the polyethylenes were decomposed at 600°C. The air supply through the furnace was $450\,\mathrm{l\,h^{-1}}$ and an additional air supply of $450\,\mathrm{l\,h^{-1}}$ was used for dilution of the pyrolysis products in the exposure chamber. The CO concentrations were determined by Draeger tubes[a] and were less than 1000 ppm. The COHb levels in the blood at the end of the 30 min exposures were 27% and 33% for the LDPE and HDPE, respectively, and no deaths occurred. Under the same test procedure, pine wood generated about 2000 ppm CO, COHb levels of 51% and also no deaths. The authors concluded that under these test conditions the combustion products from these polyethylenes appear to be no more toxic than those from pine wood and that in a real fire, the toxicological risk from the fire gases of polyethylenes is no greater than that of pine wood.

Herpol *et al.* used the DIN toxicity test method to investigate whether synthetic materials are more dangerous when involved in fires from a toxicological point of view than natural materials.[32–34] The polyethylene samples included in this study are listed below:

No. 5 and K9—Low-density sheets
No. 6 or K10—High-density sheet A
No. 7—High-density sheet B
No. 8—Low-density granules
K11—Tubing (treated with fire retardant)

These materials were decomposed at three temperatures (400°, 600° and 800°C) in a furnace through which an air flow of 200 l h^{-1} was passed. The combustion products were further diluted by an additional air flow of 200 l h^{-1} before entering the exposure chamber in which rats were exposed in a whole-body mode for 30 min. Lethality (as measured by the cessation of respiration) was the biological endpoint.

The polyethylene samples flamed in all except a few tests at 400°C. At 600°C all of the polyethylene samples were about equally toxic and caused 92–100% mortality. At 400° and 800°C, samples 5 and K9 were more toxic than samples K10 and K11 (FR) (Table 7). The COHb levels in the blood of dead rats ranged between 48% and 79%. The CO concentration-time products for 30 min ranged from 29 000 to 189 000 ppm·min in those experiments in which deaths occurred. In an earlier study of lethalities from pure CO in air, Herpol *et al.* found that no deaths occurred at CO concentration–time products up to 120 000 ppm·min and 100% of the animals did not die until 210 000 ppm·min was reached.[35] In the pure CO experiments in which all the animals died the mean COHb ranged from 58% to 71%. In the experiments on polyethylenes, most of the CO concentration–time products are lower than the lethal CO concentration–time products seen in the pure CO tests, an indication of the presence of other toxicants.

Table 7. Toxicological effects on rats exposed to combustion products from polyethylenes[a] decomposed according to the DIN toxicity test method[32–34]

Temp. (°C)	Sample	CO (ppm·min)[b]	CO_2 (%·min)[b]	Mean COHb (%) D	A	Mortality Number of rats	%
400	5, K9	131 690	30.1	59	35	17/18	94
	6, K10	84 300	26.0	65	24	12/18	67
	K11 (FR)	1 610	0.5	—	0.3	0/18	0
600	5, K9	115 500	127.4	62	23	34/36	94
	6, K10	124 220	113.0	63	—	24/24	100
	7	118 970	154.3	48	64	11/12	92
	8	146 630	191.8	65	—	12/12	100
	K11 (FR)	188 890	103.2	58	72	17/18	94
800	5, K9	117 550	109.2	64	—	30/30	100
	K10	29 000	40.9	79	48	7/18	39
	K11 (KR)	126 460	100.9	73	37	17/30	57

[a] 10 g samples.
[b] Accumulated concentration for 30 min.
D: Dead animals.
A: Alive animals.

Table 8. Variation of mean respiration frequency[a] in rats exposed to polyethylenes decomposition products[32, 33]

Temp. (°C)	Sample no.	Mean respiratory frequency at 6 min	12 min	18 min	24 min	30 min
400	5	89	73	34	28	9
	6	97	96	100	53	26
600	5	76	46	28	9	4
	6	82	43	20	8	0
	7	63	31	53	33	8
	8	55	36	13	0	0
800	5	37	14	4	1	0

[a] Expressed as a percentage of the mean normal value before the test.

The CO_2 concentration–time products in Table 7 ranged from 26.0% to 191.8%·min except for sample K11 (FR), which had an CO_2 concentration–time product of 0.5%·min at 400°C. A CO_2 concentration–time product greater than 75%·min will increase the rate of respiration.[35] In these experiments, however, the respiration of rats decreased drastically, even when CO_2 concentration–time products were above 100%·min (Table 8). This reduction suggests the presence of irritants in the combustion products.

Comparison of results (shown in Table 9) obtained with two wood products decomposed in the DIN test method showed that some of the samples of polyethylene (not fire retarded) appeared to be more toxic at 800°C but had about the same degree of toxicity at 400° and 600°C.[33]

Table 9. Comparison of toxicities (DIN toxicity test)[33]

Sample	Percentage mortality at 400°C	600°C	800°C
5, K9	94	94	100
6, K10	67	100	39
7		92	
8		100	
Beech	72	54	17
Poplar		100	28

To assess the hazard produced from the decomposition of a material Herpol proposed the use of a 'toxicity index' (TX) based on a mathematical expression which takes into consideration the observed mortality and exposure time under the most toxic conditions.[34,36,37] A good correlation was shown to exist between the TX and LT_{50} values (times necessary to kill 50% of the rats). The maximum TX values for the three polyethylenes tested (K9, K10, K11(FR)) ranged from 30 to 48. These values indicated a higher overall toxicity for the polyethylene samples than for the poplar and beech wood samples (results shown below).[34]

	Maximum TX
K9	48.00
K10	29.53
K11 (FR)	30.93
Beech	8.80
Poplar	16.93

University of San Francisco (USF) toxicity test method

The USF test method has been used by Hilado *et al.* to evaluate the toxicity of the thermal decomposition products from a great number of commercial materials, including polyethylene. The test method involves exposing four mice in the whole-body mode to the thermal degradation products from 1 g samples decomposed in a tube furnace. The temperature is either increased from 200° to 800°C at a rate of 40°C min^{-1} or fixed at a temperature ranging from 200° to 800°C. The experiments are conducted with or without a forced air supply. Animals are exposed for 30 min or until the time of death of the last surviving animal. Biological endpoints are average times to incapacitation (T_i) as indicated by staggering, prostration, convulsions and collapse, and time to death (T_d) as indicated by cessation of movement and lack of respiration.

The results of the evaluation of several samples of polyethylene decomposed in the USF furnace set in the rising temperature mode without any added air supply are presented in Table 10. The average times to incapacitation ranged from 11.54 ± 0.62 to 15.52 ± 4.44 min and average times to death ranged from 13.99 ± 0.85 to 24.69 min. In most tests, death occurred 2–6 min after incapacitation (as indicated by staggering). The average times and standard deviations were calculated from the mean of two or more experiments and are not indicative of the variability of the animals within any one test.

The relative toxicity of polyethylenes is highly dependent on the conditions of combustion (temperature and air flow rate). Changing from the rising temperature program to a fixed temperature mode at 800°C results in shorter times to animal responses, i.e. higher toxicity.[39] This effect is attributed to the more rapid generation of toxicants from polyethylenes when decomposed at 800°C as compared with the rising temperature program. Progressive increases in toxicity were also observed in the fixed temperature mode as the temperature was increased.[40]

Table 10. Toxicity results for polyethylenes[a] decomposed according to the University of San Francisco method using the rising temperature mode[b]

Sample designation	T_i (min)	T_d (min)	References
PE1	15.52 ± 4.44[c]	22.60 ± 0.45	47, 53, 54, 55
PE2	11.54 ± 0.62	13.99 ± 0.85	41
	11.74 ± 0.29	19.84 ± 0.29	53, 54, 55
PE foam		20.68 ± 0.36	56, 58
PE foam		20.93 ± 0.47	58, 59
PE microfoam		20.42 ± 0.26	58, 59
Pe solid 1		19.84	44
PE solid 2		22.66	44
PE solid 3		24.69	44
PE solid 5 (LDPE)	12.80 ± 1.34	18.60 ± 0.30	38, 44
PE solid 6 (HDPE)	13.82 ± 2.53	18.29 ± 1.22	38, 44

[a] Sample weight 1 g.
[b] 40°C min^{-1} from 200° to 800°C.
[c] Standard deviation of average times from two or more experiments.
T_i: Average time to staggering.
T_d: Average time to death.
PE: Polyethylene

When the polyethylenes were decomposed under a forced air supply the times to death and times to incapacitation were generally shorter than when the polyethylenes were decomposed in the static mode.[41] The effects of the temperature regime and ventilation conditions on the times-to-death from the exposures to the combustion products from a polyethylene are summarized in Table 11.[42]

In a study on the lethal effects of CO in air Hilado and Cumming found that the time-to-death from 10 000 ppm CO was about 5 min.[43] When polyethylene samples were decomposed with the USF test method using either of the two temperature modes, GC gas analysis of the chamber atmospheres at the time of death of the last surviving animal showed the presence of relatively high concentrations of CO, methane and ethylene (Table 12). The CO concentrations ranged from 9155 to 15 050 ppm (rising temperature mode) and from 565 to 16 560 ppm (fixed temperature mode). From the results in Table 12, it appears that CO could be the principal toxicant in the combustion gas mixture from the polyethylenes decomposed in the rising temperature mode and in the experiments in the fixed mode at 500°, 600° and 800°C without forced air. At 300° and 400°C, where the CO concentrations were below 3000 ppm, other gases most likely contributed to the observed deaths.

The role of CO in the combustion gas mixture was estimated by a concentration–time relationship or 'death product' (*DP*), which was defined as

$$DP = \int_0^t C\,dt$$

where C is the concentration of CO at time t.[44] Hilado and Cumming determined the critical *DP* for CO to be 47 240 ± 14 980 ppm.min.[43] Tests were terminated upon death of the last surviving animal or 30 min. The *DP* values for CO from five polyethylene samples decomposed with the rising temperature mode were found to range from 41 880 to 74 650 ppm.min.[44] For three other polyethylene samples decomposed at 800°C the *DP* values ranged from 60 290 to 95 390 ppm·min.[45] The range of *DP* values calculated for these polyethylenes suggest that CO was probably the principal toxicant.

Table 11. Survival times of test animals exposed to smoke from a polyethylene[a] decomposed under different University of San Francisco test method conditions[42,57]

Temperature mode	Temperature (°C)	Mean time-to-death (min) No air flow	Mean time-to-death (min) Air flow[b]
Fixed	300	31.0	30[c]
	400	29.3	7.0
	500	21.5	6.8
	600	15.8	8.2
	700	13.8	30[c]
	800	11.7	30[c]
Rising	200–800°C at 40°C min^{-1}	22.7	13.8

[a] Sample designation P1.
[b] Air flow rate 1 l min^{-1}
[c] When no deaths occurred during the 30 min exposure, a survival time of 30 min is indicated.

Table 12. Gas analyses of the combustion products from polyethylenes[a] examined via the University of San Francisco test method[b]

Temp. mode	Sample designation	Temp. (°C)	CO (ppm)	CO_2 (%)	CH_4 (ppm)	C_2H_4 (ppm)	C_2H_6 (ppm)	References
Rising[c]	PE1		11 250	3.36	8550	6200	1250	47, 53
	PE2		15 050	2.36	8900	8200	1500	39, 54
	PE solid 5		11 075		9440			38
	PE solid 6		9155		8205			38
Fixed	PE1	300	565		0			40
	PE1	400	2798		0			40
	PE1	500	4320		2185			40
	PE1	600	10 578		9052			40
	PE2	800	16 560					40

[a] Sample weight 1 g.
[b] Without forced air flow.
[c] 40°C min^{-1} from 200° to 800°C.

Federal Aviation Administration (FAA/CAMI) toxicity test method

The toxicity of the thermal degradation products from various aircraft cabin materials, including a fire retarded polyethylene flotation cushion, has been evaluated by Crane *et al.* using the FAA toxicity test method.[46] This test method utilizes a static system consisting of a tube furnace connected to an exposure chamber in which three rats are exposed in the whole-body mode for 30 min. The combustion products, generated from 0.75 g samples decomposed at 600°C, are recirculated between the furnace and the animal chamber during the exposure. Separate rotating activity wheels in which the rats are forced to run or walk continuously are used to determine the time to incapacitation (T_i) and time to death (T_d). Rats are considered incapacitated when they start to slide or tumble in the rotating cages and dead when visible respiration ceases. When the animals were exposed to the combustion products from a fire retarded rigid polyethylene foam the mean observed response times for T_i and T_d were 6.66 ± 0.85 min and 10.26 ± 0.62 min, respectively. For comparison purposes, Crane *et al.* converted the observed response times to 'standard' response times (i.e. the values were normalized to a 200 g rat and 1.000 g fuel load). The normalized values were 5.25 min for T_i and 8.08 min for T_d. That the 'standard' T_i value for this polyethylene foam was within the range of T_i values (4.29 to 5.55 min) determined for six other commercial foams is an indication that the toxicity of this polyethylene was about equal to that of other foams used for the same end purpose.[46]

The FAA/CAMI screening test method was also used by Hilado *et al.* to evaluate a series of materials and to compare the test results with those obtained by the USF test method.[47] The sample evaluated was a low-density polyethylene (referred to as PE 1 above). All animals died when a 0.75 g sample of the polyethylene was decomposed at 600°C. The average times to incapacitation and to death were 4.88 ± 0.29 min and 8.03 ± 0.08 min, respectively. About 10 000 ppm of CO were detected in the exposure atmosphere. This polyethylene produced the most toxic degradation products when compared with three other materials tested according to the FAA/CAMI method (i.e. in degree of toxicity, polyethylene > polycarbonate > ABS > polystyrene). In contrast, this polyethylene ranked third when tested with the USF method using the rising temperature program (40°C min^{-1} from 200 to 800°C) with no forced air flow.[47]

The Dow Chemical Company test method

Potts *et al.* studied the toxicity of several polyethylene formulations decomposed under non-flaming (oxidative pyrolysis) and flaming conditions.[26] The test method employed was developed by the Dow Chemical Company specifically to evaluate smoke toxicity.[48] Rats were exposed for 30 min in a whole-body mode to degradation products generated in a quartz cup furnace located within the exposure chamber. All the smoke generated in the furnace was kept in the exposure chamber (i.e. static system). The rats were observed for any abnormal symptoms (e.g. irritation, breathing irregularity and nasal discharges) and mortality. LC_{50} values (the concentration of material consumed ($mg\,l^{-1}$) that caused 50% of the animals to die) were calculated for deaths that occurred during the 30 min exposure and a 14 day post-exposure period. The chamber atmosphere was analyzed for CO, CO_2 and O_2 by GC and for acrolein by GC/MS and colorimetric methods using a spectrophotometer.

Toxicity experiments were performed on three commercial samples of polyethylene (ETHAFOAM 220 foam, XFS4101 foam (which was fire retarded), and DOW 520 pellets).[26] Three to six gram samples decomposed in the flaming mode produced signs of abnormal behavior and deaths during the 30 min exposures (no rats died during the 14 day post-exposure period). In these experiments the average CO concentrations ranged from 1500 ppm to 4100 ppm, O_2 levels from 11% to 15% and acrolein concentrations from 3 to 23 ppm. The lethalities were attributed to CO poisoning together with marked oxygen depletion.

The non-flaming experiments, which were carried out at temperatures just below the auto-ignition temperatures of the polyethylene samples (0.35 to 2 g), produced signs of breathing difficulties and eye irritation. Lethalities occurred only during the post-exposure period (in most cases, within 16 to 48 h). In these experiments the average CO concentrations ranged from 100 to 2200 ppm, acrolein concentrations were between 19 to 155 ppm, while O_2

levels remained above 19%. Gross pathologic examinations of the animals showed lesions in the upper and lower respiratory system. The lethalities were attributed principally to the concentrations of acrolein in the exposure atmosphere. To verify that the levels of acrolein measured in these experiments can cause deaths as a result of a 30 min exposure, Potts *et al.* conducted control exposures to acrolein in air. Since the LC_{50} for acrolein was determined to be in the range of 45–95 ppm and most of the lethalities occurred within 24–48 h following the exposure, it seems reasonable to assume that the acrolein played a major role in the deaths of the rats.[26]

The polyethylene foams examined by Potts *et al.* were found to be more toxic in the non-flaming mode than in the flaming mode (Table 13). (No LC_{50} values were calculated for exposures with polyethylene sample DOW 520.) When compared with cellulosic materials tested by the same method in the flaming mode the decomposition products from these polyethylenes (LC_{50} (30 min + 14 day) values of 35 and 31 $\mathrm{mg\,l^{-1}}$) were found to be about as toxic as those from wood (LC_{50} (30 min + 14 days) = 35.0 $\mathrm{mg\,l^{-1}}$), whereas, in the non-flaming mode the decomposition products from these polyethylenes (LC_{50} (30 min + 14 day) values of 6 and 5 $\mathrm{mg\,l^{-1}}$) were more toxic than those from wood (LC_{50} (30 min + 14 days) = 22 $\mathrm{mg\,l^{-1}}$). In contrast, the toxicity of a polyethylene wire insulation in the non-flaming mode as determined by Levin *et al.* using the National Bureau of Standards (NBS) toxicity test method[49] appeared to be much less toxic than that found by Potts *et al.* The results of Levin *et al.* showed a non-flaming LC_{50} (30 min + 14 day) value greater than 75 $\mathrm{mg\,l^{-1}}$.[50] The difference in the results of Levin *et al.* and those of Potts *et al.* indicate that the high toxicity of the foams examined by Potts *et al.* are not necessarily characteristic of polyethylenes in general.

Potts *et al.* also found that the acrolein concentrations from the non-flaming decomposition of wood were lower than those formed from these polyethylenes (e.g. 43 ppm for a 6 g sample of wood versus 155 ppm for a 2 g sample of polyethylene).[48] Therefore acrolein may be contributing to the post-exposure deaths from these polyethylenes.

Polyethylenes produce high concentrations of acrolein only over a narrow temperature range. Decreasing the pyrolysis temperature 40°C below the autoignition temperature reduced the acrolein concentrations from a 5 g sample of polyethylene to < 2 ppm and produced no deaths. Closer to the autoignition temperature, 65 to 97 ppm of acrolein were generated and all the test animals died. Potts *et al.* point out that since polyethylenes are lethal over the very narrow pyrolysis temperature range of approximately 40°C, the time in which lethal effects can be produced in real fire situations is probably very short.

Table 13. **LC_{50} values calculated for different polyethylene foams decomposed by the Dow Chemical Company Test Procedure[26]**

Sample	Combustion mode	LC_{50} ($\mathrm{mg\,l^{-1}}$)	95% Confidence limits ($\mathrm{mg\,l^{-1}}$)
ETHAFOAM 220	F	~35	34–41
XFS4101 (FR)	F	31.3	29.3–33.3
ETHAFOAM220	NF	5.3	4.4 -6.6
XFS4101 (FR)	NF	~6.1	5.3 -6.9

F: Flaming.
NF: Non-flaming.

Large-scale tests

The hypothesis of Potts *et al.* was examined in large-scale tests where approximately the same sample weight of polyethylene per room volume ratio (13.6 $\mathrm{mg\,l^{-1}}$) noted to produce 100% rat mortality in the Dow small-scale test was decomposed.[24] In the first series of experiments, blocks of the same polyethylene foams, ETHAFOAM 220 and XFS-4101 (FR), were decomposed by radiant heat fluxes ($\geqslant 25\,\mathrm{kW\,m^{-2}}$) either under flaming or non-flaming conditions in a 70 $\mathrm{m^3}$ room. Rats were exposed to the smoke in rooms adjacent to the burn room. In the large-scale non-flaming tests only 5% of the foam was consumed and in the flaming experiments only about one third of the foam was decomposed. The concentration of acrolein in the vicinity of the rats was less than 10 ppm for the flaming tests and less than 5 ppm for the non-flaming tests. The exposed rats showed no ill effects in either case.

In a second series of tests, approximately 18 kg (40 lb) of the same two polyethylene foams were burned in the flaming mode in a building of about 1000 $\mathrm{m^3}$ in volume. Rats were placed in the building and were exposed to the combustion products from the fire for a total time of 30 min. The small amount of acrolein (less than 15 ppm) produced no ill effects in the rats. Heat blisters were noted at the edges of rats' ears due to temperatures which briefly reached 60–80°C.[24] The investigators concluded that the acrolein concentrations produced in certain 'real' fires involving polyethylenes would probably not constitute a significant hazard.

To evaluate whether polyethylene-based materials pose an unreasonable hazard in a 'real' fire Kuhn *et al.* studied the production of the toxic gases, CO and acrolein, from polyethylene foams decomposed under both non-flaming and flaming conditions in full-scale fire tests not involving animals.[24] In the first series of experiments about 320 kg (710 lb) of the same two brands of polyethylene, ETHAFOAM 220 and XFS-4101 (FR), were burned in a building of about 1000 $\mathrm{m^3}$ in size. The fire, after becoming well developed, was extinguished with water. The concentration of acrolein, which was measured in the burn room prior to the extinguishment, was estimated to be less than 15 ppm for both foams. (The presence of soot may have interfered with the spectrophotometric colorimetric technique used.)

In the second series of tests the relative hazard of acrolein in full-scale tests was compared to that of CO. One to nine cartons (each containing approximately 50 lb) of the same two brands of polyethylene were burned in a 34 $\mathrm{m^3}$ room connected to a corridor. The maximum concentrations of CO and acrolein detected in the corridor were 14 000 ppm and 15 ppm, respectively. The LC_{50} (30 min and 14 day) value for CO as determined for CO in rats is 4600 ppm[25] and that for acrolein is in the range of 45–95 ppm.[26] Other studies of 5 min exposures of baboons to acrolein in air showed that 500 ppm produced no deaths either during or following the exposures whereas concentrations of about 1000 ppm produced some post-exposure deaths.[27] Therefore the large-scale test results suggest that the acrolein concentrations generated in 'real' fires involving polyethylene foams were not toxicologically significant whereas the levels of CO are of toxicological concern.

Miscellaneous Tests

Gad and Smith used a test method developed at the Carnegie–Mellon Institute of Research (CMIR) to evaluate the influence of heating rates on the toxicity of the decomposition products from a HDPE.[51] The experimental procedure involved exposing the whole-bodies of rats to the thermal degradation products generated in a furnace heated by a radiant IR source. The furnace and the exposure chamber were interconnected so that the animals received a static exposure. CO and CO_2 were monitored during the exposure by IR and the total hydrocarbons were measured by flame photometry. A motor-driven rotating activity wheel was used to determine incapacitation and lethality. The LC_{50} and IC_{50} values (the concentrations that killed or incapacitated 50% of the test animals exposed for 30 min) were based on the weight of the polyethylene sample volatilized.

Six rats were exposed for 30 min to the decomposition products from HDPE samples heated at rates of 20°, 30°, 40° and $50°C\,min^{-1}$ starting from an ambient temperature of 25°C. The polyethylene flamed early when exposed to the higher heating rates (40° and $50°C\,min^{-1}$). The experimental results were influenced by the change in heating rate as well as by the mode of combustion. The production of CO increased as the heating rate increased (e.g. the maximum CO concentration from a 2 g sample increased from 800 ppm at $20°C\,min^{-1}$ to 7300 ppm at $50°C\,min^{-1}$). However, much more of the sample was decomposed at the higher heating rates. A similar trend was observed for total hydrocarbons.

The LC_{50} and IC_{50} results calculated for 30 min exposures at different heating rates in both the flaming and non-flaming modes are summarized in Table 14. In the non-flaming mode the toxic effect of the combustion products from the polyethylene increases slightly (lower value indicates increased toxicity) at the higher heating rates. In the flaming mode the combustion products from the polyethylene appear to be less toxic as the LC_{50} values increased by almost a factor of two over the non-flaming results at the lower heating rates. In most cases the lethalities appear to be attributable to the CO concentrations. Comparing the polyethylene results and those of Douglas fir, Gad and Smith concluded that over the range of experimental conditions the combustion toxicity of this HDPE was not greater than that of Douglas fir, a reference material commonly used for comparison.

Table 14. Influence of heating rates on the toxicity of combustion products from a polyethylene[51]

	Polyethylene		Douglas fir	
Heating rate[a]	LC_{50}^{b} ($mg\,l^{-1}$)	IC_{50}^{b} ($mg\,l^{-1}$)	LC_{50} ($mg\,l^{-1}$)	IC_{50} ($mg\,l^{-1}$)
20	25.2	10.6	43.0	33.5
30	24.7	9.6	38.5	19.9
40	48.4[c]	< 12.4[c]	39.3	19.6
50	51.2[c]	< 19.6[c]	21.5	14.8

[a] °C per minute from 25°C.

[b] Value calculated on basis of material volatilized during the 30 min exposures.

[c] Flaming experiments.

Kishitani and Nakamura used a dynamic system and time based animal model (similar to that employed by other Japanese research groups) to evaluate the toxicity of combustion products of building materials.[52] A polyethylene was decomposed in a tube furnace at 350°, 500° and 750°C (temperatures to which materials would be subjected during the initial stages of a fire). Flaming occurred at 750°C. One mouse at a time in a whole-body mode was exposed to the combustion products in an adjacent chamber for 15 min, a period which was estimated as the time required to evacuate a multi-storied building. Surviving mice were kept and observed for one week following the tests. A vibration sensor during the exposures was used to detect movement of the mouse. Time of death in minutes or days, as indicated by the cessation of respiration, was the biological endpoint.

The maximum concentrations of CO generated by the degradation of 10 g samples of a polyethylene were 6500 ppm at 350°C, 3900 ppm at 500°C and 1800 ppm at 750°C. No deaths occurred from the exposure to the 750°C (flaming) combustion products, but all mice died from the non-flaming combustion products generated at 350°C and 500°C. All those deaths, except one, occurred 1–3 days following the exposure. The one lethality occurred at 14 min during the exposure at 350°C. The authors proposed that the post-exposure deaths were caused by various hydrocarbons known to be generated from polyethylene decomposed in the temperature range of 350–500°C.[52]

SUMMARY

In this report a review has been made of the chemical nature and toxicity of the volatile products generated during combustion of polyethylenes. The thermal degradation products from polyethylenes are largely dependent upon the temperature and oxygen availability. In the absence of oxygen, a mixture of primarily n-alkanes and l-alkenes are produced. In the presence of oxygen, additional oxygen-containing organic compounds (mostly low-molecular-weight aldehydes and carboxylic acids) are formed. Among the great number of gaseous products identified, CO appears to be the predominant toxicant. Non-flaming combustion also favored the production of acrolein and other irritant gases. Flaming combustion favored the production of CO_2, hydrocarbons, and aromatics. Under restricted flaming with limited O_2 content, production of CO increased with increasing temperature.

The toxicity of the combustion products from polyethylenes has been examined by seven different test procedures. Most of these test methods evaluated the toxicity by determining the numbers of animals affected and times to incapacitation and death without developing quantitative concentration–response relationships. In general, polyethylenes are more toxic in the non-flaming mode than in the flaming one. The toxicity in the non-flaming mode increases with temperature and air supply. It is also greater when the material is decomposed with a high

constant temperature than with a rising temperature program.

The HDPE LC_{50} values for 30 min exposures (no post-exposure period) were about 25 mg l^{-1} in the non-flaming mode and about 50 mg l^{-1} in the flaming mode according to the Carnegie–Mellon Institute of Research test method.[51] The LC_{50} values of the polyethylene foams calculated for 30 min exposures and 14 day post-exposure periods were about 5 mg l^{-1} in the non-flaming mode and about 35 mg l^{-1} in the flaming mode according to results obtained by the Dow Chemical Company test method.[26] The 30 min and 14 day post-exposure LC_{50} value for polyethylene wire insulation in the non-flaming mode was greater than 75 mg l^{-1} when determined by the NBS toxicity test method.[50] Since acrolein is produced in the non-flaming mode and most deaths are postexposure, many studies have examined the production of acrolein. However, it is not clear whether the post-exposure deaths are due to acrolein alone or if additional irritant gases ought to be examined. The difference in the LC_{50} values in the non-flaming mode probably reflects the differences in the test methods and sample variability.

The only available comparative study of full-scale versus bench-scale experiments suggests that small-scale testing may produce toxicity results which overestimate those found under full-scale testing. Since numerous full-scale scenarios may be envisioned and only one has been studied, these findings may have only limited applicability.

The results presented in this review show that the toxicity of the combustion products from various samples of polyethylenes are not highly or unusually toxic.

Acknowledgements

The authors gratefully acknowledge the help of Ms N. Jason, Ms M. Diephaus, Ms A. Durham and Ms C. S. Bailey who performed the literature search and compiled the references. This study was supported in part by the Consumer Product Safety Commission. Dr Rita Orzel was project officer under NBS contract No. 753–1386 (CPSC Task Order No. 84–8).

NOTE

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[a] It should be noted that the use of colorimetric tubes, such as Draeger tubes, provides unreliable and, at best, semiquantitative results, primarily because other combustion gases may interfere in the analysis. The temperature of the gas being sampled also has been noted to have an effect on the results.[31]

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