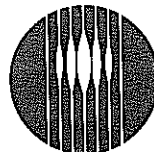


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# A SURVEY OF THE TOXICITY OF THERMAL DECOMPOSITION PRODUCTS OF EXPANDED POLYSTYRENE

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**CSIRO**  
AUSTRALIA

Division of Building, Construction and Engineering

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**A survey of the toxicity of thermal decomposition products of expanded polystyrene**

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## EXECUTIVE SUMMARY

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Expanded polystyrene has come to be a common building material. Because of its low cost, very low density and easy mouldability, it has become one of the most popular insulation materials in the building industry, especially in commercial buildings. However expanded polystyrene is a combustible material. It will burn in the presence of a flame. The addition of fire-retardant additives will reduce the likelihood of ignition occurring, or the amount and rate of burning once ignition has occurred. Nevertheless, in the event of a fire, expanded polystyrene will burn, or in the absence of direct flame contact, undergo thermal decomposition. In either case the expanded polystyrene will break down, emitting gases that will contribute to the fire atmosphere. The aim of this technical report is to survey the literature on thermal decomposition and combustion products of expanded polystyrene and to assess their contribution to the toxic hazard of fires. Over 100 papers are referenced, including some previous reviews covering similar areas.

The report is in several sections. The first section covers literature on thermal decomposition and combustion products of polystyrene and identifies the major species produced. It finds that carbon monoxide and carbon dioxide are the major species produced, whilst depletion of oxygen always occurs in fires. Styrene monomer is the major organic species produced, especially in poorly ventilated fires. Over 50 other species have been identified from the thermal decomposition of polystyrene, though many only in trace amounts.

The second section of the report surveys the literature on the combustion toxicity of polystyrene. The major combustion toxicity tests are listed, but are not analysed in detail. All the tests use animals, usually rats or mice. Data on the combustion toxicity of polystyrene in the various tests is compared with that for other materials. As the combustion toxicity tests vary in many ways, they do not all produce the same ranking of materials with regard to *toxic potency*. Generally, in combustion toxicity tests where flaming did not occur, polystyrene had *toxic potency* to animals lower than that of wood, whilst in combustion toxicity tests where flaming did occur, polystyrene had a *toxic potency* to animals equal to or higher than that of wood. It is also noted that the *toxic hazard* of a material is a combination of *toxic potency* and other fire behaviour characteristics, such as ease of ignition and burning. Studies which attempted to assess the *toxic hazard* of materials gave standard expanded polystyrene a *toxic hazard* less

than or similar to wood. Some workers are developing toxicity indexes, which are models to sum toxicities of individual combustion products, thereby reducing the need for animal tests in the future. These models predict that the toxicity of combustion products of polystyrene will be determined solely by the concentrations of carbon monoxide, carbon dioxide and oxygen.

Finally, there is a small section on fire deaths. Whilst none of the studies cited specifically mentions polystyrene, or any other material, they all conclude that most deaths in fires from smoke inhalation are caused by carbon monoxide, the major toxic species produced in all fires.

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**KEYWORDS:** Building fires, expanded polystyrene, combustion products, toxicity, thermal decomposition.

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# INTRODUCTION

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The name 'polystyrene' designates a family of plastics derived essentially from styrene, which is produced from two products of petroleum refining—ethylene and benzene. Pure polystyrene is a clear colourless amorphous solid.

Expanded polystyrene is made by introducing a blowing agent (usually pentane) into beads of polystyrene. Both moulding and extrusion processes can be used to turn these expandable beads into the final product. In the moulding process, the beads are heated with steam and the polystyrene, being thermoplastic, softens. The absorbed blowing agent vaporises, expanding the beads to about fifty times their original volume. These foamed beads are placed in the required mould and heated again where further expansion occurs, producing the characteristic 'beadboard' structure of moulded expanded polystyrene (PIA 1992).

For the extrusion process, the same expandable beads, incorporating an additional blowing agent, are melted in the extruder. When the molten mix leaves the extruder die head, foaming occurs to produce a continuous sheet of extruded expanded polystyrene (PIA 1992).

Expanded polystyrene has excellent thermal insulating properties, and it is as thermal insulation in buildings that the majority of the material is used, whilst use as packing and display material is also common (Klepik 1990).

Polystyrene is a combustible material, and whilst addition of fire-retardants can reduce its flammability, fire retarded grades are still combustible. Polystyrene softens at about 100°C (Schwarz 1990), and melts and flows at 180°C. Thermal decomposition begins at about 270°C (Pfaffli *et al.* 1978), although Edgerley (1980) has found small amounts of thermal decomposition products at 260°C, which is the maximum recommended processing temperature for extruded polystyrene. Ignition in the presence of a pilot flame can occur at about 350°C and ignition without a pilot flame at about 490°C (Hilado 1990; Troitzsch 1990).

All building grades of expanded polystyrene produced in Australia contain fire-retardant additives sufficient for the material to meet the requirements of the relevant parts of Australian Standard 1366-Part 3 (SAA

1992), the Standard for moulded expanded polystyrene, and AS 1366-Part 4 (SAA 1989), the Standard for extruded expanded polystyrene. Expanded polystyrene must also meet the general requirements for materials of the Building Code of Australia (AUBRCC 1991) when used in buildings of Classes 2-3 and 5-9. (There are no requirements for Classes 1, 4 and 10.) Building-grade expanded polystyrene is found in coolroom panels and other sandwich panel applications; as in-ceiling and in-wall insulation; and in various forms associated with concrete construction and formwork.

A number of literature surveys have been written on the thermal decomposition products of plastics and their toxicity. These usually include polystyrene, but it is usually solid polystyrene rather than expanded polystyrene that is discussed. Whilst the base resin may be the same in both cases, the different additives in, and structure of, expanded polystyrene can result in a different burning behaviour, and hence can result in different combustion products, or different yields of combustion products. As polystyrene melts at about 180°C, it is liquid polystyrene which undergoes thermal decomposition and combustion. Nevertheless, the original form may affect the fire behaviour of the material. Therefore some caution should be taken when using data from solid polystyrene to assess the likely combustion products of expanded polystyrene.

In the studies surveyed many different experimental set-ups have been used, and the terms describing the nature of the experiments vary widely, and not particularly consistently. Hence we have 'thermal decomposition', 'thermal degradation', 'thermo-oxidation', 'pyrolysis', 'flame combustion', 'combustion', 'flaming', 'non-flaming', 'smouldering' and 'fire' being used in various papers. In this report 'thermal decomposition' will be used as the general term, and 'combustion', either 'flaming' or 'non-flaming', will be used only for those experiments where it is clear that combustion is indeed occurring. The term 'fire' will only be used in relation to experiments in which the only heat source is from the combustion of materials in the experiment, or when referring to fires 'at large'.

Terms used in combustion toxicology include 'toxicity', 'toxic potency' and 'toxic hazard'. The term 'toxicity' means the propensity of a substance to produce adverse

biochemical or physiological effects (ASTM 1992), whilst 'toxic potency' is a quantitative expression of that propensity. The 'toxic hazard' of a material in a fire is a function both of the toxic potency of its combustion products and of its fire behaviour characteristics, such as ease of ignition and burning.

A further source of confusion in terminology arises in the differing uses of the word 'smoke' in different countries. In Australia smoke means a *visible* suspension of solid or liquid particles or gases resulting from combustion (SAA 1990). In America, the term 'smoke' includes all combustion gases; whether visible or not (ASTM 1992), and hence writers sometimes refer to 'toxicity of smoke'. The term 'toxicity of combustion products' will be used in this report.

There have been previous literature surveys on the combustion products of polystyrene. In 1963, Underwriters' Laboratories published a Bulletin of Research (Dufour 1963) which surveyed information on toxicity of combustion and thermal decomposition products of building products, including solid polystyrene. A CSIRO report by Nicholl and Martin (1977) surveyed literature on the toxicity of combustion products of cellular plastics, including expanded polystyrene. They

included data on combustion products, toxicity of individual gases, toxicity of combined combustion products and test procedures. More recently, Gurman *et al.* (1986) at the National Bureau of Standards (NBS; now the National Institute of Standards and Technology—NIST) published a review of the literature on the toxicity of combustion products of polystyrene. Their extremely comprehensive paper covers the English language literature up until 1984. The paper surveys literature on both solid and expanded polystyrene under a range of experimental environments, and is arranged by experimental method, with thermal decomposition methods followed by toxicity assessment methods.

In this Technical Report, literature on gases produced by the thermal decomposition of expanded (and solid) polystyrene and the toxicity of thermal decomposition products is surveyed, and comparisons with other building materials are made. Literature on deaths in fires is also included. This report uses the CSIRO (Nicholl & Martin 1977) and NBS (Gurman *et al.* 1986) reports as resource materials, and includes readily available additional material up to 1993. To facilitate comparisons between data sets, the units and chemical nomenclature used have been standardised as far as possible.

## THERMAL DECOMPOSITION PRODUCTS OF EXPANDED POLYSTYRENE

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Styrene is a hydrocarbon, and hence contains only the elements carbon and hydrogen. Pure polystyrene likewise contains only carbon and hydrogen. If pure polystyrene were to undergo complete combustion, its only products of combustion would be carbon dioxide and water vapour. However, fires are always incomplete combustion, which means that, in practice, carbon monoxide and soot are also major products of combustion of polystyrene, as they are of all other combustible materials. Many other combustion products are also produced, varying in quantity by many orders of magnitude. The exact composition of the combustion products will depend on the particular grade of polystyrene, the additives included, and factors dependent on the fire or test scenario (e.g. temperature and oxygen availability).

Polystyrene does not contain chemically bound nitrogen or chlorine, so its combustion products do not normally include nitrogen-containing species such as cyanide or nitrogen oxides, or chlorine-containing species such as hydrogen chloride. Chlorine may be present in fire-retardant additives in some cases.

The role of fire-retardant additives is to delay or prevent ignition, and to reduce the rate of combustion if ignition occurs. Therefore any assessment of combustion products should take into account decreased combustion due to the presence of fire-retardant additives.

There have been many studies on the thermal decomposition of polystyrene (Gurman *et al.* 1986). These usually involve placing small specimens in a furnace or other heating device under controlled temperature conditions. The atmosphere is also controlled, and may vary from a vacuum to an inert atmosphere to an oxidative atmosphere, such as air. These thermal decomposition experiments are not always meant to represent fire scenarios. They may be designed to give data on thermal decomposition products relevant to a particular situation or to a specific stage in a fire\*. Only by considering all relevant data can a picture of the likely combustion products of polystyrene in building fires be gained from laboratory experiments.

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\* For a discussion of the various stages of fires, see Drysdale (1985), Ch. 9, The Pre-flashover Compartment Fire.

The thermal decomposition of polystyrene is firstly a depolymerisation process, producing primarily styrene, either as the monomer, dimer or trimer (Gurman *et al.* 1986; Mitera & Michal 1985). In the presence of flame, these gases can ignite and burn, producing simpler compounds, including carbon dioxide, carbon monoxide and water vapour. In fires, the availability of oxygen is dependent on the fire scenarios. If the atmosphere is depleted of oxygen, less oxidation occurs, and the species produced more resemble those obtained in thermal decomposition experiments in inert atmospheres.

Experiments performed with a plentiful supply of oxygen are most relevant to the early stage of a fire, probably up to the occurrence of flashover. Those done in reduced oxygen or inert atmospheres are more relevant to post-flashover fires. Thermal decomposition studies are also relevant to those situations where heat from a fire causes decomposition of expanded polystyrene in the absence of direct flame contact, or when smouldering combustion occurs.

### Oxygen depletion

The atmosphere contains 21% oxygen, and because fires consume oxygen, fire atmospheres generally contain less than 21% oxygen. Therefore reduction in oxygen, or 'oxygen depletion', is always a result of combustion. The extent of oxygen depletion depends on the amount of material combusted, and on the available supply of oxygen.

Thermal decomposition studies generally do not measure oxygen depletion. However, information on oxygen depletion can be obtained from studies that attempt to simulate fire scenarios. At the Fire Research Institute, Japan, Morikawa and Yanai (1989) conducted combustion studies on the burning of foam plastics in an enclosure 2 × 2 × 2 m with an exhaust duct. Inside this enclosure a plywood open-ended box was constructed, with three walls 0.9 × 1.6 m, and a ceiling 0.9 m square. The foam plastic specimens, including expanded polystyrene, were mounted as internal linings on one side wall of the plywood box. The fire source was a 200 g wood crib placed in the corner opposite the foam plastic wall lining. The air inflow into the room was controlled to either 2.9, 3.8 or 5.8 m<sup>3</sup>/min for each

experiment. Combustion gases were measured in the exhaust duct. The materials examined were polyisocyanurate, rigid polyurethane, phenolic and polystyrene foams, and plywood. It was not reported whether any contained fire-retardant additives. It was found that, for all the materials examined, as the measured exhaust temperature increased in response to fire growth, the concentration of O<sub>2</sub> decreased. In this study the data does not show any discernible difference in oxygen depletion between polystyrene foam and the other materials examined, including plywood. However, all specimens contained more plywood than foamed plastics, and the data does not make clear what amount of plywood was involved in the combustion in each experiment.

Larger scale experiments were carried out by Fardell *et al.* (1986) at the Fire Research Station, UK. They conducted their experiments in a room/corridor facility, in which a room 3.3 × 3.0 × 2.4 m high was connected, via a doorway of variable dimensions, to an open-ended corridor 1.17 m wide, 2.4 m high and 11.4 m long. The materials assessed were pine (*pinus sylvestris*), polymethylmethacrylate, polypropylene and expanded polystyrene. None of the materials contained fire-retardant additives. The first three materials were burnt as 40 kg 1.0 × 1.0 × 0.25 m cribs, comprising sticks 25 mm square (10 sticks per layer), whilst the expanded polystyrene was burnt as 27 kg 1 m<sup>3</sup> blocks. The three plastics materials were reduced to a liquid pool fire within the first five minutes of each test.

Combustion gases were measured at two points in the corridor—immediately outside the burn room door, and at the far end of the corridor. The purpose of the work was to obtain 'fingerprints' of the combustion products of the materials tested, consisting of organic compounds. They also measured oxygen, carbon dioxide and carbon monoxide. As a smaller quantity of expanded polystyrene than of the other three materials was used, caution must be used when making comparisons between them. No data on mass loss rates is given. Data on instantaneous oxygen concentrations at high and low ventilation rates, during the growth, steady state and decay stages of the fires is shown in Table 1.

The results show that in the growth stage of the fires, expanded polystyrene consumes more oxygen than pine, but in the steady state and decay stages, expanded polystyrene consumes less oxygen than pine. This suggests that the majority of expanded polystyrene was consumed in a more rapid growth stage, and that a smaller proportion of material remained for the steady state and decay stages, compared with pine.

Recently fire tests that employ oxygen consumption calorimetry have been developed. These methods, such

Table 1. Oxygen concentration in combustion gases during growth, steady state and decay stages of fires with fuel loads of single materials in a room/corridor facility (after Fardell *et al.* 1986)

Fuel load		Oxygen concentration (%) <sup>a</sup>		
Material <sup>b</sup>	Mass (kg)	Fire stage		
		Growth	Steady state	Decay
<i>High ventilation (large opening)</i>				
Expanded polystyrene	27	7.2	16.2	19.6
Polymethylmethacrylate	40	13.0	9.8	14.2
Polypropylene	40	15.8	2.0	15.2
Pine	40	19.1	3.0	13.4
<i>Low ventilation (small opening)</i>				
Expanded polystyrene	27	10.3	9.6	14.0
Polymethylmethacrylate	40	7.8	6.8	17.0
Polypropylene	40	15.2	6.2	6.0
Pine	40	17.3	6.2	9.3

<sup>a</sup> Ambient = 21.0%.

<sup>b</sup> None contained fire-retardant additives.

as the cone calorimeter (Babrauskas 1982), measure oxygen consumption from burning materials primarily to calculate rate of heat release. As the methods become widely used, data on many materials is being accumulated. Whilst oxygen concentrations are not presently included in published results, 'toxicity index' approaches presently being developed (see later) will make use of oxygen depletion data determined in such methods.

### Carbon monoxide

Studies both on thermal decomposition in oxidative environments and combustion of polystyrene generally measure carbon monoxide. As polystyrene contains no chemically bound oxygen, thermal decomposition studies in vacuum or inert atmospheres usually do not measure carbon monoxide. Brauman (1979) has shown that the yield of carbon monoxide during combustion of polystyrene, and other plastics, depends on factors such as burning rate and the presence of fire retardants.

Sumi and Tsuchiya (1971) heated specimens of white pine (sawdust pellets) and expanded polystyrene (no fire retardant) at 800°C in sealed 5 L flasks containing air. Sample masses were not equal but were chosen to determine the maximum yield of carbon monoxide (grams of carbon monoxide per gram of sample) obtainable in each case. Their results (Table 2) show similar maximum yields of carbon monoxide for white pine and expanded polystyrene, though these occurred at different sample loadings.

Table 2. Carbon monoxide and carbon dioxide produced by heating expanded polystyrene and white pine to 800°C in 5 L flasks of air (after Sumi & Tsuchiya 1971)

Material	Sample mass (g)	Carbon monoxide (g/g)	Carbon dioxide (g/g)	Residue (g/g)
Expanded polystyrene	0.298	0.36	2.36	0
	0.296	0.27	2.94	0
	0.350	0.44	1.94	0.01
	0.351	0.45	1.93	0.01
	0.400	0.46	1.54	0.01
	0.406	0.41	1.49	0.01
	0.498	0.39	1.21	0.01
	0.497	0.40	1.16	0.01
	0.599	0.35	1.09	0.02
	0.604	0.32	1.03	0.02
White pine	0.800	0.24	0.86	0.13
	0.799	0.25	0.84	0.13
	1.007	0.35	0.90	0.13
	0.999	0.36	0.92	0.14
	1.194	0.45	0.55	0.13
	1.197	0.44	0.57	0.14
	1.606	0.41	0.54	0.14
	1.600	0.43	0.53	0.14

Pfaffli *et al.* (1978) studied the thermal decomposition products of polystyrene in air. They were attempting to simulate industrial processing conditions rather than combustion. Samples (0.1 g) of the polystyrene (Stymer PS-RH; no additives) were degraded in a thin (4 mm ID) J-shaped open-ended glass tube (3.8 mL) in an oven. Air was drawn through the tube at 700 mL/min for 15 minutes. They conducted experiments at 200, 350 and 500°C. No flaming was reported. Under these conditions, they found only trace amounts of carbon monoxide (carbon dioxide was not measured), but at higher levels at 500°C than at 350 or 200°C.

Morimoto *et al.* (1976) used a vertical tube furnace in studies on the combustion products of a range of polymers. The 366 mL combustion tube had an inlet near the base and outlet at the top of the tube, allowing air to flow through upwards at 830 or 1660 mL/min. The tube furnace was preheated to 700°C prior to the 0.1 g specimen being inserted onto a bed of quartz beads. A gas collection system allowed the total combustion products to be collected for later analysis. The materials examined (Table 3) were polymers, including polystyrene, and cedar. All these materials underwent flaming combustion. The polymers were all commercially available resins which did not contain any additives. Data extracted from their results (Table 3) show that under the well-ventilated conditions of the experiments, polystyrene produced similar yields of carbon monoxide to a number of other polymers, but

Table 3. Carbon monoxide and carbon dioxide produced by flaming combustion of 0.1 g samples of materials at 700°C in a vertical tube furnace (after Morimoto *et al.* 1976)

Material	Gas yield (g/g)	
	CO	CO <sub>2</sub>
<i>Airflow rate 830 mL/min</i>		
Polystyrene	0.207	0.590
Polyethylene	0.195	0.502
Nylon 66	0.194	0.563
Polyurethane (polyester; TDI)	0.160	0.630
Epoxy resin	0.228	0.961
Cedar	0.066	1.397
<i>Airflow rate 1660 mL/min</i>		
Polystyrene	0.178	0.619
Polyethylene	0.210	0.738
Nylon 66	0.205	0.590
Polyurethane (polyester; TDI)	0.173	0.666
Epoxy resin	0.153	1.138
Cedar	0.016	1.573

that all synthetic polymers produced more carbon monoxide than the cedar.

Michal (1981) studied the thermal decomposition of a number of polymeric materials including polystyrene foam (Krasten 336; density 40 kg/m<sup>3</sup>; no fire-retardant additives reported). He degraded 20–25 mg samples in a tube furnace in helium-oxygen mixtures. He also carried out flaming combustion studies in a 4.2 L combustion chamber to which the oxygen supply was restricted. Some of his results are shown in Table 4. In the thermal decomposition experiments, expanded polystyrene produced similar concentrations of carbon monoxide to those produced by ABS and polymethylmethacrylate, but lower concentrations than polyethylene. In the flame combustion experiments, expanded polystyrene produced less carbon monoxide than polymethylmethacrylate, polyvinylchloride, polycarbonate and rigid polyurethane foam, but similar amounts to the other plastics examined. Michal found that even under controlled laboratory conditions it is not possible to get good reproducibility in carbon monoxide production, and comparison of fire with laboratory tests can only be approximate.

In later work, Michal (1983a) used a 4.5 L two-chamber system, with separate combustion chamber and measurement chamber, to study the combustion products of polymeric materials. The two-chamber system had a steep temperature gradient between chambers and restricted air access. Carbon monoxide and carbon dioxide were analysed continuously in the measurement chamber. The prime purpose of the two-chamber system was to allow toxicity testing on animals, such as mice. In the experiments reported, 0.1–0.3 g samples of granules of various polymeric materials

Table 4. Carbon monoxide produced in thermal decomposition and flame combustion experiments (after Michal 1981)

Material	Carbon monoxide (%)			
	Thermal decomposition <sup>a</sup> of 20–25 mg samples 550°C		Flame combustion <sup>b</sup> 600°C <sup>c</sup>	
	Mean	Range <sup>d</sup>	Mean	Range <sup>d</sup>
Expanded polystyrene	0.38	0.33	9.86	4.40
Polyethylene	2.97	0.58	10.02	3.18
ABS	1.45	1.42	11.44	1.59
Polymethylmethacrylate	0.61	0.15	18.99	4.57
Polypropylene	—	—	10.16	1.29
Polyvinylchloride	—	—	15.04	6.35
Rigid polyurethane foam	—	—	14.12	3.21
Polycarbonate	—	—	16.48	1.36

<sup>a</sup> Called 'thermo-oxidation' in original paper; oxygen concentration not stated, flaming not stated.

<sup>b</sup> Air access restricted; sample size unknown.

<sup>c</sup> Known for polymethylmethacrylate; presumed for the other materials.

<sup>d</sup> Variation from lowest to highest result.

were degraded at fixed temperatures in crucibles in the base of the combustion chamber. The materials examined were polyethylene, polypropylene, solid polystyrene (Kraesten 127; no fire-retardant additives) and nylon 6. It was determined that, under these experimental conditions, non-flaming decomposition could take place at 500°C and flaming combustion at 600°C for all these materials. Michal found that in the non-flaming mode solid polystyrene had the lowest yield of carbon monoxide of these four polymeric materials. However in the flaming mode solid polystyrene had the same or slightly higher yield of carbon monoxide (depending on initial sample mass) as polypropylene and polyethylene, and a higher yield of carbon monoxide than nylon 6. Solid polystyrene showed the greatest increase in carbon monoxide production from non-flaming mode to flaming mode. This compares with polypropylene and nylon 6, which showed slight increases, and polyethylene which showed a marked decrease. No discussion of these results is provided.

On a far larger scale, Fardell *et al.* (1986), in their room/corridor burns (discussed previously) of expanded polystyrene and three other materials, reported instantaneous concentrations of carbon monoxide during the growth, steady state and decay periods of a fire (Table 5). Corresponding oxygen concentrations are given in Table 1.

Table 5. Carbon monoxide concentrations in combustion gases during growth, steady state and decay stages of fire with fuel loads of single materials in a room/corridor facility (after Fardell *et al.* 1986)

Material <sup>a</sup>	Fuel Load Mass (kg)	CO concentration (%)		
		Fire stage		
		Growth	Steady state	Decay
<i>High ventilation (large opening)</i>				
Expanded polystyrene	27	0.25	0.21	0.08
Polymethylmethacrylate	40	0.01	0.1	0.04
Polypropylene	40	0.12	2.9	0.7
Pine	40	0.01	2.3	0.15
<i>Low ventilation (small opening)</i>				
Expanded polystyrene	27	1.0	1.35	0.4
Polymethylmethacrylate	40	0.3	1.2	0.1
Polypropylene	40	0.022	0.8	1.5
Pine	40	0.09	4.0	0.6

<sup>a</sup> None contained fire-retardant additives.

In their experimental set-up, the combustion of expanded polystyrene produced more carbon monoxide than the other materials during the growth stage, but during the steady state and decay stages, expanded polystyrene produced less carbon monoxide than pine. This is consistent with the greater consumption of oxygen in the growth stage discussed earlier, and appears to confirm that the majority of expanded polystyrene was consumed in a rapid growth stage.

Tewarson (1988) has collated data on the yields of carbon monoxide and carbon dioxide produced in well-ventilated fires by various materials. His data (Table 6) is designed to be used in fire engineering calculations, and was derived from various sources. Some of the data is the average of measured values, some is calculated, and some is 'corrected' to well-ventilated conditions. The data for both fire-retarded and standard expanded polystyrene, and also for solid polystyrene are almost identical, and are among the higher figures for the materials listed, only those for epoxy, polyester and polyvinylchloride being higher. The carbon monoxide data for the three woods are an order of magnitude lower than that for the polystyrenes.

Tewarson's data for the production of carbon monoxide by polymeric materials is approximately an order of magnitude lower than that found in the thermal decomposition experiments of Sumi and Tsuchiya (Table 2) and Morimoto *et al.* (Table 3). The figures for wood are approximately two orders of magnitude lower than those obtained by Sumi and Tsuchiya (Table 2), under conditions designed to produce the maximum carbon monoxide yield, and an order of magnitude lower than those found by Morimoto *et al.* (Table 3).

Table 6. Typical yields of carbon monoxide and carbon dioxide from various materials in well-ventilated fires (after Tewarson 1988)

Material	Gas yield (g/g)	
	CO	CO <sub>2</sub>
<i>Cellular plastics</i>		
Expanded polystyrene, 16 kg/m <sup>3</sup> (GM-47) <sup>a</sup>	0.060	2.30
Expanded polystyrene, 16 kg/m <sup>3</sup> FR* (GM-49)	0.065	2.30
Extruded polystyrene, 34 kg/m <sup>3</sup> (GM-51)	0.058	2.34
Extruded polystyrene, 29 kg/m <sup>3</sup> FR (GM-53)	0.060	2.34
Rigid polyurethane foam, 32 kg/m <sup>3</sup> (GM-29)	0.031	1.52
Rigid polyurethane foam, FR (GM-31)	0.038	1.53
Rigid polyurethane foam, 64 kg/m <sup>3</sup> (GM-35)	0.025	1.58
Rigid polyurethane foam, 320 kg/m <sup>3</sup> (GM-37)	0.024	1.63
Polyisocyanurate foam, 32 kg/m <sup>3</sup> (GM-41)	0.046	1.18
Polyisocyanurate foam, 32 kg/m <sup>3</sup> (GM-43)	0.051	1.11
Polyethylene foam <sup>b</sup>	0.020	2.63
<i>Solid plastics</i>		
Polystyrene	0.060	2.33
Polyethylene	0.024	2.76
Polypropylene	0.024	2.79
Polymethylmethacrylate	0.010	2.12
Polyester	0.070	1.65
Epoxy	0.080	1.59
Nylon	0.038	2.06
Polyvinylchloride	0.063	0.46
<i>Woods</i>		
Red oak	0.004	1.27
Douglas fir	0.004	1.31
Pine	0.005	1.33

<sup>a</sup> GM designations identify standard reference materials (Products Research Committee 1980).

<sup>b</sup> Mean value for four polyethylenes.

In general the production of carbon monoxide is favoured by inefficient combustion, which can be due to lack of sufficient oxygen. In well-ventilated fires the production of carbon dioxide is favoured over the production of carbon monoxide. Tewarson (1990) has collated data which demonstrates that the yield of carbon monoxide increases with a decrease in fire ventilation. The lower yields of carbon monoxide quoted by Tewarson, as compared with the data of Sumi and Tsuchiya (Table 2) and Morimoto *et al.* (Table 3), are not accompanied by higher yields of carbon dioxide, which would be expected if ventilation was the only condition differing.

Mulholland *et al.* (1991) carried out experiments in a modified cone calorimeter in which the oxygen content

\* In this report the letters FR denote materials with fire-retardant additives.

of the environment could be altered. They found that for the materials tested (which included polymethylmethacrylate and Douglas fir, but did not include polystyrene) the carbon monoxide yields doubled when the oxygen concentration was decreased from 21% to 14%.

Whilst the production of carbon monoxide by the thermal decomposition of polystyrene is dependent on temperature and ventilation, other factors also play a role. These factors will include the grade and formulation of the polystyrene, and the particular experiment or fire scenario.

In the thermal decomposition studies in which polystyrene was heated to 500°C or more, it produced similar quantities of carbon monoxide to other plastics, but in most studies it produced more carbon monoxide than wood. In flaming combustion studies polystyrene likewise produced more carbon monoxide than wood, but similar quantities to other plastics. In the one study that compared production of carbon monoxide by fire-retarded and non-fire-retarded polystyrenes, both types have almost identical yields.

### Carbon dioxide

Carbon dioxide is produced by the combustion of all organic materials, including polystyrene. Carbon dioxide is naturally present in the atmosphere (typically 0.03%). Materials which contain a higher proportion of carbon will, if fully combusted, produce a higher yield of carbon dioxide, i.e. they will produce more grams of carbon dioxide for each gram of material burnt. The maximum possible yield of carbon dioxide for a number of materials is given in Table 7.

Table 7. The maximum possible yield of carbon dioxide obtainable from combustion of some materials, calculated from their chemical composition

Material	Carbon content (approx.) <sup>a</sup> (g/g)	Maximum yield of carbon dioxide (approx.) (g/g)
Polystyrene	0.91	3.3
Polyethylene	0.86	3.2
Polypropylene	0.86	3.2
Rigid polyurethane foam	0.65 <sup>b</sup>	2.4
Polymethylmethacrylate	0.60	2.2
Nylon 66	0.59	2.2
Wood (dry)	0.52 <sup>c</sup>	1.9
Polyvinylchloride	0.38 <sup>b</sup>	1.4

<sup>a</sup> Calculated unless otherwise stated.

<sup>b</sup> Babrauskas *et al.* (1991a).

<sup>c</sup> Fung (1984).

The amount of carbon dioxide produced in a fire is dependent on the amount of material combusted, and the availability of oxygen.

Sumi and Tsuchiya (1971), in their study of combustion products of wood and polystyrene (discussed earlier), measured the yield of carbon dioxide. Their data (Table 2) shows that under the conditions they selected (to produce the maximum carbon monoxide), the yield of carbon dioxide from polystyrene was about twice that for wood. This is what would be expected under free burning conditions, as polystyrene contains more carbon than wood (Table 7).

Morimoto *et al.* (1976) measured the carbon dioxide produced by a range of polymers, and wood, in their vertical combustion chamber (previously described). Their results (Table 3) show that polystyrene produced less carbon dioxide than wood, rather than more as might be expected (Table 7). This suggests that under this experimental set-up, polystyrene, and some of the other polymers, did not burn as completely as wood.

Michal (1983a) used his 4.5 L two-chamber system (described earlier) to compare the carbon dioxide produced by the combustion of 0.1–0.3 g samples of various polymers, including polystyrene (Krasten 127; no fire-retardant additives). His results (Table 8) show that polystyrene produced about the same amount of carbon dioxide under these conditions as the other two polymers assessed, and that more carbon dioxide was produced in the flaming mode than in the non-flaming mode.

Michal (1983b) designed a second larger combustion chamber (650 L) for further studies on the combustion

Table 8. Carbon dioxide produced by non-flaming and flaming combustion of materials in a 4.5 L combustion chamber (after Michal 1983a)

Material <sup>a</sup>	CO <sub>2</sub> concentration (%)					
	Sample mass					
	0.1 g		0.2 g		0.3 g	
Non-flaming (500°C)	Flaming (600°C)	Non-flaming (500°C)	Flaming (600°C)	Non-flaming (500°C)	Flaming (600°C)	
Poly-styrene	1.24	2.30	1.77	3.36	2.36	3.60
Poly-ethylene	1.24	2.60	1.95	3.72	2.71	3.66
Poly-propylene	1.12	2.01	1.69	3.43	2.02	3.78

<sup>a</sup> None contained fire-retardant additive.

products of the polymeric materials listed in Table 8. The overall shape of the chamber was an oval annulus of square cross-section. This CAB 650 chamber stands on end, with its long axis vertical. A crucible furnace, suitable for 1–10 g samples is located at the base of the chamber. Gas sampling probes are located approximately halfway up the chamber. Gases are free to circulate within the chamber, or can be exhausted via a duct at the top of the chamber. The amount of air available per unit sample mass in the CAB 650 chamber was an order of magnitude greater than it was in the CAB 4.5 chamber (Michal 1983a), having 650 L for 1–10 g samples as opposed to 4.5 L for 0.1–0.3 g samples. Under these conditions, Michal found that he did not get flaming of polystyrene at 600°C, as he had in the CAB 4.5 chamber. At 800°C the polystyrene did flame and produced about the same amount of carbon dioxide as the polyethylene, which also flamed. At 1000°C all three polymers flamed and produced comparable amounts of carbon dioxide. The amount of carbon dioxide produced by the polystyrene and the polyethylene was almost identical at the two temperatures. If temperature differences in the two chambers are ignored, then it can be concluded that a greater proportion of polystyrene was combusted to carbon dioxide and water vapour, under the higher ventilation conditions in the CAB 650 chamber.

All these workers were conducting thermal decomposition studies on samples that varied from 0.1 to 10 g. On the other hand Fardell *et al.* (1986) used 27–40 kg specimens in their combustion experiments in a room/corridor facility (previously discussed). Their results (Table 9) are difficult to interpret as no data on rate of mass loss is provided. As the combustion gases were measured in the corridor adjacent to the burn room, the amount of distribution is dependent on air-flow rates into and out of the burn room through the single opening. This flow rate was, apparently, controlled only by the fires themselves. At high ventilation the expanded polystyrene produced more carbon dioxide in the growth stage than the other materials, but in the steady state and decay stages expanded polystyrene produced less carbon dioxide than the other materials. This is consistent with the data for oxygen depletion (Table 1) and carbon monoxide production (Table 5) in the same experiments, and suggests more rapid burning of the expanded polystyrene in the growth stage, with very little material left by the steady state and decay stages. At low ventilation the production of carbon dioxide is restricted in the growth stage, but is then spread more equally over the steady state and decay stages of the fire. This suggests that the expanded polystyrene fire was more affected in the growth stage by ventilation control than the other fires. In fact the other three materials show an increase in carbon dioxide

Table 9. Carbon dioxide concentrations in combustion gases during growth, steady state and decay stages of a fire with fuel loads of single materials in a room/corridor facility (after Fardell *et al.* 1986)

Fuel load		CO <sub>2</sub> concentration (%)		
Material <sup>a</sup>	Mass (kg)	Fire stage		
		Growth	Steady state	Decay
<i>High ventilation (large opening)</i>				
Expanded polystyrene	27	12.0	3.5	1.4
Polymethylmethacrylate	40	7.4	10.0	6.0
Polypropylene	40	5.0	13.1	4.3
Pine	40	1.9	12.8	6.8
<i>Low ventilation (small opening)</i>				
Expanded polystyrene	27	9.3	9.0	6.0
Polymethylmethacrylate	40	12.1	11.0	4.4
Polypropylene	40	5.7	12.9	12.0
Pine	40	3.4	6.0	8.9

<sup>a</sup> None contained fire-retardant additives.

concentrations in the growth stage at low ventilation, possibly reflecting less dilution by incoming air. These studies highlight the importance of considering fire scenarios when assessing the toxicity of combustion products.

The yield of carbon dioxide expected to be produced by various materials in well-ventilated fires has been tabulated by Tewarson (1988). When his data (Table 6) is compared with theoretical yields (Table 7), it can be seen that for all materials the majority of carbon in the combustion products in well-ventilated fires is in the form of carbon dioxide.

Restricting ventilation to the fire can favour the production of carbon monoxide over carbon dioxide. Reducing the quantity of material consumed in a fire does not alter the yield of carbon dioxide, or other combustion products, but will alter their concentration in air.

### Other gases

Many of the papers reviewed by Gurman *et al.* (1986) concentrated on identifying as many combustion products as possible using analytical techniques such as gas chromatography coupled with mass spectrometry. Such studies were not necessarily related to combustion. For instance Pfaffli *et al.* (1978) were simulating industrial processing conditions, and therefore did not want their primary thermal decomposition products to undergo further oxidation, as can happen in a fire.

Gurman *et al.* collated a list of species reported in 19 studies. This list (Table 10) is not exhaustive, but probably includes all compounds likely to be produced in any but minute quantities by the thermal decomposition or combustion of most grades of polystyrene, including grades with fire retardants. As expected, none of the compounds listed contain nitrogen. The one chlorine-containing compound (1,1,2-trichloroethane) is reported in only one reference. The grade of polystyrene studied is unknown, but this compound may be a residual blowing agent of a type that is no longer used. Levin (1987) incorporated the data from Gurman *et al.* in a much larger qualitative tabulation that lists thermal decomposition products of polystyrenes, ABS, nylons, polyesters, polyethylenes, polyvinylchlorides and rigid polyurethane foams. Each of the materials has a unique set of thermal decomposition products that relate to its chemical composition.

Apart from carbon dioxide and carbon monoxide, the major volatile thermal decomposition product of polystyrene is styrene monomer, or styrene. Styrene is a clear flammable liquid (boiling point 145°C) with a characteristic sweet smell. Gurman *et al.* concluded that styrene monomer is the main volatile product, regardless of atmospheric conditions. In the papers they surveyed, the yields ranged from 0.6 to 100% of the mass volatilised. They found that the yield of styrene was temperature dependent, increasing with furnace temperatures up to 500°C and decreasing above 800°C. Pfaffli *et al.* (1978) degraded samples of polystyrene (Stymer PS-RH; no additives; residual monomer content < 0.02%) in his J-shaped glass tube decomposition chamber (discussed earlier). He measured the amount of a number of decomposition products found at 350 and 500°C. His results (Table 11) show that styrene is present in greater quantities than the other species determined. Beyler (1988), citing Cullis and Hirschler (1981), relates monomer yield from thermal decomposition to polymer structure for a number of polymers, quoting a monomer yield of 42–45% for polystyrene. This is a lot higher than the apparent 5–6% found by Pfaffli *et al.* (Table 11), and relates to conditions of temperature and atmosphere under which secondary decomposition or oxidation do not occur.

Mitera and Michal (1985) used the CAB 4.5 (Michal 1983a) and CAB 650 (Michal 1983b) combustion chambers (previously described) to study the combustion products of four polymers, including polystyrene. In the CAB 4.5 chamber (4.5 L) they conducted non-flaming combustion experiments at 500°C and flaming combustion experiments at 600°C, on 0.2 g samples. In the CAB 650 chamber (650 L) they conducted flaming combustion experiments at 600 and 1000°C on 3 g samples. In their data analysis, they list 38 identified compounds for polystyrene. The list differs in some

Table 10. Volatile thermal decomposition products of polystyrene formed under various experimental environments (after Gurman *et al.* 1986)

Decomposition products	Atmosphere		No. of studies	
	Vacuum	Inert <sup>a</sup>		Oxidative
Acetaldehyde			x	1
Acetophenone			x	2
Acetylene	x	x	x	3
Acrolein <sup>b</sup> (acrylaldehyde)			x	2
Allylbenzene (3-phenylpropene)		x	x	2
Benzaldehyde			x	3
Benzene	x	x	x	9
Benzoic acid			x	1
Benzyl alcohol			x	2
Butadiene <sup>b</sup>		x		2
Butane		x	x	2
1-butene		x	x	2
Carbon dioxide		x	x	4
Carbon monoxide		x	x	6
Cinnamaldehyde			x	2
1,3-diphenylpropane ('styrene dimer')		x	x	1
1,3-diphenylpropene ('styrene dimer')		x	x	1
Ethane	x	x	x	3
Ethylbenzene	x	x	x	8
Ethylene	x	x	x	4
Ethylmethyl benzene		x	x	1
Formaldehyde			x	1
Formic acid			x	1
Hexane		x		1
Hexene <sup>c</sup>		x		2
Methane	x	x	x	3
Methanol			x	1
3-methyl-1-butene		x		1
4-methyl-2-hexene		x		1
2-methyl-3-pentene		x		1
Methyl phenol <sup>b</sup> (cresol)		x	x	1
$\alpha$ -methylstyrene (2-phenylpropene) <sup>d</sup>		x	x	8
$\beta$ -methylstyrene (1-phenylpropene)		x	x	3
Pentane		x		2
1-pentene		x		1
Phenol			x	2
1-phenylethanol			x	1
Propane			x	1
iso-propylbenzene (cumene)		x	x	4
n-propylbenzene		x	x	3
Propylene			x	1
Styrene—monomer	x	x	x	13
—dimer	x	x	x	8
—trimer	x	x	x	6
—tetramer	x	x	x	5
—pentamer			x	1
—hexamer			x	1
—heptamer			x	1
Styrene oxide			x	1
Toluene	x	x	x	9
1,1,2-trichloroethane		x		1
Vinylcyclohexane <sup>b</sup>		x		2
Vinylcyclohexene <sup>b</sup>		x		2

<sup>a</sup> Decomposed under atmospheres of argon, helium or nitrogen.

<sup>b</sup> Products found when impact polystyrenes or polystyrenes with a polybutadiene additive were decomposed.

<sup>c</sup> Includes 1-hexene, 2-methyl-1-pentene listed in original paper.

<sup>d</sup> Includes ( $\alpha$ ) styrene listed in original paper.

details to that provided by Gurman *et al.* (1986), but identifies the same types of combustion products. Mitera and Michal found that polystyrene decomposed, under all conditions, largely to the monomer, dimer or trimer of styrene. The proportions of the styrenes, and of the other combustion products, varied greatly under the different combustion conditions. At 1000°C polystyrene was converted primarily to carbon dioxide, with correspondingly lower concentrations of all other combustion products. Mitera and Michal also noted the importance of the system used for collecting combustion products. Flaming combustion experiments at 600°C were performed in both chambers. In the CAB 650 chamber the yields of high boiling products, such as the dimers and trimers of styrene, were very much higher than for the similar experiments in the CAB 4.5 chamber. They concluded that less material was lost by condensation on the walls of the chamber in the former case. Two chlorine-containing compounds were found (tetrachloromethane and tetrachloroethene), but these may be residual processing solvents that are not now used.

Table 11. Hydrocarbons and oxidised compounds produced by the thermal decomposition of 100 mg samples of polystyrene under an airflow of 700 mL/min (after Pfaffli *et al.* 1978)

Combustion product	Mass (mg)	
	Decomposition temperature	
	350°C	500°C
<i>Aromatic hydrocarbons</i>		
Styrene	5.22	5.84
$\alpha$ -methylstyrene (2-phenylpropene)	0.12	0.07
Allylbenzene (3-phenylpropene)	0.09	0.03
Ethylbenzene	0.04	0.01
Benzene	0.03	0.01
Toluene	0.03	0.10
Cumene (iso-propylbenzene)	0.02	0.01
n-propylbenzene	< 0.01	< 0.01
<i>Oxidised aromatic compounds</i>		
Benzaldehyde	3.44	0.87
1-phenylethanol	0.98	0.08
Acetophenone	0.15	0.02
Styrene oxide	0.14	0.07
Phenol	0.12	0.02
Cinnamaldehyde	< 0.01	< 0.01
Benzyl alcohol	< 0.01	< 0.01
Benzoic acid	—	0.03
<i>Aliphatic hydrocarbons</i>		
	< 0.01	< 0.01
<i>Oxidised aliphatic compounds</i>		
Formaldehyde	0.17	0.10
Acrylaldehyde (acrolein)	0.02	0.01
Formic acid	< 0.01	< 0.01

Morimoto *et al.* (1976), in their study of the combustion of a number of polymers and wood (discussed earlier), collected only those combustion products which remain as gases under ambient conditions. Consequently they did not collect or analyse for styrene, or other combustion products which condense out as liquids. In their study (Table 12) only those materials which contain nitrogen in their chemical composition (nylon 66, polyurethane, epoxy resin and melamine resin) produced the combustion products which contain nitrogen (hydrogen cyanide, ammonia and nitrous oxide). Cullis and Hirschler (1981) quote sources who found that in hydrocarbon flames nitrogen oxides may be formed by oxidation of atmospheric nitrogen. The combustion systems they quote, however, are probably not relevant to building fires (Shahed & Newhall 1971; Thompson *et al.* 1972). When calculating heat flows in enclosure fires, Drysdale (1985) assumes that atmospheric nitrogen is not involved in chemical reactions in fires.

Table 12. Gaseous combustion products produced by flaming combustion of 0.1 g samples of materials at 700°C under an airflow of 830 mL/min in a vertical tube furnace (after Morimoto *et al.*, 1976)<sup>a</sup>

Material <sup>b</sup>	Gas yield (g/g)				
	NH <sub>3</sub>	HCN	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>2</sub>
Polystyrene			0.007	0.016	0.006
Polyethylene			0.065	0.187	0.010
Nylon 66	0.004	0.026	0.039	0.082	0.007
Polyurethane		0.001	0.017	0.037	0.006
Epoxy resin		0.003	0.033	0.005	0.006
Cedar			0.002	0.001	0.002

<sup>a</sup> See Table 3 for carbon monoxide and carbon dioxide yields.

<sup>b</sup> None contained fire-retardant additives.

## TOXICITY OF THERMAL DECOMPOSITION PRODUCTS OF EXPANDED POLYSTYRENE

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The toxicity of a substance is its ability to impair health or cause death. One measure of the toxicity of a substance is the amount that must be taken in to produce a particular debilitating effect in a person or animal. When dealing with the toxicity of combustion products, two difficulties arise. Firstly, as has been demonstrated, fires produce a very large range of combustion products, with the combustion products being produced changing in type and quantity with fire scenarios or stages. Secondly, there is the difficulty of summing the toxic effects of individual combustion products, as different substances may act on the body in different ways, or have synergistic effects. Therefore studies on combustion toxicology take one of two approaches: either they measure one or two major toxic species; or they assess total toxic effect without determining what substances are present.

Purser (1988) discusses approaches to toxicity assessment of combustion products. He identifies two main views on toxicity in modern times which influence the approach taken. The first, the 'materials-based' approach, holds that new materials have produced new species of toxic combustion products, and that it is sufficient to limit the use of those materials that produce these new toxic species. This approach leads to the use of small-scale combustion toxicity screening tests for individual materials.

The second view, leading to the 'combustion products-based' approach, holds that the nature of toxic species have not changed all that much, but the rate of combustion, and hence the rate of production of combustion products, has changed. This approach leads to a desire to control toxic hazard by controlling such factors as ignition, flame spread, and smoke and gas production. For this approach it is only necessary to measure a few major toxic species. For instance, the concentration-time profiles of the major toxic species may be followed in large-scale fire tests. Fire scenarios may be designed to test a particular building and to predict likely toxic hazard, which is a function both of the toxicity of combustion products and of the quantity of combustion products produced. Toxic hazard is thus also dependent on other fire behaviour characteristics of materials, such as ignitability and ease of burning.

Purser concludes that there is a need for both small-scale materials-based combustion toxicity tests and for modelling based on a few major toxic fire products. He finds that existing information is often inadequate and misleading, and calls for a better standard of research and testing.

Two comprehensive texts on combustion toxicology, both of which include extensive references, are Kaplan *et al.* (1983) and Gad and Anderson (1990). Kaplan *et al.* concentrate on providing an in-depth analysis of combustion toxicity test methods. Gad and Anderson provide information on physiology, toxicity of individual gases, combustion toxicity testing, regulations concerning combustion toxicity, combustion toxicity of various polymers, and influence of flame retardants on combustion toxicity. Hilado and coworkers (Hilado & Cumming 1977; Hilado & Huttlinger 1980) have published a series of bibliographies on combustion toxicology. Hartzell (1989a; 1989b; 1992a) has assembled papers on combustion toxicology originally published in the *Journal of Fire Sciences* into three volumes. Papers included come from the United States, Canada, United Kingdom, Germany, Finland, France, Czechoslovakia and Japan. Gurmañ *et al.* (1986) also cover toxicity test methods in their review. Consequently, in this survey there will be little discussion of the relative merits of particular toxicity tests, and only minimal experimental details will be given. The emphasis will be on comparative data reported in individual papers.

### Toxicological data

Kimmerle (1974) has collated physiological data for a number of species, some of which are combustion products of polystyrene. This information is presented in Tables 13–21. This limited sampling shows that whilst some toxic combustion products are also irritants, or have detectable odours, carbon monoxide or carbon dioxide (or oxygen depletion) can be present in lethal concentrations without odour or irritation to act as a warning. More detailed information on the physiological effect of different concentrations of carbon monoxide is given by Stewart (1974) and Purser (1988), whilst Hirschler *et al.* (1993) cover the subject comprehensively in a volume which considers all sources of carbon monoxide, not just fires.

Table 13. Human physiological effects of reduced levels of oxygen (after Kimmerle 1974)

O <sub>2</sub> concentration (%)	Symptoms
21	Ambient concentration in air
20	Normal
17	Respiration volume increases, muscular coordination diminishes, attention and clear thinking require more effort
12-15	Shortness of breath, headache, dizziness, quickened pulse, efforts fatigue quickly, muscular coordination for skilled movements lost
10-12	Nausea and vomiting, exertion impossible, paralysis of motion
6-8	Collapse and unconsciousness occurs
≤ 6	Death in 6-8 minutes

Table 14. Relation between carbon monoxide concentration and response in humans (after Kimmerle 1974)

CO concentration (ppm)	Symptoms
100	No poisoning symptoms even for long periods of time
200	Headache after 2-3 hours
300	Distinct poisoning after 2-3 hours
400	Distinct poisoning after 1-2 hours
500	Hallucinations felt in 30-120 minutes
1000	Difficulty of ambulation, death after 2 hours inhalation
1500	Death after 1 hour inhalation
3000	Fatal in 30 minutes
≥ 8000	Immediate death by suffocation

Table 15. Human physiological effects from various levels of carbon dioxide (after Kimmerle 1974)

CO <sub>2</sub> concentration (ppm)	Symptoms
250-350	Ambient concentration in air
900-5000	Without effect
18 000	Ventilation increased by 50%
25 000	Ventilation increased by 100%
30 000	Weakly narcotic, decreasing acuity of hearing, increase of blood pressure and pulse
40 000	Ventilation increased by 300%, headache, weakness
50 000	Symptoms of poisoning after 30 minutes, headache, dizziness, sweating
80 000	Dizziness, stupor, unconsciousness
90 000	Distinct dyspnoea, loss of blood pressure, congestion, fatal within 4 hours
120 000	Immediate unconsciousness, death in minutes
200 000	Immediate unconsciousness, death by suffocation

Table 16. Styrene concentrations in air and symptoms in humans (after Kimmerle 1974)

Styrene concentration (ppm)	Symptoms
60	Threshold of odour, no irritation
100	Strong odour, tolerable
200-400	Non-tolerable odour
216	Unpleasant subjective symptoms
376	Definite signs of neurological impairment
600	Irritation of the eyes
800	Immediate irritation of eyes and throat, somnolence, weakness

Table 17. Acetaldehyde concentration in air and symptoms in humans (after Kimmerle 1974)

Acetaldehyde concentration (ppm)	Symptoms
0.07-0.21	Threshold of odour
25-50	Transient slight irritation of eyes after 15 minutes
134	Slight irritation of the respiratory tract after 30 minutes
200	Irritation of nose and throat

Table 18. Acrolein concentration in air and symptoms in humans (after Kimmerle 1974)

Acrolein concentration (ppm)	Symptoms
0.805	Lacrimation, irritation of the mucous membranes
1.0	Immediately detectable irritation
5.5	Intense irritation
≥ 10	Lethal in a short time
24	Unbearable

Table 19. Benzene concentration in air and symptoms in humans after short exposure (after Kimmerle 1974)

Benzene concentration (ppm)	Symptoms
500	Slight irritation
1500-4000	Dangerous to life after several hours
8 000	Fatal after 30-60 minutes
20 000	Fatal after 5 minutes

Table 20. Formaldehyde concentration in air and symptoms in humans (after Kimmerle 1974)

Formaldehyde concentration (ppm)	Symptoms
0.05–1.0	Threshold of odour
0.25–1.6	Threshold of irritation of eyes
0.08–1.6	Slight irritation of eyes and nose
0.5	Threshold of irritation of throat
10	Conjunctivitis, rhinitis and pharyngitis in a few minutes
10–15	Dyspnoea, cough, pneumonia, bronchitis
> 50	Necrosis of the mucous membranes, spasm of the larynx, oedema of the lungs

Table 21. Toluene concentration in air and symptoms in humans (after Kimmerle 1974)

Toluene concentration (ppm)	Symptoms
190–380	No complaints
500–1000	Headache, nausea, momentary loss of memory, anorexia, irritation of eyes
1000–1500	Palpitation, extreme weakness, loss of coordination, impairment of reaction time
2000–2500	Dizziness, nausea, narcosis after 3 hours
10 000	Immediately fatal

### Combustion toxicity tests

Methods for assessing toxicity of products of thermal decomposition and combustion are described in Alarie and Barrow (1977), Cullis and Hirschler (1981), Kaplan *et al.* (1983), Gurman *et al.* (1986), Gad and Anderson (1990), Troitzsch (1990) and Hartzell (1992b). All the methods use animal exposure. Typically materials undergo thermal decomposition or combustion in one chamber, and the smoke and gases are transported to a second chamber where the animals are exposed. Variables encountered include decomposition chamber temperature, sample size, chamber size, animal species, temperature of gases in animal exposure chamber, biological endpoint, airflow, degree of body exposure and method of reporting results.

Currently there is considerable debate on combustion toxicity test methods. Kaplan *et al.* (1989) compared three methods and found that the thermal decomposi-

tion products varied in nature and rate of production. They found that all three methods had deficiencies, and concluded that neither toxicity nor toxic hazard could be measured adequately by small-scale toxicity tests, and that toxic hazard assessments should also include other relevant aspects of fire behaviour. Debanne *et al.* (1987) conducted statistical analyses of data obtained using the University of Pittsburgh and National Bureau of Standards combustion toxicity procedures. The evaluation revealed that up to 25% of the data from both methods was not valid. Both the British Standards Institution (BSI 1982) and the International Organisation for Standardisation (ISO 1989; 1990) have prepared guidelines for the design of combustion toxicity tests. The ISO reports contain much informative material and bibliographies.

A summary of toxicity assessment procedures that have been used to study thermal decomposition products of polystyrenes is given in Table 22. Gurman *et al.* (1986) note that although each method assesses toxicity, the apparatus, experimental conditions and measured endpoints vary substantially, and the methods generate results that are not readily comparable.

They note, for example, that parameters relating to the production of a given biological effect (see Table 22) that were measured include:

- the mass of material consumed in the furnace;
- the concentration of material, expressed as mass consumed per unit exposure chamber volume or air dilution volume; and
- exposure time.

The results of the different methods are expressed as 'lethal concentration',  $LC_{50}$ , necessary to kill 50% of the exposed animals, or 'effective concentration',  $EC_{50}$ , needed to produce some non-lethal biological effect in 50% of animals (both in a specified exposure time), or the mean time needed to produce death,  $T_D$ , or incapacitation,  $T_i$ , of all test animals.  $LC_{50}$  and  $EC_{50}$  are calculated by dividing the mass of material consumed, or in some cases the 'charge' loaded, by the chamber volume. Gurman *et al.* use the terms 'lethal loadings',  $LL_{50}$ , and 'effective loading',  $EL_{50}$ , for ' $LC_{50}$ ' results that do not include exposure chamber volume in their calculation of results. In any case, methods vary in so many details that comparisons should only be made within a particular method. Some workers (e.g. Alexeeff & Packham 1984a) consider exposure times in conjunction with  $LC_{50}$  values to produce concentration time products, expressed as  $L(Ct)_{50}$ .

Table 22. Methods for determining inhalation toxicity of products of thermal decomposition of materials  
(after Gurman *et al.* 1986)

Method <sup>a</sup>	Animal species	Exposure time (min)	Biological endpoint(s)	Type of exposure <sup>b</sup>	Combustion system	Airflow system
Dow	Rats	30	Death	WB	Cup furnace	Static
Univ. of Utah	Rats	30	(1)Incapacitation (2)Death	HO	Cup furnace	Static
NBS	Rats	30	(1)Incapacitation (2)Death	HO	Cup furnace	Static
DIN	Rats	30	(1)Death (2)Respiratory frequency	NO WB	Tube furnace	Dynamic
FAA/CAMI	Rats <sup>c</sup>	30	(1)Incapacitation (2)Death	WB	Tube furnace	Recirculating
NASA/USF	Mice	30	(1)Incapacitation (2)Death	WB	Tube furnace	(1)Static (2)Dynamic
Japanese	Mice <sup>c</sup>	15	(1)Incapacitation (2)Cardiovascular (3)Death	WB	Tube furnace	Dynamic
Univ. of Michigan <sup>d</sup>	Rats Rabbits	240	Death	WB	Tube furnace	Static
Univ. of Michigan <sup>d</sup>	Rats	140	Death	HO	Combustion furnace	Dynamic
Univ. of Pittsburgh	Mice	30	(1)Incapacitation (2)Death (3)Respiratory frequency	HO	Combustion furnace	Dynamic
GE/SRI <sup>d</sup>	Rats	120	Death	WB	Combustion furnace	Recirculating
Harvard	Rats	20	(1)Incapacitation (2)Death	WB	Combustion furnace	Recirculating

<sup>a</sup>Methods are described by Kaplan *et al.* (1983).

<sup>b</sup>WB = whole body exposure; NO = nose only exposure; HO = head only exposure.

<sup>c</sup>Animals in an activity wheel during exposure.

<sup>d</sup>Data for polystyrenes from this method are included in Gurman *et al.* (1986), but not in this report.

Potts and Lederer (1977) evaluated the toxicity of many materials, including polystyrenes, using the method they developed for the Dow Chemical Company. They conducted non-flaming and flaming tests at the same decomposition temperatures on a number of materials, and reported their results as rat fatalities and gas concentrations (Table 23). They attempted, by observation and pathologic examination, to relate deaths to particular toxicants. They concluded that carbon monoxide intoxication appeared to be a large contributory cause to most of the fatalities.

Their data (Table 23) shows that under their test conditions, polystyrenes which produce a greater rate of fatalities than wood in flaming conditions produce no fatalities under non-flaming conditions. In Table 24 rat fatalities are listed as a function of sample weight. Under non-flaming conditions, 6 g of expanded polystyrene caused no fatalities, whereas 2–4 g of wood produced fatalities. Under flaming conditions, 5 g of expanded polystyrene caused fatalities compared to 3–6 g of wood.

Table 23. Fatalities and gas concentrations for various materials in the Dow Chemical Company combustion toxicity test<sup>a</sup> (after Potts & Lederer 1977)

Material	Temp. (°C)	Animal fatalities <sup>b</sup>			Average gas concentrations							
		During exposure	Post- exposure	Total	O <sub>2</sub> <sup>c</sup> (%)	CO <sup>d</sup> (ppm)	CO <sub>2</sub> <sup>d</sup> (ppm)	NO <sub>x</sub> <sup>e</sup> (ppm)	HCN <sup>e</sup> (ppm)	H <sub>2</sub> CO <sup>e</sup> (ppm)	Acrolein (ppm)	Styrene <sup>e</sup> (ppm)
<b>Flaming</b>												
Impact polystyrene <sup>f</sup>	475	5,7	0,0	5,7	13,07	3700	58 800	4,5		100		
Impact polystyrene, FR <sup>g</sup>	675	7,7	0,0	7,7	17,43	5700	21 700	10		250		
Expanded polystyrene <sup>h</sup>	550	7,7	0,0	7,7	14,04	3800	50 900	15		150		
Douglas fir plywood	475	2,6	0,0	2,6	16,34	3900	38 600	5	< 2	20		
<b>Non-flaming</b>												
Impact polystyrene <sup>f</sup>	475	0,0	0,0	0,0	19,85	300	6 500			> 300	14	> 400
Impact polystyrene, FR <sup>g</sup>	550	0,0	0,0	0,0	19,28	2100	7 400			> 300	3	> 400
Expanded polystyrene <sup>h</sup>	550	0,0	0,0	0,0	19,14	500	6 400					
Douglas fir plywood	450	1,1	3,5	4,6	18,76	5800	15 100	< 2	5	> 50	27	

<sup>a</sup> 6 g samples; a 6 g sample, if 100% consumed, is equivalent to a dose of 40 mg/L of chamber volume. Over 97% of the sample was consumed in each of these tests.

<sup>b</sup> Seven animals were exposed in each of two replicate tests, with results separated by a comma.

<sup>c</sup> Minimum of the values in two tests. <sup>d</sup> Maximum of the values in two tests. <sup>e</sup> Maximum of the spot readings in two tests. <sup>f</sup> Styron 492U; contains 7% rubber.

<sup>g</sup> Styron 6021.01; as f, but contains fire-retardant additives. <sup>h</sup> Styrofoam SM; additives unknown.

The results also show that the fire-retarded polystyrene performs worse than the non-retarded polystyrene. This is often found in toxicity tests where the object is to decompose as much material as possible. In these tests, with the exception of polyurethane, at least 97% of all materials was consumed. Under non-flaming conditions 78–96% of the polyurethane was consumed and under flaming conditions 76–79% of the polyurethane was consumed. In fires the presence of fire-retarded additives can inhibit ignition and retard burning, at least in the early stages, thereby limiting the quantity of material decomposed. Under these circumstances the presence of fire-retardant additives may result in lower concentrations of toxic gases, though in later stages of a fire this difference may not be so pronounced.

An interlaboratory trial conducted on the NBS combustion toxicity test included expanded polystyrene amongst the materials assessed (Levin *et al.* 1983). The apparatus used by the participating laboratories varied in details such as furnace type and volume, and exposure chamber volume. The number and strain of rats exposed also varied. Some of the data from the National Bureau of Standards Laboratory, which used a combustion system based on the design of Potts and Lederer (1977), is presented in Table 25.

This data shows that polymeric materials such as expanded polystyrene and rigid polyurethane foam produce less toxic combustion products in the non-flaming mode than they do in the flaming mode, whereas the opposite is true for wood. In the flaming mode the expanded polystyrene produced combustion products with a toxicity similar to that of the combustion products of wood. Levin (1985) has used NBS data from the same source to illustrate graphically the combustion toxicity of twelve materials, including polystyrene. Data from the same source is further analysed in two papers on the interaction of toxic gases (Levin *et al.* 1986; 1987).

The limitations of the NBS method have been listed by its developers (Levin *et al.* 1982; 1985). These limitations included factors related to apparatus and to specimen exposure. Levin *et al.* (1985) explored the possibility of replacing the NBS cup furnace with a cone radiator proposed by Alexeeff and Packham (1984b) before suggesting a new furnace based on the cone calorimeter (Levin 1985). This work, which is summed up by Babrauskas, Levin *et al.* (1991), has led to the preparation of a proposed ASTM test method. This proposed method is at present the subject of debate regarding its relevance to fire scenarios (Alarie 1992a).

Table 24. Fatalities of rats as a function of sample mass for a number of materials in the Dow Chemical Company toxicity test (after Potts &amp; Lederer 1977)

Material	Decomposition temp. (°C)	Rat fatalities <sup>a</sup>									
		Nominal sample mass (g)									
		1	1.5	2	3	4	5	6	7	8	
<i>Non-flaming</i>											
Impact polystyrene <sup>b</sup>	475							0,0 <sup>f</sup>			
Impact polystyrene, FR <sup>c</sup>	550							0,0			
Expanded polystyrene <sup>d</sup>	550							0,0			
Rigid poly urethane foam <sup>e</sup>	560	0,1	2,6	7,7,7,6							
Douglas fir plywood	450			0,0		2,1		4,6			
Red oak	440			2,0,0		6,6		6,6			
Yellow pine	450			0,0		5,2		6,7			
<i>Flaming</i>											
Impact polystyrene <sup>b</sup>	475				0	0,0	1,2	7,5	7		
Impact poly styrene, FR <sup>c</sup>	675				0,0	4,2	4,6	7,7	6,7		
Expanded polystyrene <sup>d</sup>	550				0,0	0,0	3,1	7,7	7		
Rigid poly urethane foam <sup>e</sup>	560				0	0,2	2,7,5,7				
Douglas fir plywood	475			0	1,0	1,0	5	2,6	7	7	
Red oak	480					0,0		4,1		7,5	
Yellow pine	475					0,0		1,1		6,7	

<sup>a</sup> Seven rats were exposed in each of two replicate tests, with results separated by a comma; fatalities occurred either during exposure or in the 14-day post-exposure period.

<sup>b</sup> Styron 492U; contains 7% rubber.

<sup>c</sup> Styron 6021.01; as b, but contains fire-retardant additives.

<sup>d</sup> Styrofoam SM; additives unknown.

<sup>e</sup> Laboratory, non-commercial, preparation containing phosphate.

<sup>f</sup> Replicate tests.

Table 25. Toxicity data and gas concentrations for a number of materials in the National Bureau of Standards combustion toxicity test<sup>a</sup> (after Levin et al. 1983)

Material <sup>b</sup>	Decomposition temp. <sup>c</sup> (°C)	EC <sub>50</sub> (mg/L)	LC <sub>50</sub> 30 min (mg/L)	LC <sub>50</sub> 30 min + 14 days (mg/L)	COHb @ 30 min LC <sub>50</sub> (ppm)	CO @ 30 min LC <sub>50</sub> (ppm)
<i>Non-flaming</i>						
Expanded poly styrene (GM-51) <sup>d</sup>	465	> 40.0	> 40.0	> 40.0	> 6	> 70
Rigid polyurethane foam (GM-30)	525-550	ND <sup>e</sup>	> 39.6	> 39.6	> 47	> 1700
ABS	525	ND	> 32.5	30.9	> 28	> 700
Douglas fir	440	13.5	29.0	22.8	86	3400
Red oak <sup>f</sup>	455	~23.0	> 45.0	30.3	> 81	> 3600
<i>Flaming</i>						
Expanded polystyrene (GM-51)	515-565	28.7	38.9	38.9	78	1300
Rigid polyurethane foam (GM-30)	570-575	ND	14.3	13.3	63	1800
ABS	600	ND	22.1	19.3	44	1800
Douglas fir	490	~23.5	39.8	39.8	83	3400
Red oak <sup>f</sup>	505-530	34.8	59.0	56.8	83	2900

<sup>a</sup> Single laboratory (NBS); six rats exposed per test; 1 L cup furnace.

<sup>b</sup> None contained fire-retardant additives.

<sup>c</sup> 25°C below non-piloted ignition temperature for non-flaming, and 25°C above for flaming.

<sup>d</sup> GM designations identify standard reference materials (Products Research Committee 1980).

<sup>e</sup> Not determined.

<sup>f</sup> Some data collected using 300 mL cup furnace.

One of the few combustion toxicity tests that has been formally standardised is the German DIN 53 436 method (Kaplan *et al.* 1983; Prager 1988). During its development, Hofmann and Oettel (1968; 1969; 1974) used the method to study the combustion toxicity of a number of materials, including seven expanded polystyrenes. They compared both equal masses and equal volumes of materials at a range of furnace temperatures. At the lower temperatures non-flaming decomposition occurred, whilst at the higher temperatures flaming or glowing decomposition occurred. Their results (Table 26) show that where no flaming occurred all the expanded polystyrenes produced decomposition products with a lower toxicity than those produced by wood materials under the same conditions. However under flaming conditions, on an equal mass basis, all the expanded polystyrenes, whether fire-retarded or not, produced combustion products with a toxicity

comparable to wood materials. When equal volumes of material were compared, the expanded polystyrenes, with their very low density compared to wood products (typically 400–800 kg/m<sup>3</sup>), produce combustion products of much lower toxicity than wood materials. On the basis of carboxyhaemoglobin values in the dead animals, Hofmann and Oettel concluded that for these materials carbon monoxide was the major toxic species.

Herpol and Minne (1976) used the same procedure to compare the combustion toxicity of fifteen materials including two expanded polystyrenes, only one of which was fire-retarded. Whilst 10 g specimens of the thirteen other materials were used, due to volume restraints the expanded polystyrene specimens were 2.4 g for the unretarded and 2.2 g for the fire-retarded. The two expanded polystyrenes, when decomposed at approximately 580°C, produced similar results for

Table 26. Combustion toxicity of various materials compared on mass and on volume basis<sup>a</sup> (after Hofmann & Oettel 1969)

Material	COHb blood content (%) and death rate <sup>b</sup> of rats at decomposition temperatures of							
	300°C		400°C		500°C		600°C	
	%	Rate	%	Rate	%	Rate	%	Rate
<i>Specimens of equal mass (5 g)</i>								
Expanded polystyrene 1 <sup>c</sup>	< 15	0/12	< 15	0/12	< 15	0/18	80	11/12 <sup>d</sup>
Expanded polystyrene 2 <sup>c</sup>	< 15	0/12	< 15	0/12 <sup>d</sup>	19	0/12	81	12/12 <sup>d</sup>
Expanded polystyrene 3 <sup>c</sup>	< 15	0/12	< 15	0/12	75	12/12 <sup>d</sup>		
Expanded polystyrene 4 <sup>c</sup>	< 15	0/12	< 15	0/12	72	13/18 <sup>d</sup>	81	12/12 <sup>d</sup>
Expanded polystyrene 5 <sup>c</sup>	< 15	0/12	< 15	0/12	85	12/12 <sup>d</sup>	74	12/12 <sup>d</sup>
Expanded polystyrene 6 <sup>c</sup>	< 15	0/12	< 15	0/12	79	12/12 <sup>d</sup>	78	12/12 <sup>d</sup>
Expanded polystyrene 7 <sup>c</sup>	< 15	0/12	< 15	0/12	74	12/12 <sup>d</sup>	78	12/12 <sup>d</sup>
Expanded cork	17	0/12	69	5/18 <sup>d</sup>	82	12/12 <sup>d</sup>	78	12/12 <sup>d</sup>
Pine	32	3/12	86	12/12 <sup>d</sup>	86	12/12 <sup>d</sup>	85	12/12 <sup>d</sup>
<i>Specimens of equal volume (300 × 15 × 10 mm)</i>								
Expanded polystyrene 1 <sup>c</sup>	< 15	0/12	< 15	0/12	< 15	0/12	29	0/12 <sup>d</sup>
Expanded polystyrene 2 <sup>c</sup>	< 15	0/12	< 15	0/12	< 15	0/12	26	0/12 <sup>d</sup>
Expanded polystyrene 3 <sup>c</sup>	< 15	0/12	< 15	0/12	< 15	0/12	26	0/12 <sup>d</sup>
Expanded polystyrene 4 <sup>c</sup>	< 15	0/12	< 15	0/12	< 15	0/12	40	0/12 <sup>d</sup>
Expanded polystyrene 5 <sup>c</sup>	< 15	0/12	< 15	0/12	20	0/12	41	0/12 <sup>d</sup>
Expanded polystyrene 6 <sup>c</sup>	< 15	0/12	< 15	0/12	< 15	0/12	33	0/12 <sup>d</sup>
Expanded polystyrene 7 <sup>c</sup>	< 15	0/12	< 15	0/12	< 15	0/12	34	0/12 <sup>d</sup>
Expanded cork	< 15	0/12	88	12/12 <sup>d</sup>	86	12/12 <sup>d</sup>	83	12/12 <sup>d</sup>
Pine	< 15	0/12	88	12/12 <sup>d</sup>	87	12/12 <sup>d</sup>	89	12/12 <sup>d</sup>
Spruce	< 15	0/6	88	6/6 <sup>d</sup>	88	6/6 <sup>d</sup>	92	6/6 <sup>d</sup>
Plywood	25	0/6	90	6/6 <sup>d</sup>	85	6/6 <sup>d</sup>	87	6/6 <sup>d</sup>
Particleboard 1	87	6/6 <sup>d</sup>	87	6/6 <sup>d</sup>	86	6/6 <sup>d</sup>	82	6/6 <sup>d</sup>
Particleboard 2	83	6/6 <sup>d</sup>	83	6/6 <sup>d</sup>	87	6/6 <sup>d</sup>	90	6/6 <sup>d</sup>

<sup>a</sup> The method used was later standardised as DIN 53 436 (Kaplan *et al.* 1983). Tests are non-flaming unless otherwise stated.

<sup>b</sup> Ratio of dead rats to rats exposed.

<sup>c</sup> Expanded polystyrenes: 1 = Styropor P (16.7 kg/m<sup>3</sup>); 2 = Styropor F200 (approx. 20 kg/m<sup>3</sup>); 3 = Styropor F210 (25.7 and 16 kg/m<sup>3</sup>); 4 = Styropor KR 2180 (27.7 kg/m<sup>3</sup>); 5 = Styropor KR 2180/1 (approx. 19.5 kg/m<sup>3</sup>); 6 = Styropor KR 2180/2 (approx. 19 kg/m<sup>3</sup>); 7 = Styropor F220 (approx. 20 kg/m<sup>3</sup>). All the expanded polystyrenes except Styropor P were classified 'difficultly flammable' in DIN 4102. In most cases they contained a fire-retardant additive.

<sup>d</sup> Flaming or glowing combustion occurred.

carboxyhaemoglobin. Neither produced any mortalities. For both materials, in replicate tests, there was either no flaming or only short bursts of flame. Of the materials tested at 10 g, rigid polyvinylchloride (no flaming) and glass-reinforced polyester (flaming) produced no mortalities, whilst other plastics and wood products produced mortalities.

In the combustion toxicity test developed by Crane *et al.* (1977; cited in Kaplan *et al.* 1983) at the US Federal

Aviation Administration (FAA) Civil Aeromedical Institute (CAMI), a Lindberg tube furnace is used for thermal decomposition and the system has recirculating air flow. Hilado *et al.* (1977) used this test to compare four polymeric materials, including polystyrene (Styron 402D; no additives). Under the (non-flaming) conditions of the FAA/CAMI test, the thermal decomposition products of polystyrene did not kill or incapacitate any of the rats used as test animals (Table 27), whereas the products from the other plastics did.

Table 27. Relative toxicity of combustion products of four materials as determined under a range of test conditions (after Hilado *et al.* 1977)

Method <sup>a</sup>	Furnace temp. (°C)	Airflow (mL/s)	Material <sup>b</sup>	Time to first sign of incapacitation <sup>c</sup> (min)	Mortality <sup>d</sup>
FAA/CAMI	600	R <sup>e</sup>	polyethylene	4.88	6/6
			polycarbonate	7.57	6/6
			ABS	13.38	1/6
			polystyrene	NI <sup>f</sup>	0/3
NASA/USF B	200–800 <sup>g</sup>	0	ABS	13.52	20/20
			polycarbonate	14.70	47/48
			polyethylene	16.68	8/8
			polystyrene	19.04	8/8
NASA/USF E	600	0	ABS	5.83	8/8
			polyethylene	9.95	8/8
			polystyrene	10.34	5/8
			polycarbonate	10.49	5/8
NASA/USF F	800	0	ABS	3.09	16/16
			polyethylene	3.57	8/8
			polycarbonate	5.31	23/24
			polystyrene	5.99	11/12
NASA/USF G	800	16	ABS	1.69	8/8
			polycarbonate	2.83	8/12
			polyethylene	2.91	0/8
			polystyrene	3.88	0/12
NASA/USF H	800	48	ABS	1.47	8/8
			polycarbonate	2.76	8/8
			polyethylene	5.11	0/8
			polystyrene	6.11	0/8
NASA/USF I	600	16	ABS	2.84	8/8
			polystyrene	4.09	3/8
			polycarbonate	4.63	8/8
			polyethylene	5.31	1/8
NASA/USF J	600	48	ABS	2.80	8/8
			polystyrene	3.08	4/8
			polyethylene	4.08	7/8
			polycarbonate	7.66	8/8

<sup>a</sup> All methods involve non-flaming decomposition.

<sup>b</sup> None contained fire-retardant additives.

<sup>c</sup> Mean time to first signs of staggering.

<sup>d</sup> Deaths/exposures.

<sup>e</sup> Recirculated airflow; flow not stated, but is usually 67 mL/s (Kaplan *et al.* 1983).

<sup>f</sup> No incapacitation.

<sup>g</sup> Rising temperature, 40°C/min.

The combustion toxicity test developed for the National Aeronautics and Space Administration (NASA) at the University of San Francisco (USF) by Hilado (1975) also uses the Lindberg tube furnace, but has a smaller total volume and no recirculation. It is capable of being used either at constant temperature or with the temperature rising at a set rate. Hilado *et al.* (1977) have compared the toxicity of products produced in the NASA/USF method at different furnace temperatures and airflows for the same four polymers, including polystyrene (Styron 402D). Procedure B is intended to simulate pre-flashover conditions of a developing fire; procedures E, F, G and H are intended to simulate post-flashover conditions; and procedures I and J are intended to approximate FAA/CAMI conditions. All procedures involve non-flaming decomposition of the material being assessed. Their results (Table 27) show how dependent toxicity results are on the method used. Additionally, the rankings are different depending on the endpoint selected—in this case time to incapacitation or mortality. Depending on the procedure used in the NASA/USF test, polystyrene can produce mortalities ranging from 0% (procedures G and H, Table 27) to 100% (procedure B). Hilado *et al.* (1979) also explored the effects of decomposition temperature and airflow on the combustion toxicity of a polystyrene (Styron 402D). They found that no deaths occurred at furnace temperatures up to 400°C. At furnace temperatures of 500–800°C the mean time to death did not vary much, being between 22 and 29 minutes, but the mortality increased from 38% at 500°C to 95% at 800°C. The occurrence of flaming was not reported.

Hilado and coworkers have published many tabulations of results from the NASA/USF combustion toxicity tests (e.g. Hilado & Huttlinger 1981; Hilado *et al.* 1981). One compilation of data from previous papers (Hilado & Cumming 1978) compares the combustion toxicity of 270 materials determined under the rising temperature regime of NASA/USF procedure B. Results for some building materials are given in Table 28. The polystyrenes assessed generally had a lower combustion toxicity than wood products when assessed by this method. Hilado (1983) has also compiled data specifically for thermal insulation materials, using the NASA/USF procedure B. Of the numerous materials listed, only some polychloroprenes had  $T_d$  values (time to death) longer than expanded polystyrene.

In their review, Gurman *et al.* (1986) included some Japanese studies which compared the combustion toxicity of expanded polystyrene with that of other materials. Gurman *et al.* noted that whilst the procedures differed in detail, there were some similarities. In one of these studies (Nishimaru *et al.* 1979), expanded polystyrene is compared with other cellular plastics,

and with a wood (lauan). Some of their results are given in Table 29.

The sample masses were not the same for all materials. At 550°C the expanded polystyrene failed to cause incapacitation in four out of six mice when 15 g was decomposed, whilst the same mass of lauan, and smaller masses of polyvinylchloride foam and urea resin foam, caused incapacitation in 3–6 minutes. The 5 g sample of the polyurethane foam, which decomposed without flaming, did not cause incapacitation in five out of six mice. At 750°C, the two expanded polystyrenes had the longest time to incapacitation, even though greater masses of these specimens were consumed. The test durations were also much greater.

The University of Pittsburgh Smoke Toxicity Test Method is used for the mandatory determination of combustion toxicity of materials or products sold in the State of New York (Anderson 1990; Chien *et al.* 1991). At present there is debate about this method and its suitability for such a purpose (Grand 1985; 1992; Alarie 1992a; 1992b; Hirschler 1992). The latest version of the test, known as UPitt II (Caldwell & Alarie 1990), uses a truncated cone radiator of the type used in the cone calorimeter (Babrauskas 1982). Previous versions of the UPitt method used the vertical tube furnace described by Kaplan *et al.* (1983), or a Lindberg furnace (Gurman *et al.* 1986).

Alexeeff and Packham (1984a) calculated concentration-time products,  $L(Ct)_{50}$  from published  $LC_{50}$  values for the combustion products of a range of materials determined by the UPitt method. Using rate of mass loss data, they integrated the concentrations (mass of material consumed per unit chamber volume) over the exposure time. Some of their data is given in Table 30. The ranking of  $L(Ct)_{50}$  values differs from the ranking of  $LC_{50}$  values, emphasising the problems associated with attempting to quantify combustion toxicity. The authors suggest exercising caution when comparing  $L(Ct)_{50}$  values, as they may vary with exposure time.

On both scales the expanded polystyrene with fire-retardant additives is assessed as having a lower toxicity than the unretarded expanded polystyrene, though both have higher toxicities than Douglas fir. Gurman *et al.* (1986), who also analysed the data for the polystyrenes from Alarie and Anderson (1979), noted that the UPitt test was one of the few in which combustion products of polystyrene are ranked as being more toxic than wood. Hilado (1983) tabulates data for the relative toxicity of combustion products of thermal insulation materials determined using the UPitt test. His results show that by this method all cellular plastics, including expanded polystyrenes, both fire-retarded and non-fire-retarded, have higher toxicities than wood.

Table 28. Relative toxicity of combustion products of some building materials and plastics using NASA/USF procedure B<sup>a</sup> (after Hilado & Cumming 1978)

Material	Time to death <sup>b</sup> (min)	Time to incapacitation <sup>c</sup> (min)	No. of tests	No. of animals
Rigid polyurethane foam, 10% FR (R2)	10.62	8.28	2	8
Hardboard, unfinished	10.86	8.56	2	8
Red oak, 2	11.50	9.09	2	8
Particleboard, untreated	11.82	9.32	2	8
Nylon 6	13.47	11.55	3	12
Douglas fir, 2	13.62	9.84	2	8
Rigid polyurethane foam, 7% FR (R3)	13.69	10.91	3	12
Polyisocyanurate foam	13.74		2	8
Beech	13.82	9.69	3	12
Polyethylene, 1	13.99	11.54	3	12
Rigid polyurethane foam, FR (Q1)	14.05	11.23	3	12
Aspen poplar	14.06	9.96	3	12
Rigid polyurethane foam, R1	14.10	9.64	2	8
ABS, 3	14.48	10.58	2	8
Red oak, 1	14.50	10.23	3	12
Douglas fir, 1	14.76	11.79	3	12
Western red cedar	14.91	10.00	3	12
Polyethylene foam, 2	14.96	7.81	2	8
Polyethylene foam, 1	15.14	8.44	2	8
Rigid polyurethane foam, FR, 390 kg/m <sup>3</sup>	15.14	12.62	2	8
Eastern white pine	15.42	10.72	3	12
Southern yellow pine	15.56	10.91	3	12
Polymethylmethacrylate	15.58	12.61	2	8
Hardboard	15.90	9.66	4	16
Bisphenol A polycarbonate, 2	16.08	12.82	2	8
Nylon 66	16.34	14.01	2	8
Polyvinylchloride, 1	16.84	12.69	2	8
Phenolphthalein polycarbonate	16.92	14.15	1	4
Rigid polyurethane foam, FR, 300 kg/m <sup>3</sup>	17.29	12.12	2	8
ABS, 2	17.62	13.52	5	20
Medium density hardboard	17.87	9.69	4	16
Chipboard	18.23	9.68	4	16
ABS, 1	19.30	11.35	2	8
Polyethylene, 2	19.84	8.86	2	8
Fibreboard soundstop	19.88	13.00	4	16
Polystyrene, 1	20.03	15.18	2	8
Cellulose fibreboard, core board	20.58	9.91	4	16
Isocyanurate foam, urethane modified, glass fibre, 1	20.71	17.81	2	8
Chlorinated polyvinylchloride, 1	21.76	6.29	3	12
Bisphenol A polycarbonate, FDA grade, reference	21.87	16.77	34	136
Polyethylene, 3	22.60	16.68	2	8
Isocyanurate foam, urethane modified, glass fibre, 2	22.66	20.00	2	8
Chlorinated polyvinylchloride, 2	22.74	9.00	1	4
Bisphenol A polycarbonate, 1	23.04	16.02	2	8
Rigid polyurethane foam, FR (Q2)	23.52	17.58	3	12
Polystyrene, 2	26.16	19.04	2	8
High temperature insulation, perlited	ND <sup>d</sup>	NI <sup>e</sup>	1	4

<sup>a</sup> Furnace temperature rising at 40°C/min from 200°C to 800°C; no forced airflow; no flaming reported.

<sup>b</sup> Mean time to cessation of movement and respiration.

<sup>c</sup> Mean time to first sign of staggering, prostration, collapse or convulsions.

<sup>d</sup> No deaths.

<sup>e</sup> No incapacitation.

Table 29. Relative toxicity of combustion products of some building materials using a Japanese procedure (after Nishimaru *et al.* 1979)

Material	Density (kg/m <sup>3</sup> )	Sample mass		Test duration (min)	Flaming duration (min)	Time to incapacitation <sup>a</sup> (min)
		Before test	After test			
<i>Furnace temperature 550°C</i>						
Expanded polystyrene 1, FR	39	15	0.1	10	0.90–3.83	7.2 <sup>b</sup>
Polyvinylchloride foam	84	7.5	1.9	10	1.93–NR <sup>c</sup>	4.62
Urea resin foam	10	1	0.1	10	0.43–0.75	3.18
Polyurethane foam, FR	NR	5	0.3	10.5	None	8.3 <sup>d</sup>
Lauan	500	15	3.1	10	0.50–1.17	5.60
<i>Furnace temperature 750°C</i>						
Expanded polystyrene 1, FR	39	15	0.1	60	0.20–1.63	12.80
Expanded polystyrene 2, FR	35	15	0.1	60	0.18–1.60	14.51
Polyvinylchloride foam	84	7.5	1.1	15	0.00–1.33	4.10
Urea resin foam	10	1.0	0.1	5	0.13–0.50	1.44
Polyurethane foam, FR	NR	5.0	0.2	10	0.00–0.67	1.47
Lauan	500	10	2.6	10	0.13–3.07	4.23

<sup>a</sup> Mean for six mice at 550°C and eight mice at 750°C, unless otherwise stated.

<sup>b</sup> Results for two tests; four out of six mice not incapacitated.

<sup>c</sup> Not reported.

<sup>d</sup> Results for one test; five out of six mice not incapacitated.

Table 30. Relative toxicity of combustion products of materials determined in the University of Pittsburgh toxicity test and expressed as concentration-time products<sup>a</sup> (after Alexeeff & Packham 1984b)

Material	L(Ct) <sub>50</sub> (mg/L.min)	LC <sub>50</sub> <sup>b</sup> (g)
PTFE resin	32.0	0.6
Wool	117.0	3.0
Phenol formaldehyde	151.0	6.3
Urea formaldehyde	155.5	2.5
Polyisocyanurate foam (GM-41) <sup>c</sup>	275.0	6.4
Expanded polystyrene (GM-47)	290.0	5.8
Polyisocyanurate foam (GM-43)	305.0	6.1
Rigid polyurethane foam FR (GM-31)	360.5	8.2
Rigid polyurethane foam (GM-37)	368.0	8.0
Rigid polyurethane foam (GM-35)	372.0	7.5
Rigid polyurethane foam (GM-29)	453.5	10.4
Cellulose fibre	464.0	11.9
Expanded polystyrene FR (GM-49)	500.0	10.0
Polyvinylchloride	715.0	15.2
Douglas fir	2647.5	63.8

<sup>a</sup> Not stated whether flaming or non-flaming.

<sup>b</sup> Source: Alarie and Anderson (1979).

<sup>c</sup> GM designations identify standard reference materials (Products Research Committee 1980).

The Harvard Medical School combustion toxicity test was developed by Dressler (Kaplan *et al.* 1983) and used in the evaluation of combustion products from consumer goods (Gurman *et al.* 1986). Robinson *et al.* (1977) used the method to investigate whether adding fire retardants to the plastics used in television cabinets increased their toxic hazard. They found that at a combustion chamber temperature of 450°C, deaths from the unretarded polystyrene were substantially more than for the polystyrene containing fire retardants (antimony oxide and decabromodiphenyl oxide) and the polyphenylene oxide containing triphenyl phosphate. However, Kaplan *et al.* (1983) point out that the design of their apparatus allows possible considerable loss of combustion products by reaction with, or adsorption onto, the glass pipes connecting the combustion chamber with the animal exposure chamber.

In many of the toxicity tests the occurrence of flaming is not specifically stated, and yet for polystyrene, and possibly other materials, it seems that the toxicity of combustion products is more dependent on mode of combustion (flaming or non-flaming) than decomposition temperature, as instanced by the data of Potts and Lederer in Tables 23 and 24, and Hoffman and Oettel in Table 25. In those combustion toxicity tests where flaming occurred, polystyrenes had a toxic potency equal to or higher than wood, producing the same or

more fatalities in test animals or obtaining lower LC<sub>50</sub> values, whilst in those combustion toxicity tests where flaming did *not* occur, polystyrene had a lower toxic potency than wood, producing less fatalities in test animals or having longer times to death or incapacitation of test animals or having higher LC<sub>50</sub> values.

### Role of carbon monoxide

The majority of papers on combustion toxicity testing in which attempts are made to identify the combustion product or products primarily responsible for incapacitation or death of test animals, name carbon monoxide as the chief toxicant under most conditions. Hilado (1979) estimated total concentration-time exposures of test animals to carbon monoxide in NASA/USF Procedure B combustion toxicity tests on 93 materials. He found that carbon monoxide was present in sufficient quantities to have been the sole toxicant in the gases from the majority of materials evaluated, including two solid polystyrenes. For a number of materials, including the one expanded polystyrene assessed, Hilado found that carbon monoxide may have been the principal toxicant.

Potts and Lederer (1977), in their evaluation of the toxicity of materials as determined in the Dow Chemical Company test (discussed earlier), concluded that carbon monoxide intoxication appeared to be a large contributory cause to most of the fatalities. They suggest that an average concentration of 3000 ppm of carbon monoxide will, in the absence of significant concentrations of other toxicants, be sufficient to produce death in this test. Their results (Table 23) show that in the flaming exposure both polystyrene and wood produced average concentrations of carbon monoxide in excess of 3000 ppm, and both produced mortalities, whilst in the non-flaming mode the polystyrenes did not produce average concentrations of carbon monoxide in excess of 3000 ppm and did not produce any fatalities.

In a project comparing fire-retarded and non-fire-retarded items (including television cabinets of high impact polystyrene), Babrauskas *et al.* (1988) measured carbon monoxide production in the cone calorimeter, the furniture calorimeter, the NBS toxicity test and in full room burns. They found that the small-scale tests gave lower yields of carbon monoxide than the full-scale tests. Debanne *et al.* (1992) interpret this result to mean that small-scale tests are biased in favour of species other than carbon monoxide. This suggests that the toxic hazard due to carbon monoxide in fires is even greater than what is shown in small-scale tests.

Morikawa (1984), on the other hand, in experiments on hydrocarbons, but not including polystyrene, concludes that at temperatures below 650°C acrolein may have a greater lethal role than carbon monoxide. His experiments were generally, but apparently not exclusively, non-flaming.

### Toxicity index approaches

Whilst carbon monoxide is most often the major toxic species found in combustion toxicity tests, there is no argument that other species can contribute to overall toxicity. The difficulty is in finding ways to sum the contribution of individual toxic species. Sumi and Tsuchiya (1971) used a simple summation to compare the toxicity of expanded polystyrene and white pine due to carbon monoxide and carbon dioxide. In their approach the toxicity of each species is independently calculated by relating its concentration to the short-term exposure lethal level for that material. Hence,

$$t = \frac{C_e}{C_f}$$

where  $t$  is the toxicity index of a species;  $C_e$  is the effective concentration; and  $C_f$  is the concentration fatal to a person in 30 minutes.

In their study,  $C_e$  for each gas was calculated on the basis of 1 g of the material being decomposed at 800°C, and the combustion gases being diffused in a volume of 1 m<sup>3</sup>. The experimental conditions, and data obtained, are discussed earlier (Table 2). The total toxicity of the material is calculated by summing the toxicity indexes for each species. Some of their data is given in Table 31. Under their experimental conditions flaming probably occurred, though this is not explicitly stated.

Their results give expanded polystyrene a toxicity index due solely to carbon monoxide and carbon dioxide of 0.08–0.10 compared to white pine at 0.05–0.09. For white pine the contribution from carbon dioxide is negligible, whilst for expanded polystyrene the contribution from carbon dioxide in one case is one-quarter of the total.

This simple summation approach does not consider synergism between toxic species. However, Tsuchiya and Sumi (1972) believe that synergism is often overemphasised, and do not consider it important when two toxicity indexes differ by a factor greater than ten.

Table 31. Toxicity indexes for expanded polystyrene and white pine decomposed in air at 800°C (after Sumi & Tsuchiya 1971)

Material <sup>a</sup>	Sample mass (g)	Toxicity index		
		CO	CO <sub>2</sub>	SUM
Expanded polystyrene	0.298	0.072	0.014	0.09
	0.296	0.055	0.017	0.07
	0.350	0.088	0.012	0.10
	0.351	0.090	0.012	0.10
	0.400	0.092	0.009	0.10
	0.406	0.081	0.009	0.09
	0.498	0.077	0.007	0.08
	0.497	0.079	0.007	0.09
	0.599	0.069	0.007	0.08
	0.604	0.065	0.006	0.07
White pine	0.800	0.048	0.005	0.05
	0.799	0.051	0.005	0.06
	1.007	0.071	0.005	0.08
	0.999	0.072	0.005	0.08
	1.194	0.090	0.003	0.09
	1.197	0.089	0.003	0.09
	1.606	0.082	0.003	0.08
	1.600	0.086	0.003	0.09

<sup>a</sup> None contained fire-retardant additives.

Sumi and Tsuchiya (1976a; 1976b) further developed their toxicity index by including volume and loading factors; so that,

$$T = t \frac{V}{w}$$

where T is the toxicity factor (of a species); t is the toxicity, or toxicity index of a species; V is the volume into which the products are dissipated; and w is the mass of original material.

Hence,

$$T = \frac{C_e}{C_f} \cdot \frac{V}{w}$$

Putting

$$C_e = \frac{v}{V}$$

where v is the volume of toxic gas produced, the toxicity factor may be expressed as

$$T = \frac{v}{C_f w}$$

Sumi and Tsuchiya assume that the toxicity factors are additive, thus

$$\Sigma T = \Sigma \frac{v}{C_f w}$$

Sumi and Tsuchiya (1976a; 1976b) decomposed a number of materials, including polystyrene (no further description), in a tube furnace and analysed their major

thermal decomposition products. From these results they determined toxicity indexes. Their results (Table 32) are expressed as toxicity factors due to individual toxic species and the overall toxicity factor achieved by simple summation of the individual toxicity factors. They found that polystyrene had one of the lowest potentials for generating harmful decomposition products. Their results show that the toxicity factor for polystyrene is due solely to carbon monoxide and carbon dioxide, whereas for some other materials the main toxic species contain nitrogen or chlorine. Polystyrene has a similar toxicity factor to white pine, whilst both are lower than some other polymeric materials. The toxicity factor, as developed by Sumi and Tsuchiya, does not include oxygen depletion, unlike the following toxicity index approaches.

Hartzell *et al.* (1985) worked with 'doses' (concentration-time products) of individual toxicants, and introduced the term 'fractional effective dose' to relate exposure doses to lethal dose. This work relies on 'Haber's rule', which states that the exposure dose required to cause an effect for a given toxicant is relatively constant, i.e.

$$Ct = K$$

where C is the exposure concentration; t is the exposure time; and K is constant for a particular toxicant.

Hartzell *et al.* expressed their fractional effective dose (FED) in the form:

$$FED = \frac{\bar{C} \times \Delta t}{(Ct)_c}$$

Table 32. Toxicity factors determined by summation of toxicities of thermal decomposition products<sup>a</sup> (after Sumi & Tsuchiya 1976b)<sup>b</sup>

Material	Toxicity factor (1/g) due to <sup>b</sup>					$\Sigma T^c$
	CO	CO <sub>2</sub>	HCl	HCN	Others	
Polystyrene	19	2				20
Polyethylene	21	1				20
Phenolic resin	5	1			22	30
White pine	47	3				50
Polyvinylchloride	12	1	343			360
ABS	10	1		267		280
Polyurethane (rigid)	14	1		273		290
Nylon 6	17	1		931		950

<sup>a</sup> Thermal decomposition temperatures of 800°C for most materials, but possibly lower for polyvinylchloride.

<sup>b</sup> The following values of C<sub>f</sub> (dangerous concentration for a 30 minute exposure (ppm)) were used: HCN 135; CO 4000; CO<sub>2</sub> 70 000–100 000; HCl 1000.

<sup>c</sup> Maximum values obtained by Sumi and Tsuchiya.

where  $\Delta t$  is a time interval;  $\bar{C}$  is the mean concentration of toxicant over a time interval; and  $(Ct)_c$  is the dose necessary to produce an effect.

The effect occurs at the time that

$$\Sigma \text{FED} = 1$$

Hartzell *et al.* verified their fractional effective dose model for exposure of rats to single toxicants, including carbon monoxide.

Levin *et al.* (1987) showed that, in most cases, observed toxicity may be explained by the toxicological interactions of a limited number of major fire gases. The concepts of summation, fractional effective dose and the use of a limited number of fire gases have been combined in what has come to be known as the N-Gas Model (Braun *et al.* 1987; Levin & Gann 1990; Babrauskas, Levin *et al.* 1991). Babrauskas, Levin *et al.* (1991) have included a standard procedure for development of data for use in toxic fire hazard modelling as an annex in their paper. It includes the N-Gas Model in the following form:

$$\text{FED} = \frac{m[\text{CO}]}{[\text{CO}_2]-b} + \frac{21-[\text{O}_2]}{21-\text{LC}_{50} \text{O}_2} + \frac{[\text{HCN}]}{\text{LC}_{50} \text{HCN}} \\ + \frac{[\text{HCl}]}{\text{LC}_{50} \text{HCl}} + \frac{[\text{HBr}]}{\text{LC}_{50} \text{HBr}}$$

where FED is the fractional effective (exposure) dose;  $m$  and  $b$  are constants which depend on the concentration of carbon dioxide (if  $[\text{CO}_2] \leq 5\%$ ,  $m = -18$  and  $b = 122\,000$ , if  $[\text{CO}_2] > 5\%$ ,  $m = 23$  and  $b = -38600$ );  $[\text{CO}]$ ,  $[\text{CO}_2]$ ,  $[\text{O}_2]$ ,  $[\text{HCN}]$ ,  $[\text{HCl}]$  and  $[\text{HBr}]$  are the concentrations of carbon monoxide, carbon dioxide, oxygen, hydrogen cyanide, hydrogen chloride and hydrogen bromide respectively (in ppm except  $\text{O}_2$  which is in %); and  $\text{LC}_{50} \text{O}_2$ ,  $\text{LC}_{50} \text{HCN}$ ,  $\text{LC}_{50} \text{HCl}$  and  $\text{LC}_{50} \text{HBr}$  are the lethal concentrations (necessary to kill 50% of the exposed animals) of oxygen (by depletion), hydrogen cyanide, hydrogen chloride, and hydrogen bromide respectively, and have values of 5.4%, 150 ppm, 3800 ppm and 3000 ppm.

The equation then reduces to

$$\text{FED} = \frac{m[\text{CO}]}{[\text{CO}_2]-b} + \frac{21-[\text{O}_2]}{15.6} + \frac{[\text{HCN}]}{150} \\ + \frac{[\text{HCl}]}{3800} + \frac{[\text{HBr}]}{3000}$$

The first term reflects the interaction between carbon monoxide and carbon dioxide quantified by Levin *et al.* (1986). However, not all workers are convinced that there is such an interaction (Crane 1985; Tsuchiya 1986).

In the assessment of polystyrenes, the third and fourth terms would normally be zero, whilst the final term may be affected by the presence of any brominated fire retardant. Hence in this approach the combustion toxicity of polystyrene would be determined largely from the concentrations of carbon monoxide, carbon dioxide and oxygen.

Purser (1989a; 1989b) has also developed a combustion toxicity model based on summing fractional effective doses. The terms in his equation take into account the way different gases act on the body. He defines a 'fractional incapacitating dose for narcosis',

$$F_{\text{IN}} = (F_{\text{ICO}} + F_{\text{ICN}}) \times V_{\text{CO}_2} + F_{\text{IO}} \text{ or } F_{\text{ICO}_2}$$

where  $F_{\text{IN}}$  is the fraction of an incapacitating dose of all narcotic gases;  $F_{\text{ICO}}$ ,  $F_{\text{ICN}}$ ,  $F_{\text{IO}}$  and  $F_{\text{ICO}_2}$  are the fractions of incapacitating doses of carbon monoxide, hydrogen cyanide, 'low oxygen hypoxia' and carbon dioxide; and  $V_{\text{CO}_2}$  is a multiplication factor for carbon dioxide-induced hyperventilation.

The fractions of incapacitating dose ( $F$ ) for each gas are determined differently, depending on their physiological action. The term for carbon monoxide is related to carboxyhaemoglobin level, resulting from exposure to carbon monoxide, in a 70 kg man engaged in light activity for up to one hour. The term for low oxygen hypoxia is derived from the 'dose' of hypoxia necessary to cause loss of consciousness. There are two terms for carbon dioxide. The multiplication factor ( $V_{\text{CO}_2}$ ) is derived from the increased respiratory activity caused by carbon dioxide, which increases the rate of uptake of other toxic gases, and which is itself a narcotic. The second term ( $F_{\text{ICO}_2}$ ) is derived from the time to unconsciousness caused by carbon dioxide. The term for hydrogen cyanide ( $F_{\text{ICN}}$ ) will normally be zero for polystyrenes.

In this model, the toxicity of combustion products of polystyrene will be determined solely by the concentrations of carbon monoxide, carbon dioxide and oxygen. At this stage neither model has been validated specifically for polystyrene.

### Toxic hazard

Purser (1988; 1992) discusses the role fire behaviour characteristics other than toxicity of combustion products play in toxic hazard. He points out that as toxic hazard is a function of quantity of combustion products produced as well as the toxicity of combustion products, the toxic hazard of a material is dependent on fire behaviour characteristics such as ease of ignition and burning.

Anderson and Alarie (1978) quoted data obtained using the UPitt II method (employing the vertical tube furnace) when developing a toxic hazard index. Two expanded polystyrenes (one with fire retardants) had LC<sub>50</sub> values, determined by this method, greater than wood. However the toxic hazard indexes, which were calculated by dividing densities by initial decomposition temperatures and LC<sub>50</sub> values, were lower for the expanded polystyrenes than for wood. (The LC<sub>50</sub> values quoted had units of mass, and hence, according to Gurman *et al.* (1986), should be quoted as LL<sub>50</sub> values.)

Babrauskas (1993) has proposed a measure of toxic hazard that combines toxicity data from the NBS combustion toxicity test (Levin *et al.* 1982) with mass loss and ignitability data from the cone calorimeter (Babrauskas 1982). He suggests the relationship

$$\text{toxic fire hazard} \propto \frac{\text{MLR}}{t_{\text{ig}} \times \text{LC}_{50}}$$

where MLR is the average mass loss rate from 10% to 90% mass loss in the cone calorimeter at an irradiance of 50 kW/m<sup>2</sup>;  $t_{\text{ig}}$  is the ignition time under the same conditions; and LC<sub>50</sub> is the lethal concentration (necessary to kill 50% of exposed animals) in the NBS combustion toxicity test.

He has determined the 'toxic fire hazard' of the materials used by Levin *et al.* (1983) in their interlaboratory evaluation. Some of his results are given in Table 33.

Expanded polystyrene has a similar 'toxic fire hazard' to Douglas fir and red oak, and a much lower 'toxic fire hazard' than the rigid polyurethane foam and the ABS (acrylonitrile-butadiene-styrene).

### Large-scale testing

A number of studies have been conducted on measuring toxicity from large-scale fires. Some have had the object of assessing toxicity from 'typical' building contents (Morikawa & Yanai 1986; 1990; 1993). However, they have not included any polystyrene products amongst the materials used. Other studies have sought to compare bench-scale combustion toxicity tests with large-scale fires. A series of studies at the US National Institute of Standards and Technology (formerly National Bureau of Standards) sought to validate the

Table 33. Relative toxic hazard of some materials calculated from data obtained in the NBS combustion toxicity test and the cone calorimeter (after Babrauskas 1993)

Material <sup>a</sup>	LC <sub>50</sub> <sup>b</sup> (mg/L)	MLR <sup>c</sup> (g/m <sup>2</sup> .s)	$t_{\text{ig}}$ <sup>c</sup> (s)	$\frac{\text{MLR}}{t_{\text{ig}} \times \text{LC}_{50}}$ <sup>d</sup> (mm/s <sup>2</sup> )
Rigid polyurethane foam (GM-30) <sup>e</sup>	13.3	20.5	3.4	480
ABS	19.3	27.5	12.5	120
Douglas fir	40.0	7.95	14.3	14
Expanded polystyrene (GM-51)	38.9	17.0	33.1	13
Red oak	56.8	12.0	22.7	9.7

<sup>a</sup> None contained fire-retardant additives.

<sup>b</sup> Corresponds to data for flaming in the fifth column of Table 25.

<sup>c</sup> Average of two tests.

<sup>d</sup> 'Toxic fire hazard'; may not compute exactly due to averaging in previous columns.

<sup>e</sup> GM designations identify standard reference materials (Products Research Committee 1980).

NBS combustion toxicity test (Braun *et al.* 1987; 1990; Babrauskas *et al.* 1991a; 1991b). These studies show that comparing bench-scale combustion toxicity tests to large-scale fire tests is a complex procedure. Points of comparison between small- and large-scale included the nature of animal deaths; the relative contributions of different gases to animal deaths; similarity of gas yields, and N-Gas Model predictions. Braun *et al.* (1990) found that the NBS combustion toxicity test did not produce the same combustion atmosphere found in large-scale tests, however the N-Gas Model could take this into account. Babrauskas *et al.* (1991b) found that the N-Gas Model predictions were the most promising way to relate bench-scale data to large-scale tests. These studies did not include any polystyrenes.

Fardell *et al.* (1986), in their room/corridor experiments discussed earlier, burnt single fuels, including expanded polystyrene. They did not perform any toxicity assessments, but as well as measuring the concentrations of oxygen, carbon dioxide and carbon monoxide, they measured complete 'fingerprints' for each material at different stages of the fire. Such data could presumably be used with toxicity index approaches, such as the N-Gas Model.

## FIRE STUDIES

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The following studies on fire deaths do not attempt to relate deaths to any particular material, and therefore it is not known what proportion of fires involved polystyrene.

Berl and Halpin (1976) conducted an analysis of fire deaths in the State of Maryland in 1972-73. They concluded that inhalation of carbon monoxide was responsible for incapacitation and death of 72% of the 99 fire fatalities studied. The majority of victims (59%) had inhaled lethal quantities of carbon monoxide. In another 11 fatalities, the carboxyhaemoglobin was sufficiently high to have caused severe debilitating reactions.

Berl and Halpin (1978) extended their previous survey to 463 deaths in the State of Maryland over the period 1972-77. They found that 75% of all fatalities were due to toxic gas inhalation, and that the number of fire victims with lethal carboxyhaemoglobin levels, due to inhaling carbon monoxide, was the same as in the previous study (59.4%).

Birky *et al.* (1979) also conducted an analysis of fire deaths in the State of Maryland. They concentrated on deaths in predominately residential buildings in the period September 1971 to December 1977. They also concluded that inhalation of carbon monoxide was the predominant cause of deaths in fires.

At the University of Glasgow, Harland and Woolley (1979) studied fire deaths in the Strathclyde region of

Scotland for the period July 1976 to April 1978. They found that carbon monoxide was almost certainly the cause of death in 50% of the 100 cases studied. However, when other known causes were eliminated a significant proportion of deaths still remained unexplained. Later work (Anderson *et al.* 1983) extended the study to the rest of the UK. It was found that the conclusions on fire deaths reached in the Glasgow study were valid for the UK as a whole.

Debanne *et al.* (1992), sponsored by the Society of the Plastics Industry, carried out a comprehensive study on the role of carbon monoxide in fire deaths. The study included a literature search on the toxicity of carbon monoxide to humans and two extensive forensic studies on deaths across the entire USA associated with carbon monoxide. They concluded that the toxicity of fire atmospheres is determined to a very large extent by the amount of carbon monoxide, the contribution of other toxicants usually being very small. They also concluded that the carbon monoxide concentrations in the atmospheres of large fires are determined by factors such as oxygen availability, ventilation and size of fuel load, and are very minimally affected by the chemical composition of the fuels. They further concluded that the replacement of 'natural and traditionally used materials' by man-made materials has made no difference to the toxicity of fire atmospheres.

## CONCLUSIONS

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1. Studies of fire deaths have shown that most deaths from 'smoke' inhalation are caused by carbon monoxide, although other gases, including oxygen depletion, may contribute.
2. Carbon monoxide is the major toxic combustion product in fires, though after flashover the relative production of other gases, depending on the nature of the fuel, may increase.
3. In well-ventilated fires, such as occur before flashover, the major toxic combustion product from the burning of polystyrene, and probably most organic materials, is carbon monoxide.
4. In poorly ventilated fires, such as occur after flashover, the major toxic combustion product from the burning of polystyrene is styrene.
5. In combustion toxicity tests where non-flaming combustion occurred, polystyrene had a lower toxic potency than wood. It produced less fatalities in test animals, or longer times to death or incapacitation of test animals, or higher LC<sub>50</sub> values.
6. In combustion toxicity tests where flaming combustion occurred, polystyrenes had a toxic potency equal to or higher than that of wood. It produced the same or more fatalities in test animals, or lower LC<sub>50</sub> values.
7. There are only two substantive studies on toxic hazard. In these studies, which combined toxic potency with other fire behaviour characteristics, standard expanded polystyrene was determined to have a toxic hazard to animals less than or similar to that of wood.

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