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Study 1901/01/166 – How PIN FRs affect gas and soot toxicity of smoke in case of fire? Review of the literature.
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Executed for: PINFA – Mr Philippe SALÉMIS

pin*f*a
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Executive Summary

In December 2016, the Association for non-halogenated Phosphorus, Inorganic and Nitrogen Flame Retardants (pinfa.org) asked CREPIM for a scientific literature review on the way PIN flame retardants affect the degradation of materials and as a consequence the smoke emitted and its related toxicity. Chemicals that are expressly used as smoke suppressants are not within the scope of this report. We identified 135 relevant documents from which 22 have been investigated in details.

Fire hazard assessment generally consists in investigating three contributions of a material to fire:

1) Rate of fire growth, mostly estimated as the rate of heat released from burning material and responsible for the increased temperatures near the fire

2) Smoke obscuration as a result of the yield of soot, affecting people ability to escape

3) Smoke toxicity, since the inhalation of the fire airborne products can result in a variety of ill effects ranging from disorientation to death; in addition to acute toxicity, there can also be long-term toxic effects from the inhalation of smoke

Therefore, toxicity from inhalation of toxic gases is one aspect of fire hazard assessment since it is accountable for fire deaths through incapacitating and irritant effect, however the main driver is the amount of material burnt and the heat released which govern both intensity of a fire and survivability in a fire scenario.

Fire retardants are most frequently added to plastics in order to improve their fire properties, especially by increasing the required energy to set materials on fire and to maintain the burning. It consequently leads to the modification of many flammable materials and to an accordant increase in fire safety. E.g. the use of FRs in flammable materials is necessary to pass the imposed requirements of European fire safety regulations for mass transportation and public building sectors. Smoke is always toxic, to varying degrees, however for fire retardant products in particular, the question has been raised as to whether the emission of toxic gases can be badly impacted and so if there is a net safety benefit from their use. The purpose of this work is then to gather relevant data and information so as to bring an objective overview of the known impacts of the use of Phosphorus Inorganic and Nitrogen Flame Retardant (PIN FR) on the resulting immediate and long term toxicity of the smoke of burning materials.

It appears that the factors which govern the toxicity of smoke in a real fire are on one hand, the fire scenario (meaning the ventilation, supply of oxygen in the fire and temperature), and on the other hand, the materials involved. Smoke toxicity assessments are always carried out with special attention to the testing method (defining the fire conditions and scenario) and the scale (bench test or real fire

conditions). It has been demonstrated that the acute toxicity is mainly defined as the addition of effects of a few asphyxiants and irritant gases (N-gas model), but it is very important to note that CO plays a dominant role being the big toxic killer, since it is produced from all burning organic materials and in almost all cases in greater quantities than other toxic gases.

A fair assessment of the impact of flame retardants in a material is only possible when you compare against the neat material. Even when no PIN FRs are present, high quantities of toxics in fire effluents can be found. Regarding the use of PIN FR, those acting in the gas phase (e.g. phosphinates) are inhibiting the flame and can therefore result in more incomplete combustion products but there is no evidence on a negative effect on the global toxicity of smoke. PIN FR acting in the condensed phase (e.g. metal hydroxides and many phosphate derivatives) by generating a protective charred layer can help reducing the yields of airborne products since gases and soot given off are partly trapped.

Longer term toxic effects of soot is caused by PAHs and dioxins and furans. PAHs are the most relevant pollutants in soot particles after fires because these materials are generated in the highest quantity. They are generated in all fires, particularly under pyrolysis and smouldering conditions. By their chemical nature, PIN FRs cannot generate halogenated dioxins and furans. Firefighters are particularly concerned about the repeated inhalation of volatile organic compounds (VOCs) in case of fires, and due to their known toxicities (carcinogenicity, etc.), the consistent wearing of their personal protective equipment like breathing masks seems to be a relevant solution to reduce risk.

For real life, full scale fires, this literature survey showed that there is a lack of PIN FR studies available on the smoke toxicity topic and especially on the soot generated. Most of the 22 scientific papers gathered are dealing with bench scale tests and not enough in case of real fire conditions, thus ignoring a lot of interactions between environment of the fire and materials involved. Nevertheless, none of the papers gathered in the frame of our work is pointing out any adverse effect of the addition of PIN FRs or synergist on the smoke toxicity of materials or products compared to the non-FR versions. What really matters then is that the proper use of PIN FRs and synergists can reduce both the flammability and the heat release rate. This helps fires to remain small for a longer time by delaying the occurrence of the flashover, thus increasing the required safe escape time (RSET) for people and decreasing the fire fatalities.

General introduction

Far from nuclear fission, combustion is the only known means of causing matter to release large amounts of stored energy. Indeed, even nuclear power would be impossible without combustion: metals have to be melted and fabricated before nuclear reactors can be constructed. Just how important combustion is can be illustrated by considering a lump of coal, a piece of wood or a litre of oil: how could one release the energy within these materials without combustion? From very early times to the present, from the need for warmth in caves to the apparent need for high speed motor cars, combustion has played an essential role in the development of humanity. This phenomenon is essential, combustion releases heat and that heat, a form of energy, can be used for highly important applications, such as producing electricity in thermal power stations.

When organic substances burn, they release heat; they also release chemical products of combustion. The atoms forming the molecules of organic matter cannot be destroyed by combustion, but they can be caused to separate from their original combinations and to form other combinations. Material comprising only molecules containing carbon, oxygen and hydrogen cannot, on burning, fail to produce molecules containing these elements. The principle products of combustion are carbon dioxide and water, but depending on the efficiency of the combustion process, other substances are produced: carbon monoxide, for example. Already we have identified a toxicologically active product of combustion. Carbon monoxide is a very poisonous gas and is responsible for a high percentage of deaths occurring in accidents involving fires. Combustion is often not very efficient and a range of gases and particulate materials are produced: smoke and ash. Some products remain at the source of the fire; others are carried into the atmosphere along with the heated air produced by the fire. Air pollution is produced. Even well regulated combustion of the type seen in modern internal combustion engines produces pollutants. Everybody has seen black smoke being emitted by old diesel powered vehicles; even the "cleanest" new motor car produces carbon dioxide.

Fire safety requirements are divided into fire resistance (the ability to maintain structural integrity in a fire) and fire reaction (flammability and fire toxicity). Fire hazard assessment requires consideration of the most probable fire scenarios, and prediction of the rate of fire growth, the amount of fuel present, its impact on the occupants and their ability to escape safely. Figure 1 shows a schematic relationship between the factors required to assess the fire hazard with a special focus on fire toxicity. In order to ensure safe evacuation, ISO 13571 subdivides the hazards to people escaping from

a fire into the effects of heat, asphyxiant gases, irritant gases, and visual obscuration by smoke. It treats each of the four components separately, defining untenability when any of the four reach a level which would prevent a potential victim effecting their own escape.
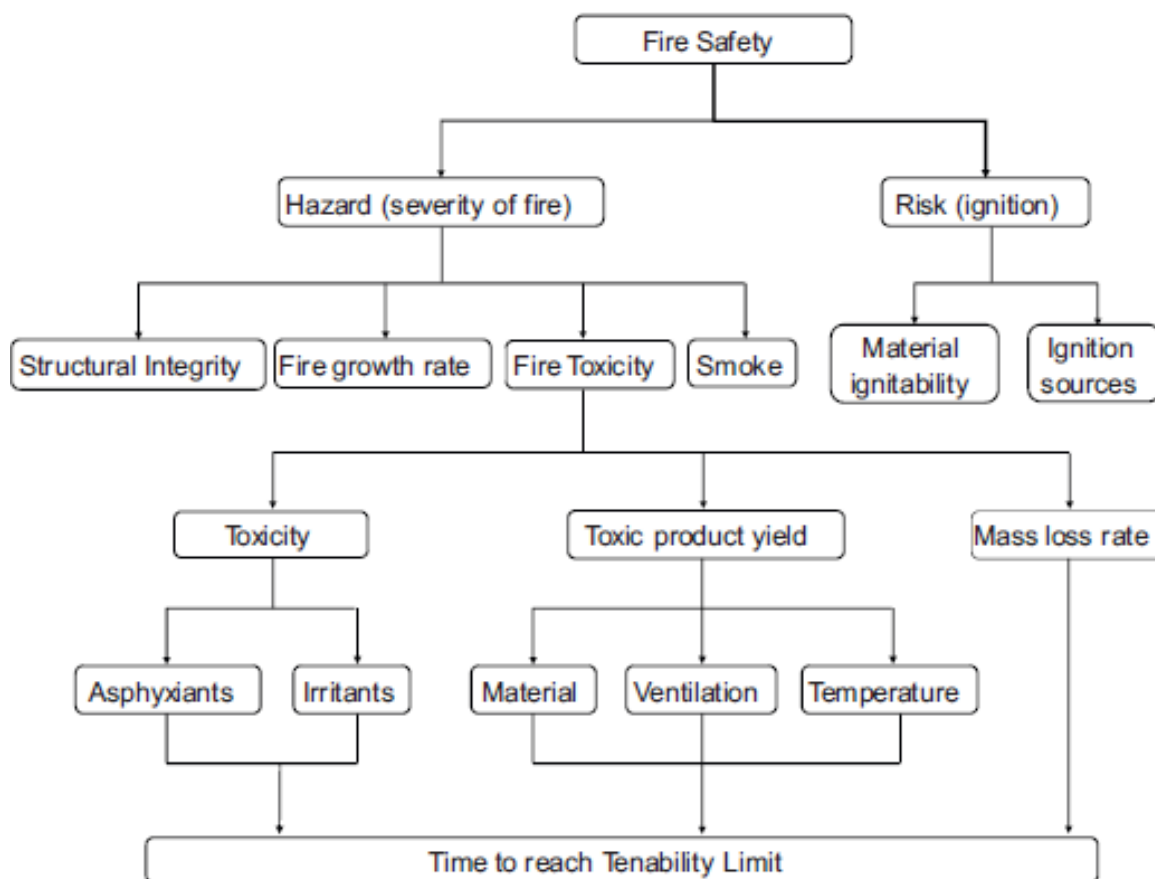
Figure 1 : Schematic of factors required for fire hazard assessment relating to fire toxicity[1]

It is then commonly admitted that nowadays fire toxicity is one of the major threat to be considered for fire safety assessment. Thus, the toxicity of materials and products involved in a fire could be put into question. In particular, for decades, fire retardants had caught the attention of scientists as regards to their contribution to the global toxicity of gases given off a fire. In spite of extensive studies and reviews already carried out on halogenated fire retardant, fewer papers have deeply studied the case of Phosphorus Inorganic and Nitrogen Flame Retardants (PIN FRs). The aim of the present work consists in providing the most comprehensive overview on the way PIN FRs affect the degradation of material and as a consequence the smoke emitted and its related toxicity.

To achieve this goal, the review has been broken down into different topics:

1. Reminding the fire retardant action of PIN FR
2. Defining the smoke in details and the experimental methods to analyse it
3. Reviewing relevant scientific publications by gathering objective information on the gases part of the smoke
4. Reviewing relevant scientific publications by gathering objective information on the soot and particulates part of the smoke
5. Discussing and concluding on the actual knowledge of PIN FR role played in the toxicity of fires

1- Reminder about PIN FR actions

1.1- Introduction

The acronym PIN FR means Phosphorus, Inorganic and Nitrogen Fire Retardant. Fire retardant (FR) is a compound which is added to a matrix, usually polymeric, in order to retard a fire by cancelling, during a certain period, a triangle fire setting (heating, oxidizer or fuel), thus disturbing the fire development. Those PIN FRs could be composed of different phosphorus oxidation degree (as Phosphate, Phosphonate, Phosphinate and Phosphine) or nitrogen compound (e.g. Melamine Phosphate, phosphazene compound include a pentavalent phosphorus and at least one nitrogen atom in a molecule) or could be also Inorganic like ATH or MDH (Aluminium Trihydroxide, Magnesium Dihydroxyde). Experience tends to use those FR, which are halogenated free, in order to reduce toxicity (compared to halogenated FR) and prevent risks for human during a fire. The aim of this first chapter is to have a brief review of PIN FR mechanisms occurring during the thermal degradation.

The expected effects for PIN FR are the following[2]:

- ➢ Condensed phase action
    - Endothermic degradation of the FR (metal hydroxide)
    - Dilution (Inert compounds like $CaCO_3$, talc (etc.)
    - Formation of a thermal shield (charring effect and intumescent system through phosphate and phosphonate derivatives)
- ➢ Gas phase action
    - Radical inhibition (phosphine and phosphinate derivatives)
    - Diminution of flame temperature by dioxygen dilution (additives releasing CO_2, H_2O, or NH_3 that can still be burnt to NO_X)

In order to choose a FR, it is essential to understand the thermal degradation of the polymeric matrix. In one hand, thermal exposure of polymeric matrix causes degradation allowing splitting of the polymeric structure which releases a lot of species such as monomers and acids. In the other hand, according to the fire triangle, plastic starts to ignite thus allowing fuel evaporation. This setting feeds the fire and depends on the kind of gases produced by the degradation and kinetics of gas releasing. Consequently, an ideal FR needs to respect four conditions to be added to the matrix:[3]

1. Be thermally stable up to the polymer degradation temperature (need to have almost the same degradation temperature than the matrix).
2. Be chemically compatible with the polymer to avoid migration which reduces the FR characteristics of the material with time.

3. Barely not influencing the physicochemical properties of the polymeric material.
4. Exhibiting a low toxicity and should not generate toxic and obscuring smoke when burning.

1.2- Phosphorus derivatives and intumescent systems thereof

Phosphorus based FRs involve phosphorus that can be stable in different oxidation degrees states, such as Phosphate, Phosphonate, Phosphinate and Phosphine or Phosphine oxide (see Figure 2).
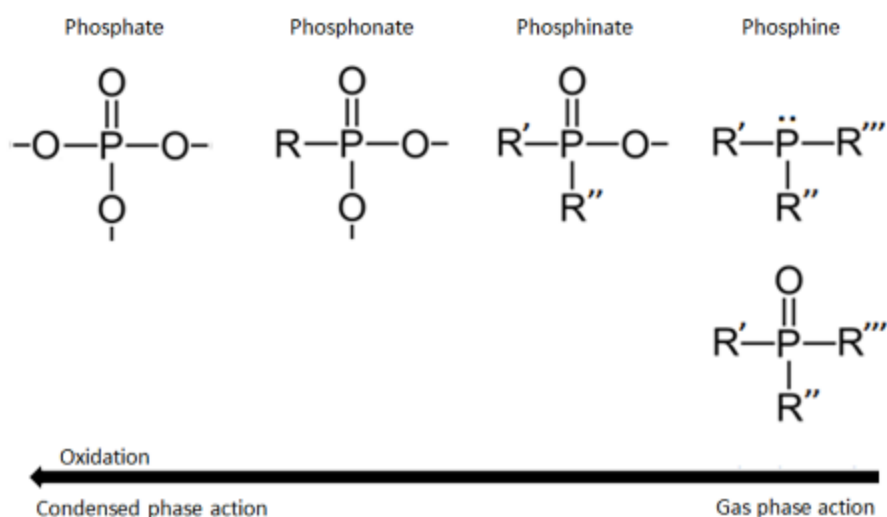
Figure 2 : Oxidation degrees of phosphorus useful for FR properties

The choice of the phosphorus-based FR depends on different parameters such as the polymer matrix or the action looked for while the thermal degradation occurs. Even though it is well-known today that the major action of those FR occurs in the condensed phase[2], it is also admitted that the less oxidised phosphorus-based FRs (phosphinate, phosphine) can act in the gas phase (Figure 3).
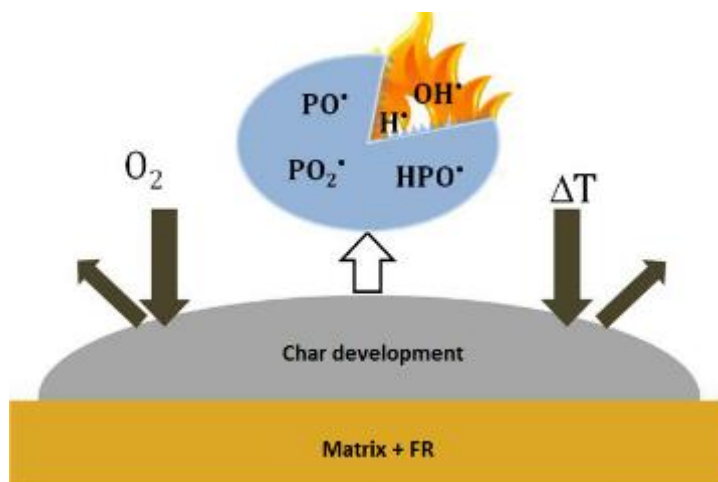
Figure 3 : Phosphorus-based FR action during thermal degradation

1.2.1- Condensed phase

High oxidation degree of phosphorus tends to promote phosphoric acid (H_3PO_4) releasing acting in the condensed phase, by Diels Alder cyclisation process, thus generating the polycyclic aromatic carbonaceous solid structure[2] (char – see Figure 4). Then, the combustible source is protected from the thermal source and oxygen penetration.
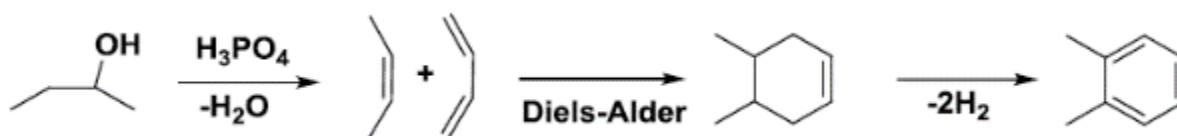
Figure 4 : Condensed phase action of phosphorus-based FR - Diels Alder cyclisation

Simultaneously to the charring effect, if an important quantity of gases is released, the char swells thus increasing the thermal barrier effect (see Figure 5). This is called intumescence and has been highly investigated during the last decades. The release of highly flammable decomposition products is consequently slowed down thus resulting in the decrease of the rate of heat released.

Figure 5 : Example of an intumescent expanded char

Intumescent system is so a system which allows the material to expand and generate the thermal shield protecting the polymer against the heat. As seen previously high oxidation degree of phosphorus is used like ammonium polyphosphate. Typically, the principal ingredients of intumescent system are the following:

1. Inorganic acid or material yielding acidic species - e.g.: phosphoric acid, ammonium polyphosphate etc.
2. A char former or carbon source, basically a primary hydroxyl rich compound - e.g.: pentaerythritol, starch, charring polymers (PA6, PU …) etc.
3. A blowing agent that decomposes to release a lot of inert species in the gas phase, mostly based on nitrogen derivatives – e.g.: melamine, urea etc.

As far as the mechanism of intumescent system is concerned, it has already been extensively described[2,4,5,6] and it is no worth in this review to explain it once more. However, the attention is drawn on the fact that the use in polymers involves specific problems:

1. The additive must be thermally stable at polymer processing temperature (often greater than 200°C).
2. The thermal degradation process of the polymer, which gives large amounts of volatile products and possibly leaves a charred residue depending on the chemical structure of the polymer, must not adversely interfere with the intumescence process.
3. The additive must form the protective foamed char over the entire surface of the burning polymer, in spite of being diluted within the polymer itself.
4. The additive must not impair the physical and chemical properties of the polymeric material. In particular, it should not interact adversely with fillers or other additives such as stabilisers, which ensure protection of the polymer during processing and outdoor exposure.
5. Low water solubility as well as low hygroscopicity could also be required if the host matrix requires such properties.

By the way, the current market offer allows the formulator to prevent any of the above problems since FR producers exhibit large ranges of ready-to-use intumescent systems for various final applications.

Apart from the traditional components of intumescent systems, some additional compounds, can be added to enhance the properties, thus resulting in synergistic effect. Indeed, these includes[4]:

1. Boron compounds: zinc borates, B_2O_3, borophosphate, borosiloxane.
2. Phosphorus compounds: phosphazene, $ZrPO_4$.
3. Silicone compounds: silica, silicone, silicalite.
4. Aluminosilicate: mordenite, zeolite, montmorillonite
5. Rare earth oxides: La_2O_3, Nd_2O_3.
6. Metal oxides: MnO_2, ZnO, Ni_2O_3, Bi_2O_3, TiO_2, ZrO_2, Fe_2O_3.
7. Others: carbon nanotubes, silsesquioxanes, layered double hydroxides, Cu, Pt, talc, sepiolite, zinc and nickel salts.

The presence of the additional filler can modify the chemical (reactivity of the filler versus the ingredients of the intumescent system) and physical (expansion, char strength and thermo-physical properties) behaviour of the intumescent char when undergoing flame or heat flux leading to enhanced performance. The probable

mechanism involves chemical reactions between the fillers and the acid source (mainly phosphate derivatives) to yield phospho-X compounds (e.g.: phosphosilicate, zinc phosphate, borophosphate, etc.) reinforcing the structure and/or the action of the fillers (or its reaction products) as a nucleating agent. Those reactions promote the formation of a homogeneous foamed structure with appropriate thermophysical properties (lower heat conductivity, lower emissivity at the surface, etc.).

1.2.2- Gas phase

Fire retardants acting in the gas phase are low oxidation degree of phosphorus like phosphinates and phosphines. In this case hydrogen and hydroxyl radicals are replaced by less effective radicals or are turned into harmless components by radical recombination in the gas phase[7]. Some possible key reactions are proposed in the equations below. Branching and chain reactions of the oxidation of hydrocarbons in the gas phase are slowed down or interrupted, which is called flame inhibition, and reduces the production of heat. The efficiency of P in the gas phase is reported to be similar or even superior to hydrogen halides like HBr. Although detailed investigations of the flame area, such as identifying the intermediate products and monitoring concentrations of the different products are quite rare, the main principle seems to be understood. It is believed that the PO-radical plays the major role. Furthermore, the resulting flame retardancy effects are obvious, including a clearly decreased heat release due to a reduced heat release rate (HRR)/mass loss rate value during flammability and fire tests.

$$PO^{\cdot} + H^{\cdot} \rightarrow HPO$$

$$PO^{\cdot} + OH^{\cdot} \rightarrow HPO_2$$

$$HPO + H^{\cdot} \rightarrow H_2 + PO^{\cdot}$$

$$OH^{\cdot} + H_2 + PO^{\cdot} \rightarrow H_2O + HPO$$

$$HPO_2^{\cdot} + H^{\cdot} \rightarrow H_2 + PO_2$$

$$HPO_2^{\cdot} + OH^{\cdot} \rightarrow H_2O + PO_2$$
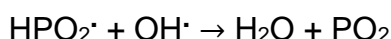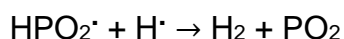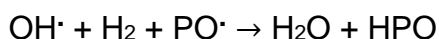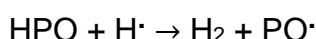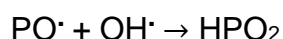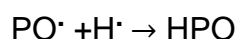
1.3- Metal oxides/hydrates

This is the largest volume PIN FR additive product group in the FR industry[8]. Aluminium trihydroxide (ATH) and magnesium dihydroxyde (MDH) are the principal products in this group which also includes brucite, hydromagnesite, huntite, and mixed metal hydroxyl carbonates. Brucite is essentially magnesium hydroxide in a naturally

occurring form. Hydromagnesite is a natural mineral usually found with huntite ($3MgCO_3Mg(OH)_2$, $3H_2O$) + $Mg_3Ca(CO_3)_4$. Mixed metal hydroxycarbonate compounds are like hydrotalcite with varying amounts of magnesium and aluminium interspersed in layers. These less frequently used types of metal hydrate FRs have been studied, but their commercial usage is small in comparison with ATH and MDH. ATH is the largest volume FR and has been so for many years. It is an extracted component of bauxite ore. ATH is a low cost FR and is easy to use.

Concerning its action, a typical mechanism described involves both dilution of the flammable volatile products feeding the flame, and cooling down of the solid phase due to endothermic decomposition[3,9]. First, the solid state endothermic processes triggered by metal oxides cool down the substrate to a temperature below that required for sustaining the combustion process.

Secondly, dilution of the gas phase leads to decrease of the temperature of the flame due to decrease of rate of exothermal oxidation reactions and to increase of volume of gases to be heated by the heat evolved by the oxidation. A lower rate of heat transfer to the polymer may result in the reduction of its rate of degradation to below the self-sustaining value. In addition, the flame may extinguish if dilution results in a concentration of flammable products which is outside the flammability zone.

ATH begins its endothermic breakdown in the range of 180-200°C releasing its first chemically bonded water. Regarding MDH, the first endothermic breakdown occurs at 300°C. This represents the main advantage over ATH since it allows processing at higher temperatures.

The reactions of decomposition for those compounds are the following:

$$\text{ATH: } 2\ Al(OH)_3 \rightarrow Al_2O_3 + H_2O\ (-1050\ kJ/kg)$$
$$\text{MDH: } Mg(OH)_2 \rightarrow MgO + H_2O\ (-1300\ kJ/kg)$$
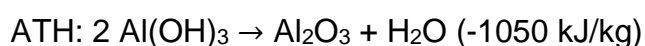
As soon as the dehydration is complete, the residual metal oxides such as alumina and magnesia generated are very stable due to their melting point which is about 2000 - 3000°C. Unfortunately, both ATH and MDH share the disadvantage of higher loading levels for FR efficacy which typically interferes with physical properties of the system. This can often be overcome with careful formulation development. Examples include the use of surface treatments, especially for MDH and the selection of proper base resin with adequate melt flow index. Processing conditions should also be properly adjusted to ensure a good result.

1.4- Nitrogen based FRs

Nitrogen containing flame retardants alone only find limited application in polymers, e.g. melamine in polyurethane foams ad melamine cyanurate in polyamides[2]. Specifically developed systems based on melamine and derivatives are used in intumescent systems that have already been reviewed in this work.

2- General smoke properties

2.1- Preamble

Almost all polymeric materials, both natural (e.g., wood) and synthetic (e.g., polyurethane or nylon), can undergo pyrolysis and/or combustion. Pyrolysis is defined as a "process of simultaneous phase and chemical species change caused by heat," with combustion being defined as "a chemical process of oxidation that occurs at a rate fast enough to produce temperature rise and usually light, either as a glow or flame."[10] The processes of pyrolysis and combustion have both physical and chemical aspects.[11] Polymeric materials, on exposure to sufficient thermal energy, typically first undergo phase change, such as melting in the case of thermoplastics, followed by chemical decomposition. These are endothermic processes, resulting in the production of volatile low-molecular-weight products, which may or may not then undergo actual combustion. If pyrolysis produces gases that are themselves combustible, flaming may occur if the following exist in the same volume:

1. Sufficient oxidizing agent (air in normal conditions)
2. An ignition source of sufficient intensity
3. Sufficient gaseous fuel vapours or volatiles

The nature of the gases generated by the pyrolysis can have a significant effect on when and whether ignition takes place. For example, a material that contains a readily volatile fire retardant may not ignite until the fire retardant has been sufficiently depleted. Should the fire retardant and the host polymer continuously volatilize until the polymer is depleted, ignition may be prevented altogether. For the process of combustion to be self-sustaining, it is necessary for the burning gases to impart sufficient heat energy to the material to continue the production of ignitable volatiles.

The process is a continuous feedback loop: heat transferred to the material causes the generation of flammable volatiles, these volatiles react with oxygen in the air to generate heat, and a part of this heat is transferred back to the material to continue the process. The chemical oxidation processes for flaming combustion of organic materials are generally quite exothermic, with more than enough energy being produced to continue the pyrolysis and bond-breaking processes if the heat transfer is efficient and heat losses to the environment are not too great. Smouldering is a different form of combustion occurring only in certain porous materials. Here, air diffuses into the pores of the material and reacts directly with the interior surfaces of the pores. The combustion products from this slower process are typically quite different from those from flaming combustion. They are, however, a significant cause of fire deaths when a

person is close to the smouldering product, as can occur following cigarette ignition of a bed or piece of upholstered furniture.[12]

Most fire deaths and most fire injuries result from the inhalation of toxic smoke, both of which have increased with the widespread use of plastic materials. Fire toxicity is most important in areas where escape is restricted. Thus, most mass transport applications, such as airlines, railways, and passenger ships include requirements to quantify the fire toxicity of internal components. Regulations have to ensure that the time required for escape is less than the time before escape becomes impossible (available safe escape time).[13]

The burning of an organic material produces a cocktail of products that vary with fire conditions. In addition to carbon dioxide (CO_2), water (H_2O), and oxygen (O_2) depletion these include asphyxiating gases, carbon monoxide (CO), and hydrogen cyanide (HCN); irritant gases, hydrogen chloride (HCl), hydrogen bromide (HBr), nitrogen oxides (NO, NO_2), and organo-irritants, such as acrolein and formaldehyde, and particulates.[14] They can cause death directly by asphyxiation or indirectly by inhibiting breathing (gaseous irritants and particulate irritants) or by visual obscuration (smoke), in each case preventing escape.

Prediction of toxic fire hazard depends on two parameters:

1) Time/concentration profiles for major products. These depend on the fire growth curve and the yields of toxic products.

2) Toxic potency of the products, based on estimates of doses likely to impair escape efficiency, cause incapacitation, or death.

While some real-life fires may be represented by a single fire stage, most fires progress through several different stages. Burning behaviour and particularly toxic product yields depend most strongly on a few factors, especially material composition, temperature, and oxygen concentration. The generalized development of a fire has been recognized, and used to classify fire growth into a number of stages, from smouldering combustion and early well-ventilated flaming, through to fully developed under-ventilated flaming.[14]

It is difficult to generalize the flammability properties of materials, since fire performance is influenced by a number of factors, including the chemical composition and structure of the material, the use of additives in formulated systems, and even the conditions of the fire. Highly cross-linked thermoset polymers normally burn less readily than thermoplastics. Cellular plastics (foams) generally burn quite readily due to their large surface area and good thermal insulating properties, which prevent dissipation of heat. Polymer systems containing halogen atoms (e.g., polyvinyl chloride

(PVC)) burn with difficulty; however, the addition of plasticizers increases the propensity of these polymer systems to burn. PIN FRs are employed to increase resistance to ignition and/or lower burning rates of polymer systems. However, inherently fire-resistant polymers and polymer systems containing fire-retardant additives will still burn under sufficiently severe thermal conditions.[15]

Seventy-six percent of the people that died in fires in their residential structures in 1990 died from the inhalation of toxic combustion products, not from burns[13]. This percentage has been rising by about one percentage point per year since 1979. Although total deaths in fires are declining, the percentage attributed to smoke inhalation has increased. An area of research termed combustion toxicity has evolved to study the adverse health effects caused by smoke or fire atmospheres on domestic residents, and also on others routinely exposed occupationally to these atmospheres such as firefighters

The toxic effects of combustion products resulting from various sources are a major cause of morbidity and mortality. All people are exposed, every day, to air pollutants produced by combustion of organic material. Some are exposed to high concentrations: forest fires provide an example. Others are exposed to lower concentrations: levels of air pollution in the countryside of developed countries. Some people are exposed to potentially dangerous levels of pollution during their work: those working with diesel engines in confined spaces, those working as fire-fighters provide examples. And some are exposed as a result of accidents: those trapped in a burning building and those exposed to carbon monoxide being emitted by a faulty coke boiler provide obvious examples. It is tragic to see that it may be easily forgotten how dangerous smoke from fires actually is. In fact it is very dangerous: incapacitation by inhalation of smoke and consequent inability to escape is the major cause of deaths in fires.[16] Each year in France, accidental exposure to smoke from uncontrolled fires results in:[17]

- 450 deaths
- 12000 injuries requiring hospital treatment, from which 3000 are admitted in critical care unit with serious neurological damages

Over the last 50 years, there has been a continuous change in the materials used for construction and content of buildings and transport with an increasing dependence on synthetic polymers and their composites with different reaction-to-fire properties. Compared with natural materials (wood, wool, cotton, leather, etc.), widely used synthetic polymers such as polyethylene (PE), polypropylene (PP), polyamide (PA), polystyrene (PS), or polyurethane (PU) burn more quickly, and generate more smoke

and toxic effluents particularly in low-density, open structures such as fabrics and foams. Although the overall number of deaths has decreased as smoke alarms and fire detection systems became available, UK Fire Statistics, with the best time series data in the world, show a progressive shift in the cause of death from "burns" to "overcome by toxic gas or smoke" from 1955 to 2008. More remarkable is the very large rise in fire toxicity injuries.[13]

In Europe, most victims are found in the room of fire origin, often close to an exit, where they collapsed trying to escape. Usually, these are living rooms or bedrooms, with upholstery or bedding being the first thing to catch fire. Unless a stringent fire safety regulation is adopted for private housing; EU directives for zero energy homes (e.g. the Passive House level (2012-2015) and the Zero Car- bon level (2016-2020)) may result in millions of homes being lined in flammable non fire-retarded insulation materials, such as PS and PU foam (PUR) or equally flammable "environmental" materials such as flax or shredded paper, and this may have a dramatic impact on domestic fire deaths.

Another example from UK statistics in Figure 6 and Figure 7 show annual fire deaths and injuries per million population in the UK from smoke and burns, by far the majority of which occur in domestic dwellings. In the 1950s most deaths (7.2 per million) and injuries (35.7 per million) resulted from burns, with very few deaths (1.9 per million) and injuries (3.3 per million) attributable to toxic smoke exposure. Between the late 1950s and the early 1970s, although the incidence of injury and death from burns remained approximately constant, there was a more than fourfold increase in deaths and a fivefold increase in injuries from exposure to toxic smoke. Although a number of factors may be involved, the main cause of this increase was considered to be changes in living styles in the average British home, and in particular the replacement of traditional materials used for the construction of upholstered furniture and bedding by man-made materials, especially polyurethane foam filling and synthetic covering materials. Not only did the incidence of flaming fires increase, but when fires occurred, fire growth was rapid and involved the production of large volumes of irritant smoke, containing high concentrations of particulates, carbon monoxide and hydrogen cyanide. The dense smoke was therefore much more likely to impede the escape of occupants, who were then rapidly overcome by asphyxiating gases and heat.

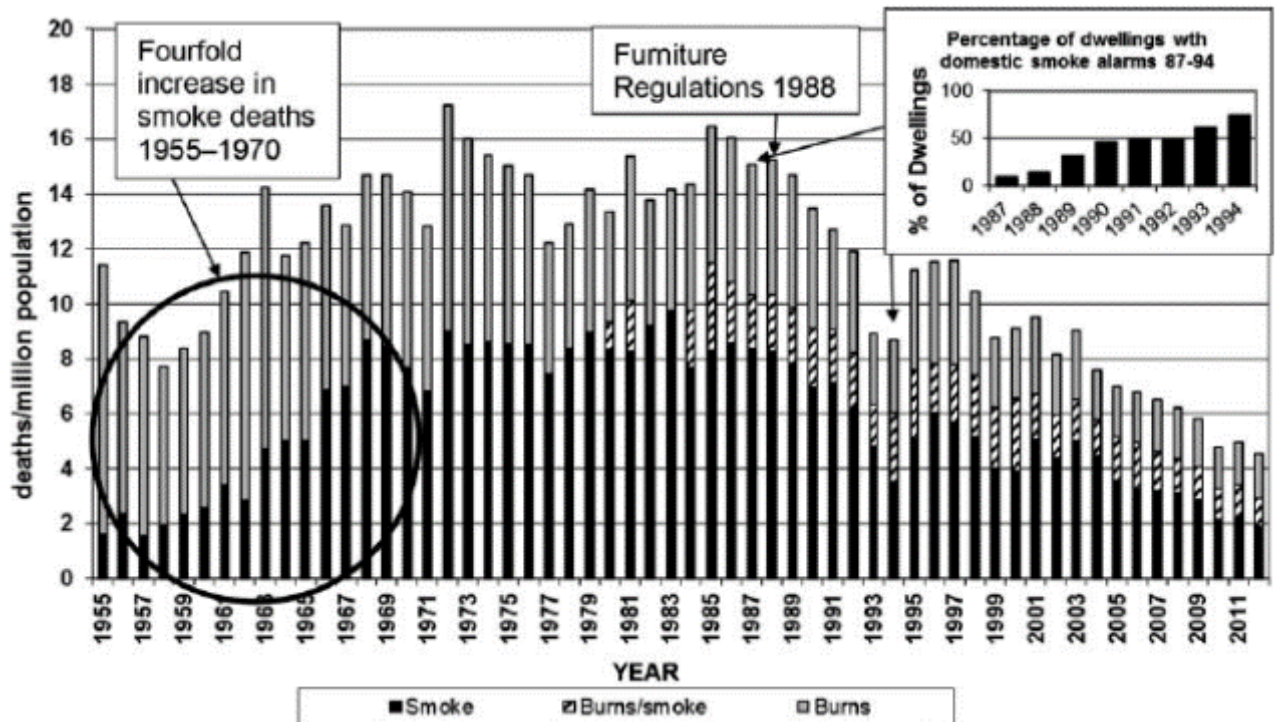**Figure 6 : Annual fire deaths in the United Kingdom per million population from smoke exposure and burns between 1955 and 2012.1**
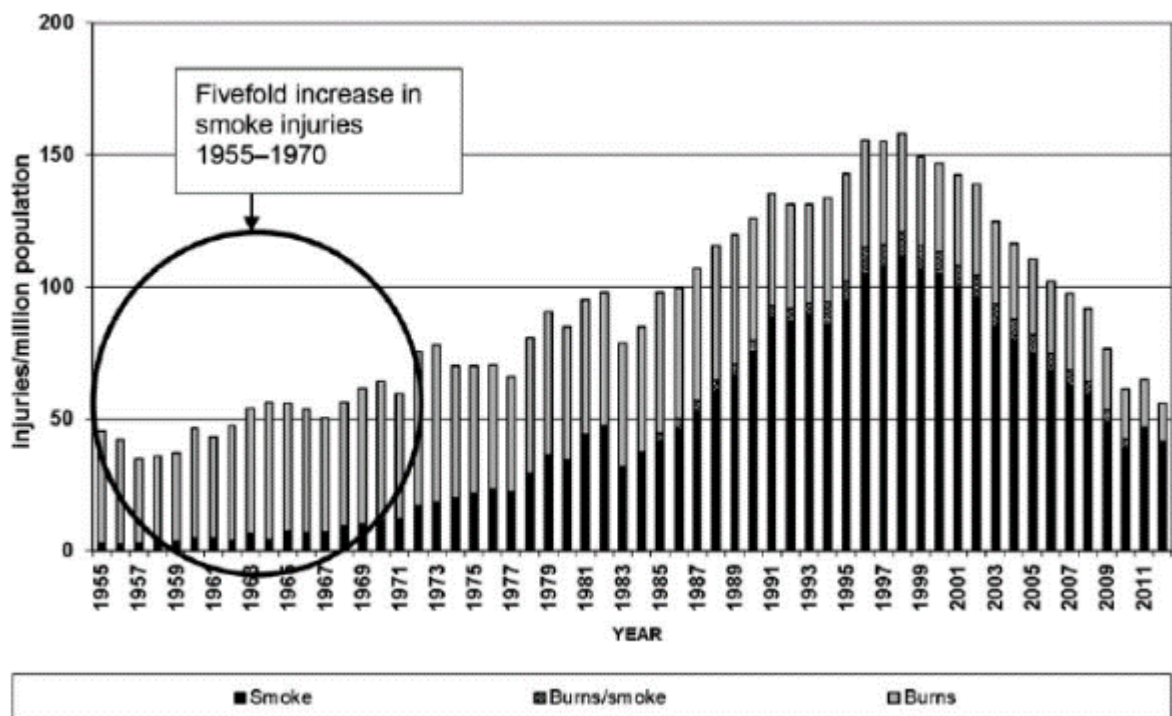
Figure 7 : Annual fire injuries in the UK per million population from smoke exposure and burns between 1955 and 2012.

Concerns regarding these issues in UK led to the introduction of the upholstered furniture flammability regulations in 1988, which required improved resistance to

ignition from small smouldering and flaming sources. This had no immediate effect, since significant replacement of old furniture in the housing stock took around a decade. However, another safety innovation introduced from this time was smoke alarms, gradual uptake of which coincided with a gradual decrease in smoke deaths, although the total number of fires and the number of smoke injuries continued to increase. From around 2000, by which time much old upholstered furniture had been replaced, the incidence of fires and of serious injuries also started to decrease so that these and the death rate gradually decreased towards the levels of the 1950s. Toxic smoke exposure remains the main cause of injuries and deaths in fires.

These few statistics illustrate the enormous ongoing adverse morbidity and mortality costs of exposure to combustion products.

2.2- Generation of fire gases and soot

Smoke is commonly defined (ASTM) as the airborne solid and liquid particulates and gases evolved when a material undergoes pyrolysis or combustion. The toxicity of smoke in a fire is a function of four factors; the amount of materials burnt; the distribution of combustion products within the smoke; the individual toxic potencies of each combustion product found in the vapour phase; and the duration of exposure.[18] The purpose of this part is to review the main toxicants commonly found in the gas phase atmosphere of fires.

2.2.1- Carbon dioxide

In well-ventilated flaming fires, nearly all the carbon lost from the combustibles is converted to carbon dioxide (CO_2). Even in post-flashover fires, the fraction of carbon conversion to CO_2 is fairly high. Thus, the yield of CO_2 has been used to estimate the burning rate of products when a direct measurement of mass loss is not possible. Carbon dioxide is also generated in smouldering fires, but the generated carbon monoxide is far more hazardous[19].

2.2.2- Carbon monoxide

Carbon monoxide (CO) is produced from both smouldering and flaming combustion. The production of CO from smouldering fires is quite slow, but these fires are not accompanied by vigorous mixing and diluting of the combustion products with room air. Thus, lethal concentrations of CO can be generated in the immediate vicinity of the ignition within 10 minutes. Lethal concentrations of CO elsewhere in the room may take 1 to 3 hours. By then, smouldering may have ceased or may have undergone transition to flaming combustion. The production of CO from flaming combustion is a

gas phase process. The fuel vapour or carbon-containing decomposition products react in a complex sequence with the oxygen in the air to form carbon monoxide. Subsequent reaction further oxidizes the CO to CO_2. The completeness of this process is largely dependent on the local supply of oxygen[20]. Oxygen available to a fire can be limited either by lowering the oxygen concentration in the incoming air supply or by reducing the volume flow of air to a fire. The formation of CO is related to the fuel-to-air equivalence ratio Φ as developed in the next part.

2.2.3- Hydrogen cyanide

The generation of hydrogen cyanide (HCN) is both material dependent and temperature-dependent. In smouldering fires and pyrolysis from flaming fires, HCN can be produced by decomposition of some nitrogen-containing polymers. HCN can be generated from nitrogen-containing polymers during flaming combustion as well. In neither case is there evidence of toxicologically significant HCN formation by fixation of the nitrogen in the air. In contrast to CO, there have been insufficient studies on HCN to enable quantitative prediction of its formation in fires. If sufficient oxygen is present, oxides of nitrogen (NOx) may also be formed from nitrogen-containing materials. Although one study reported NOx production from nitrogen containing fuels to be far less than that for HCN, there are conflicting data in the literature. HCN has also been seen to be oxidized to NOx when flames extended from a flashed-over room and continued to burn outside the doorway[21,22].

2.2.4- Halogen acids

Polymer systems containing halogen atoms (fluorine, chlorine, or bromine) result in the formation of the halogen acids— hydrogen fluoride (HF), hydrogen chloride (HCl), and hydrogen bromide (HBr), the production of which is largely material-dependent as long as thermal decomposition temperatures are reached. The halogen acids are formed in the pyrolysis component of the combustion process and are not oxidized further. Thus, the halogen acids are produced even if flaming combustion does not occur. Since the production efficiencies for the formation of HF, HCl, and HBr are close to being unity, maximum yields might be expected in fires.[23]

2.2.5- Organic irritants

Pyrolysis and/or incomplete combustion of organic materials can lead to a wide variety of organic irritant species. Those considered to be the most important toxicologically are formaldehyde, unsaturated aldehydes (especially acrolein), and isocyanates (from nitrogen-containing polymers[24]). The first two result from partial oxidation of the carbon

in the material. (Further oxidation leads to the formation of CO and then CO_2.) Acrolein, in particular, has been demonstrated to be present in many fire atmospheres[16]. It is also formed from the smouldering of all cellulosic materials and from the oxidative pyrolysis of polyethylene.

2.2.6- PAHs

Unwanted fires are characterized by incomplete combustion, often occurring at lower temperatures, and producing a rich cocktail of toxic and pollutant compounds compared to the small well-ventilated flaming and complete combustion of many laboratory test scenarios. In particular, real fires will produce more persistent bio accumulative and toxic (PBT) products, such as polycyclic aromatic hydrocarbons (PAHs), and polychloro- and polybromo-dibenzo-dioxins and furans (PCDD/F and PBDD/F) from fuels containing halogens. In addition, research concerning exposure to breathable particles (from PM_{10}s that are <10 μm diameter down to nanoparticles, ≈100 nm) from man-made sources indicates that exposure to background levels of particulates can cause irritation or damage to the respiratory system. The World Health Organization estimates a 0.5% increase in daily mortality per 10 μg.m^{-3} of PM_{10} (particulate matter smaller than about 10 μm) and smaller particles. The general effect of particulates is to cause fluid release and inflammation in the lungs, preventing gas exchange. The toxicity and particulate formation mechanisms present during accidental fires are not well understood, but the toxic gaseous species present in the smoke are known to attach themselves to nanoparticles, which act as vehicles taking toxicants deep into the lung[20].

PAHs are generated in all fires, particularly under pyrolysis and smouldering conditions. There are more than 100 different PAHs[25]. PAHs generally occur as complex mixtures, as part of combustion products such as soot, not as single compounds. PAHs usually occur naturally, but they can be manufactured as individual compounds for research purposes; however, not as the mixtures found in combustion products. As pure chemicals, they generally exist as colourless, white, or pale yellow-green solids. They can have a faint, pleasant odour. A few PAHs are used in medicines and to make dyes, plastics, and pesticides. Others are contained in asphalt used in road construction. They can also be found in substances such as crude oil, coal, coal tar pitch, creosote, and roofing tar. They are found throughout the environment in the air, water, and soil. They can occur in the air, either attached to dust particles or as solids in soil or sediment. Although the health effects of individual PAHs are not exactly the same, the following 17 PAHs are considered as a group in this profile:

- acenaphthene (IARC Group 3)

- acenaphthylene (No IARC Classification)

- anthracene (IARC Group 3)

- benz[a]anthracene (IARC Group 2A)

- benzo[a]pyrene (IARC Group 1)

- benzo[e]pyrene (IARC Group 3)

- benzo[b]fluoranthene (IARC Group 3)

- benzo[g,h,i]perylene (IARC Group 3)

- benzo[j]fluoranthene (No IARC Classification)

- benzo[k]fluoranthene (IARC Group 2B)

- chrysene (IARC Group 2B)

- dibenzo[a,h]anthracene (IARC Group 2A)

- fluoranthene (IARC Group 3)

- fluorene (IARC Group 3)

- indeno[1,2,3-c,d]pyrene (IARC Group 2B)

- phenanthrene (IARC Group 3)

- pyrene (IARC Group 3)

The previous list the 17 major PAHs together with carcinogenic classifications as defined by the International Agency for Research on Cancer (IARC). IARC classifications are as follows: Group 1 – carcinogenic to humans, Group 2A – probably carcinogenic to humans, Group 2B – possibly carcinogenic to humans, Group 3 – unclassifiable as to carcinogenicity to humans, Group 4 –probably not carcinogenic to humans.

These 17 PAHs were chosen to be included in this profile because:
-   More information is available on these than on the others;
-   They are suspected to be more harmful than some of the others, and they exhibit harmful effects that are representative of the PAHs;
-   There is a greater chance that you will be exposed to these PAHs than to the others; and
-   Of all the PAHs analysed, these were the PAHs identified at the highest concentrations at hazardous waste sites.

For IARC, the highest mutagenic and carcinogenic compound of the previous list is benzo-a-pyrene (BAP-below).
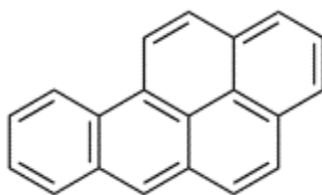
This compound is classified by IARC in the group 1 which means it is carcinogenic to humans.

PAHs are found in high amounts up to the percent range in the soot after real fires. The percentage of Benzo[a]pyrene in PAHs is around 5%. The reason for the generation of high PAH amounts is that they are precursors which form soot by condensation or agglomeration. In addition, a part of PAHs remains unreacted and is strongly bound onto the soot particles[26].

2.2.7- Dioxin / Furan

Dioxins are a group of chlorinated polynuclear aromatic compounds. They are emitted in trace quantities from combustion sources, especially the incineration of municipal wastes or hazardous fires. Because some isomers of dioxins are highly toxic and may have carcinogenic and mutagenic effects, the control of dioxin emissions from combustion sources has received great attention and the mechanisms of dioxin formation have been studied extensively. It is now believed that dioxins are formed in the low-temperature post-combustion zone of incinerators through some heterogeneous catalytic reactions occurring in the flue gas - fly ash environment[27].

Some data of dioxin emissions from various combustion sources are shown in Table 1.

Combustion sources	Dioxins in flue gas (ng-TE/Nm³)	Dioxins in fly ash (ng-TE/g)	Ref.
Municipal waste incineration	0.2-63	1-28	[5]
Hazardous waste incineration	0.1-0.5	n.a.	[6]
Wood combustion: Natural wood Waste wood	 0.02-1.8 2.7-14	 n.a. 0.08-8	[7-11]
Coal combustion	n.d.	n.d.-10	[12-14]
Plastics pyrolysis	detected	detected	[15,16]
Oil combustion: Oil furnace Leaded gasoline in vehicle Leadfree gasoline in vehicle	 0.03-0.3 10-60 (pg/L-oil) 3.5 (pg/L-oil)	n.a.	 [17] [18]
Gas combustion	0.07-100	n.a.	[19]

*TE is referred to I-TEQ. ᵇn.a.=not available, n.d.=not detected.

Table 1 : Dioxin emissions from various combustion sources.

Several observations can be made:

1. Dioxins have been detected in a variety of combustion sources. The prediction from the "trace chemistry of fire" hypothesis that "emissions of PCDDs (polychlorinated dibenzodioxins) and PCDFs (polychlorinated dibenzofurans) are general phenomena related to all combustion processes has been verified to a large extent.
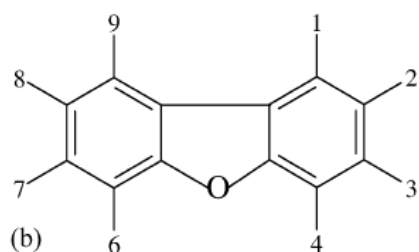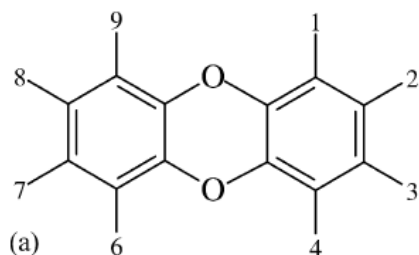
(a) Dibenzo-*para*-dioxin; (b) dibenzofuran.

2. Municipal solid waste incineration has very high dioxin emissions while coal combustion generates the lowest dioxin emissions. This fact has been recognized in many studies.

3. Dioxins emitted from these combustion processes have similar "fingerprints". Here we refer to dioxin "fingerprints" as the furan/dioxin ratio, the homologue profile and isomer pattern collectively. The typical dioxin "fingerprints" from combustion sources are: furan/dioxin ratio (w/w) is larger than 1, the weight distribution of the homologues increases with increasing degree of chlorination for PCDDs, but shows a maximum at P_5CDF or H_6CDF for PCDFs, and the isomer pattern contains almost every isomer. Dioxins from other sources, e.g. pulp bleaching and chloralkali electrolysis have different dioxin "fingerprints". Because of the similar dioxin "fingerprint" from all combustion processes, especially the similar furan/dioxin ratio, it is very likely that the mechanisms of dioxin formation in all these combustion processes are similar or at least their controlling steps are similar.

The *de novo* synthesis seems to be the dominant mechanism of dioxin formation in actual combustion systems. As *de novo* synthesis experiments indicate that carbon morphology of certain degenerated graphitic structure is essential for dioxin formation,

the morphologies of the particulate emissions from actual combustion sources are examined and it appears that soot particles formed in gas phase combustion reactions consisting of degenerated graphitic structures are the plausible source for *de novo* synthesis of dioxins. With this understanding dioxin formation in combustion systems is described as a two-stage process:

1. Carbon formation: carbon particles consisting of degenerated graphitic structures are formed in the combustion zone;
2. Carbon oxidation: the unburnt carbon particles continue to be oxidized in the low-temperature post-combustion zone and PCDD/Fs are formed as by-products of the oxidative degradation of the graphitic structure of the carbon particles.

Many steps and chemical reactions are involved in each of the two stages. For carbon formation, there are at least three steps: nucleation, particle growth and agglomeration; for carbon oxidation four steps: oxidant adsorption, formation of complex intermediate with metal ion catalysts, interaction with graphitic carbon structure and products desorption. The chemical reactions involved are extremely complex and heterogeneous.

The EPA report confirmed that dioxin is a cancer hazard to people. In 1997, the International Agency for Research on Cancer (IARC) - part of the World Health Organization - published their research into dioxins and furans and announced on February 14th, 1997, that the most potent dioxin, **2,3,7,8-TCDD** (2,3,7,8-tetrachloro-p-dibenzo-dioxin), is considered in a Group 1 carcinogen, meaning that it's a known human carcinogen.
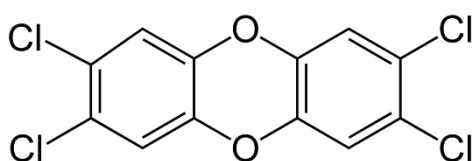
TCDD is a colourless solid with no distinguishable odour at room temperature. It is usually formed as a side product in organic synthesis and burning of organic materials. Of particular concern are the decomposition products from halogenated materials, including PVC and brominated flame retardants, which have been shown to produce large quantities of PCDD/F or PBDD/F in unwanted fires contrary to PIN-FR materials. PCDDs and PBDDs are extremely toxic, chemically and thermally stable, and have a tendency to be strongly adsorbed on the surface of particulate matter. The rate of formation of PCDD/Fs is a function of temperature, and the quantity of unburnt carbon, which is dictated by the oxygen level. Numerous studies on animals have also

confirmed that some dioxin congeners are carcinogenic and produce mutagenic effects in certain species.

2.2.8- Soot particulates

The environmental impact of airborne particles ('aerosol') has long been a major ecological and environmental concern, and in particular the anthropogenic part of the particulate material has been studied[24]. However, due to some alarming reports in the early 90's, where statistically significant correlations were found between variations in airborne particulate matter and sickness/mortality within a population, this interest has also come to include the direct health impact of airborne particles. It has been estimated that almost half a million people die per year as a result of particles generated by car engines only. This number might be compared to the estimated deaths/year due to smoking, which is 3 million/year.

Generally speaking, all air in the atmosphere contains a certain amount of small particles; from $\sim 10^2/cm^3$ in maritime environments, to $\sim 10^6/cm^3$ in the air over large cities, and further to $\sim 10^9$ particles/cm^3 in the flue gas from a boiler (before cleaning steps). Particle sizes range from the nanometer-scale up till several tens of a micron ($1\mu m = 1.E-6$ m). A typical size distribution for urban air is shown in Figure 8.
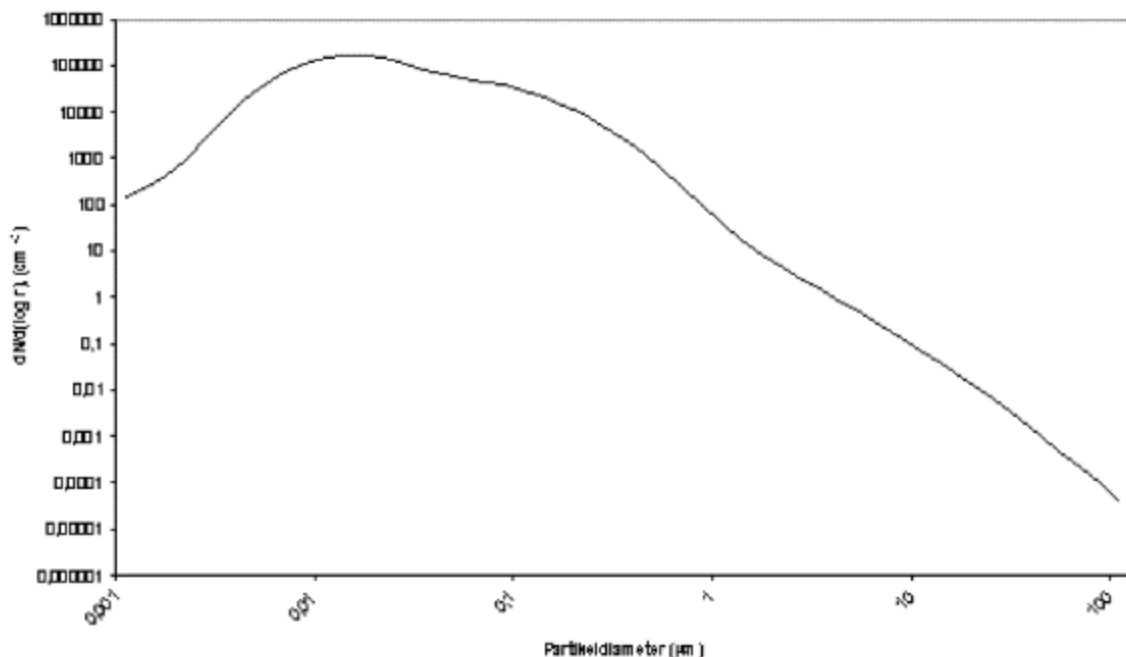
Figure 8 : Typical particle number size distribution of urban air

Researchers have shown that the health effect is mainly related to the sub-micron sized fraction of the particles, i.e. to the particles having an aerodynamic diameter, d_p, less than one micron. Some even suggest that the real danger is related to the $d_p < 100$

nano meter (nm) fraction. Such small particles are generated in huge amounts in combustion processes, partly as a result of evaporation /condensation processes, partly from soot generation. Soot production is particularly high for a vitiated fire which is a common scenario in, for example, a compartment fire.

Another potential health-hazard related to the particles is the possibility for absorption and enrichment of various poisonous substances (metals, dioxins, HCl, etc.) on the particle phase. Due to the huge number of particles in the smoke from a fire, there is a lot of available surface area and since the amount of 'fine' particles (aerodynamic diameter, d_p, of 100 nm or less) easily reaches ~1E15 particles/m^3, the equivalent area will be 20-30 m^2 per m^3 of gas. This estimation is based on the particles having a spherical shape. In real life, this may not be the case, which means that the available surface area for absorption will be even larger, thus the amount of particles might be even higher.

The particle size distribution is dependent on the material, temperature, and fire conditions[20]. The particle size of the spherical droplets from smouldering combustion is generally of the order of 1 μm, while the size of the irregular soot particulates from flaming combustion is often larger, but much harder to quantify and dependent on the measuring technique and sampling position. The deposition areas for humans as a function of particle size are shown in Figure 9.
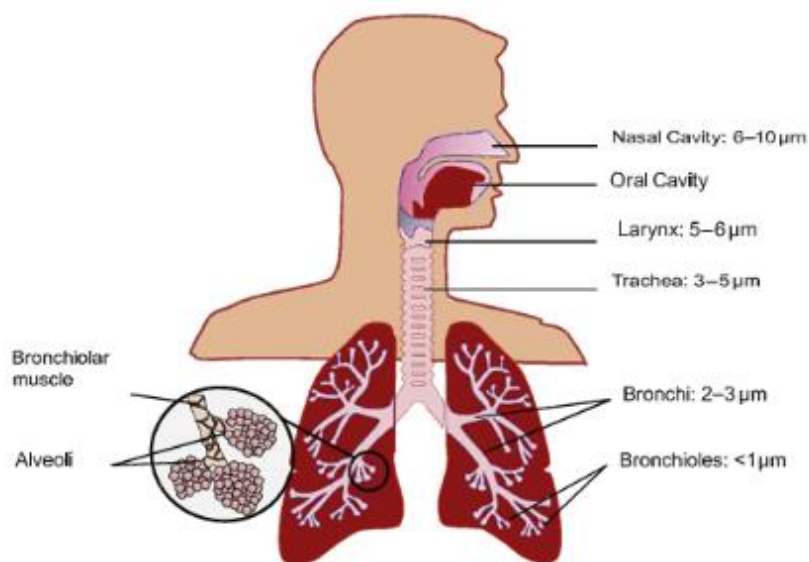
Figure 9 : Particulate distribution in the respiratory tract

The PAHs produced from fires agglomerate together into small spherical particles, which then adhere to one another, like a tangled string of beads. Both the volatile PAHs and the spherical particles will remain airborne almost indefinitely, but have the potential to cause significant damage to the lungs. The low-molecular-weight PAHs

show a moderate potential to be adsorbed onto particulates whereas high molecular weight PAHs have stronger tendencies to adsorb to organic carbon, especially small particles (< 2.5 μm).

The following figure shows the probability for deposition of different particle sizes in different areas of the lung system[24].
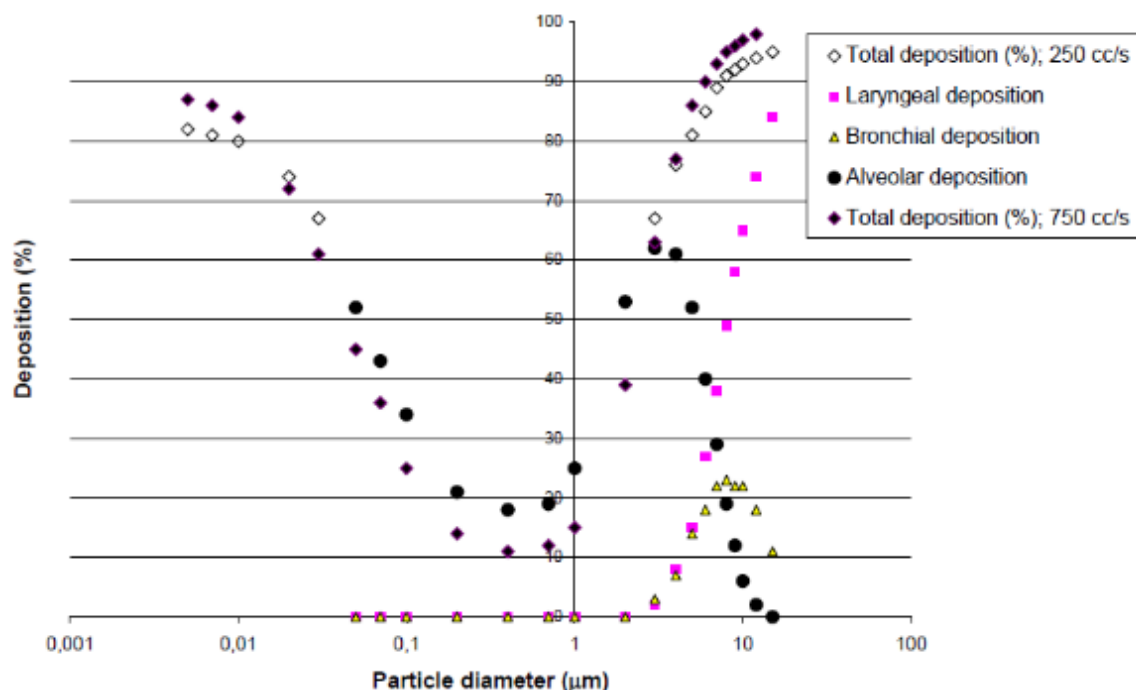
Figure 10 : Deposition "efficiency" of spherical particles with unit density (1 g/cm^3) in respiratory tract

It seems likely that poisonous substances will have different impacts on the human body depending on whether they are inhaled as gaseous molecules or as molecules absorbed on a solid/liquid surface. The lung-molecule interaction depends on the physical and chemical context in which the interaction takes place. Also, the particle can provide a certain inertia to the adsorbed molecule that will influence where in the lung region the interaction will take place. In spite of this, there is not (at this moment) any particular health related limit values for substances found on the particle phase of an aerosol. Limit values are usually based on volumetric concentrations without regard for the different phases contained in that volume. The main reason for this is probably the general difficulties involved in estimating the health impact of particle-bound substances.

2.2.9- Other Gases (supertoxicants)

Depending on the composition of the combusting products, additional toxic components of smoke can be produced in a fire. For example, phosphorus-containing

fire retardants can result in phosphoric acid aerosol, and sulphur-containing polymers can generate sulphur oxides. There is yet no predictive capability for the yields of such species[13].

2.3- Health effects of fire gases

2.3.1- Acute toxic effect of fire gases

Death in a fire may be caused by the following:
1. Carbon monoxide (CO)
2. Toxic gases in addition to CO
3. Oxygen (O_2) at levels too low to sustain life
4. Incapacitation-either physical (inability to escape) or mental (incorrect decision making)
5. Heart attacks and other cardiovascular events induced by exposure to toxic gases, particles, or vapours
6. Bodily burns from flame contact
7. Very high air temperatures
8. Smoke density or irritants in smoke that affect vision and interfere with ability to escape
9. Psychological effects (e.g., fear, shock, and panic)
10. Physical insults (e.g., building or ceiling collapses, and broken bones from jumping from upper floors)

Complete combustion of a polymer containing carbon, hydrogen, and oxygen in an atmosphere with sufficient O_2 yields CO_2 and H_2O. It is during incomplete combustion under various atmospheric conditions in either flaming or non-flaming modes that compounds of greater toxicological concern are generated. When O_2 is limited, as in non-flaming or ventilation-limited fires, the primary gases formed during the combustion of most materials are CO, CO_2, and H_2O. If the materials contain nitrogen, HCN, and NO_2, two principal thermo-oxidative products of toxicological concern, are also likely to be generated. Halogenated or flame-retarded materials generally produce HCl or HBr. Other commonly found fire gases include nitrogen oxides (NOx), ammonia (NH_3), hydrogen sulphide (H_2S), sulphur dioxide (SO_2), and fluorine compounds. One also needs to consider that in fire situations, O_2 levels drop and exposure to low O_2 atmospheres will have additional adverse physiological effects. Some of these toxic combustion gases (e.g., CO, HCN, and low O_2) produce immediate asphyxiating symptoms, while others (e.g., HCl, HBr, and NO_2) fall into an irritant category and produce symptoms following the exposures.[13]

Research in the field of acute combustion toxicology is primarily concerned with items 1-4 (cited above), all of which are related to the toxic potency of the fire gas effluent. Toxic potency is defined by ASTM as "a quantitative expression relating concentration (of smoke or combustion gases) and exposure time to a particular degree of adverse physiological response, for example, death on exposure of humans or animals". This definition is followed by a discussion that states, "The toxic potency of smoke from any material or product or assembly is related to the composition of that smoke which, in turn, is dependent upon the conditions under which the smoke is generated." One should add that the LC_{50} is a common end point used in laboratories to assess toxic potency. (The LC_{50} value is the result of a statistical calculation based on multiple experiments, each with multiple animals, and indicates the concentration at which 50% of the experimental animals exposed for a specific length of time would be expected to die either during the exposure time or the post-exposure observation period.) In the comparison of the toxic potencies of different compounds or materials, the lower the LC_{50} (i.e., the smaller the amount of material necessary to reach the toxic end point), the more toxic the material.[28]

Fire gas toxicants are usually considered as belonging to one of three basic classes:

➤ Asphyxiatings, or narcosis-producing toxicants:

In combustion toxicology, the term narcosis refers to the effects of asphyxiating toxicants that are capable of resulting in central nervous system depression, with loss of consciousness and ultimately death. Effects of these toxicants depend on the accumulated dose, that is, both concentration and duration of the exposure. The severity of the effects increases with increasing dose. Major asphyxiating sources are: carbon monoxide CO, hydrogen cyanide HCN, carbon dioxide CO_2 and oxygen depletion (since oxygen is consumed in the combustion process). [29]

➤ Sensory/upper respiratory irritants or pulmonary irritants[30]

Both inorganic irritants (e.g., halogen acids and those formed from nitrogen oxides) and organic irritants (e.g., aldehydes) can be formed in fires. Irritant effects, produced from exposure to essentially all fire atmospheres, are normally considered by combustion toxicologists as being of two types:

1. Sensory irritation, including irritation of the eyes and the upper respiratory tract
2. Pulmonary irritation affecting the lungs

Most fire irritants produce signs and symptoms characteristic of both sensory and pulmonary irritation. Eye irritation, an immediate effect that depends primarily on the

concentration of an irritant, may significantly impair a person to escape from a fire. Nerve endings in the cornea are stimulated, causing pain, reflex blinking, and tearing. Severe irritation may also lead to subsequent eye damage. Victims may shut their eyes, partially alleviating these effects; however, this action may also impair their escape from a fire. Airborne irritants also enter the upper respiratory tract, causing burning sensations in the nose, mouth, and throat, along with the secretion of mucus. These sensory effects are also primarily related to the concentration of the irritant and do not normally increase in severity as the exposure time is increased.

Following signs of initial sensory irritation, significant amounts of inhaled irritants may also be quickly taken into the lungs, with the symptoms of pulmonary or lung irritation being exhibited. Lung irritation is often characterized by coughing, bronchoconstriction, and increased pulmonary flow resistance. Tissue inflammation and damage, pulmonary oedema, and subsequent death may follow exposure to high concentrations, usually within 6 to 48 hours. Inhalation of pulmonary irritants also appears to increase susceptibility to post-exposure bacterial infection. Unlike sensory irritation, the effects of pulmonary irritation are dependent both on the concentration of the irritant and on the duration of the exposure. Most common irritants found in fire gases are: halogen acids (HCl, HBr, HF), Nitrogen oxides (NO, NO_2), SO_2, and acrolein.

> Toxicants exhibiting other or unusual effects (named as supertoxicants)[20]

Always a possibility, this class has few documented examples.

As far as phosphorus containing molecules are concerned, it has been for example studied the acute inhalation toxicity of different concentrations of burnt red phosphorus in male rabbits, rats, mice and guinea pigs. The lethal toxicity has then been found out to be mainly a consequence of the corrosive effect of the degraded species and secondary to asphyxia.[31]

Anyway, there have been a number of studies investigating the effects of combustion products on fire victims and it has been found that the key toxicant that affects fire victims is carbon monoxide[26] (CO), with smaller contributions from other toxicants. In addition, the following is now widely accepted: [32]

- CO concentrations in the atmospheres of flashover fires (the one most likely to produce fatalities) are dependent upon geometric variables and oxygen availability, and virtually non-impacted by chemical composition of fuels.

- All small scale fire tests under-evaluate CO yields, thus implying to make a CO correction calculation to correct the data collected.
- There is no universal CO threshold level, this depends mainly on the age and physical condition of the victim.
- A comparison of fire fatalities before and after the plastics era indicates the use of synthetic materials to make household goods has made no difference to the fire atmosphere toxicity.

2.3.2- Long term effects – the chronic toxic components

Delayed adverse health outcomes resulting from exposures may include the following:[13]

1. Delayed adverse cardiovascular events such as heart attacks
2. Cancer
3. Reproductive dysfunction

In addition to acute effects, longer term adverse health outcomes are under increased study. Firefighters are, justifiably, the most concerned about the chronic or repeated exposures to carcinogenic chemicals and particulate matter that are found, at low levels, during the overhaul phase after the primary fire is extinguished or "knocked down". According to an International Agency for Research on Cancer (IARC), 9 known human carcinogens (Group 1), 4 probable human carcinogens (Group 2A), and 21 possible human carcinogens (Group 2B), or a total of 34 known and possible human carcinogens, have been detected in smoke from experimental and actual building fires reported in the literature. The nine known human carcinogens include:[33]

- arsenic,
- asbestos
- benzene
- benzo[a]pyrene
- 1,3-butadiene
- cadmium
- formaldehyde
- 2,3,7,8-tetrachloro dibenzo-para-dioxin
- sulphuric acid mist and vapour

Notably, all burning materials produce significant concentrations of polynuclear aromatic hydrocarbons (PAH), including benzo[a]pyrene (BAP) but also benzene, toluene, styrene, xylene, or phenol, many of which are carcinogenic. As seen before, BAP is one of the combustion product with the highest level of toxic carcinogenicity.

PAHs can be harmful to your health under some circumstances. Several of the PAHs, including benz[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, chrysene, dibenz[a,h]anthracene, and indeno [1,2,3-c,d]pyrene, have caused tumours in laboratory animals when they breathed these substances in the air, when they ate them, or when they had long periods of skin contact with them. Studies of people show that individuals exposed by breathing or skin contact for long periods to mixtures that contain PAHs and other compounds can also develop cancer. Mice fed high levels of benzo[a]pyrene during pregnancy had difficulty reproducing and so did their offspring. The offspring of pregnant mice fed benzo[a]pyrene also showed other harmful effects, such as birth defects and decreased body weight. Similar effects could occur in people, but we have no information to show that these effects do occur. Studies in animals have also shown that PAHs can cause harmful effects on skin, body fluids, and the body's system for fighting disease after both short- and long-term exposure. These effects have not been reported in people. The Department of Health and Human Services (DHHS) has determined that benz[a]anthracene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene, and indeno[1,2,3-c,d]pyrene are known animal carcinogens. The International Agency for Research on Cancer (IARC) has determined the following: benz[a]anthracene and benzo[a]pyrene are probably carcinogenic to humans; benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, and indeno[1,2,3-c,d]pyrene are possibly carcinogenic to humans; and anthracene, benzo[g,h,i]perylene, benzo[e]pyrene, chrysene, fluoranthene, fluorene, phenanthrene, and pyrene are not classifiable as to their carcinogenicity to humans. EPA has determined that benz[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, dibenz[a,h]anthracene, and indeno[1,2,3-c,d]pyrene are probable human carcinogens and that acenaphthylene, anthracene, benzo[g,h,i]perylene, fluoranthene, fluorene, phenanthrene, and pyrene are not classifiable as to human carcinogenicity. Acenaphthene has not been classified for carcinogenic effects by the DHHS, IARC, or EPA.

Dioxins and furans are also known to be released during fires, among which the 2,3,7,8 tetrachlorodibenzodioxin is considered as the most toxic. As with other combustion products the yields of dioxins and furans are very dependent upon the combustion conditions in a fire.

Over the last few years[39], controls over the release of dioxins to the atmosphere have become more widespread, with an increasing consensus in Europe for an emission limit of 0.1 nanograms per cubic meter based on the TEQ value (0.1 ng/m^3 TEQ). At the same time, the permitted emission levels for other pollutants have been significantly reduced (Table 2), with the result that possible areas of conflict could arise when alternative strategies are considered for dealing with the dioxin problem.

	BPM 11/89 (mg/m^3, 15 °C 1 bar, wet)	TALuft 1990 (mg/m^3, standard dry, 11% O$_2$ (daily mean value))	EEC-directive (mg/m^3, standard dry, 11% O$_2$ (daily mean values))
HCl	100	10	5
SO$_x$ (SO$_2$)		35	25
HF	5	1	1
NO$_x$ (NO$_2$)		200	
CO		50	
Dust	50	10	5
Corg		10	5
Total acidity (SO$_3$)	750		
Total acidity (So$_x$)	5		
PCDD/PCDF (ng TEQ/m^3)	–	0.1	0.1
Total (ng/m^3)		1.0	

Table 2 : European regulatory emission criteria

Through this EU regulatory, we can understand that the assessment of dioxin and furan species generated after the combustion of private or public building after a fire, is also a major concern.

Anyway, it is known that most of the long term toxicity is due to the inhalation of carbonaceous soot particles on which the volatile toxic species condense[26]. When inhaled, the particle provide a delivery system for deep lung penetration of "packets" of concentrated toxins. These have been suggested to be capable of inducing remote cardiovascular events by several mechanisms.[34]

Other studies have also indicated that firefighting is associated with an excess incidence of cancer of several types. The carcinogenicity of smoke from incomplete combustion of natural organic residential fuels such as coal and wood was first implied by the report of Pott, who documented the occurrence of scrotal cancer in British chimney sweeps, and later reports suggested that occupational contact with soot may be a cause of skin and other cancers in several occupations. The carcinogenic effects of soot from natural organic sources have been largely ascribed to polycyclic aromatic hydrocarbons (PAH). Several chemical carcinogens of other chemical types have also been identified in residential smoke, however, including benzene, formaldehyde, styrene, and certain metals such as chromium.[39]

2.3.3- Importance of the time to exposure

The variety of causes of morbidity and mortality related to combustion products illustrates one aspect of their complexity: the wide range of toxic product concentrations of interest in evaluating effects, and the very wide range of exposure times that need to be considered. Figure 11 captures this, by showing the concentration ranges (expressed in $\mu g/m^3$) and exposure periods (expressed in hours) of interest for several toxic substances occurring in combustion products mixtures. The figure illustrates the enormous range of concentrations and times of interest involving over 16 orders of magnitude from pg/m^3 concentrations of dioxins over a 50 years exposure period to over 100 g/m^3 of carbon monoxide over periods as short as a few seconds.
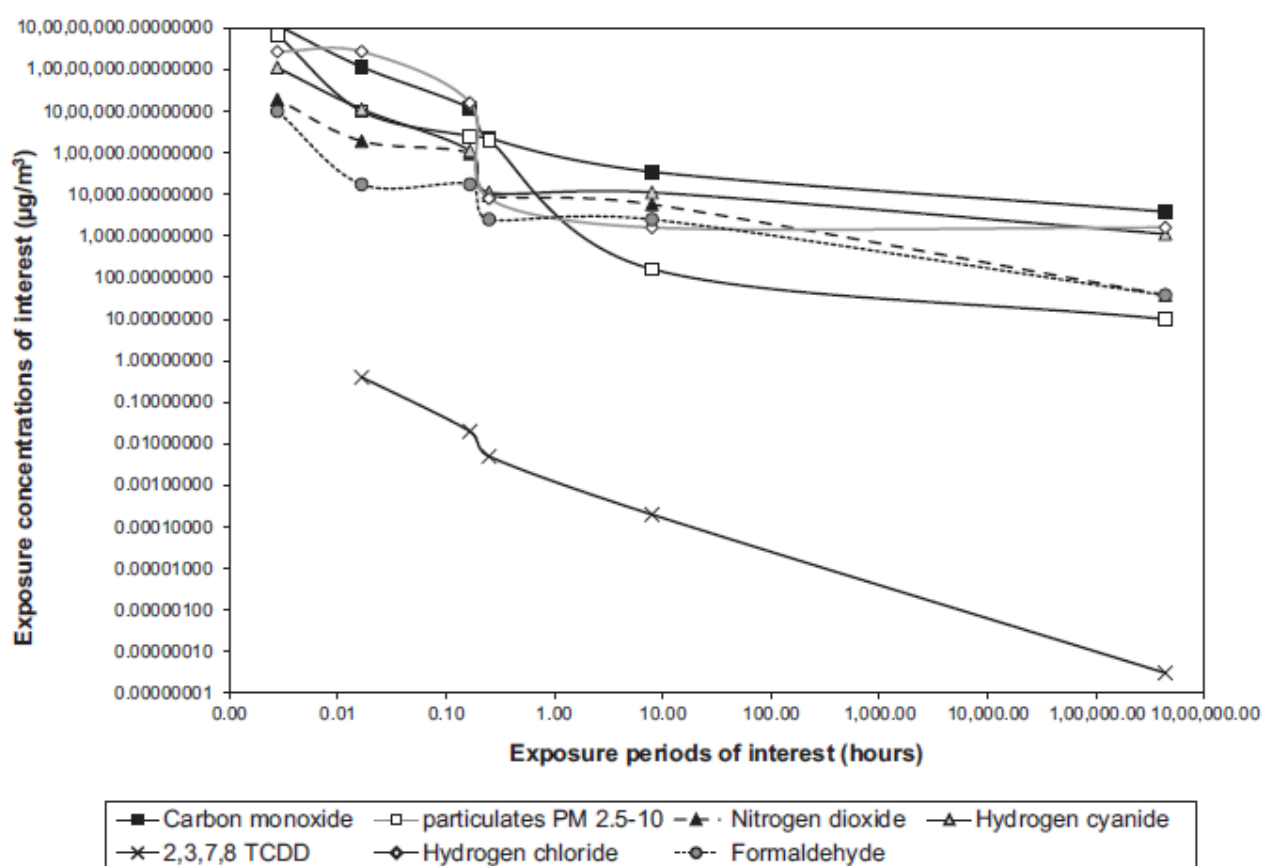
Figure 11 : Ranges of exposure concentrations and exposure periods of toxicological significance for common components of combustion product atmospheres.

The top left of Figure 11 shows concentrations of asphyxiating gases, such as carbon monoxide and hydrogen cyanide, acid gases and organic irritants, such as hydrogen chloride and formaldehyde, and smoke particulates, which can be present at concentrations up to percent levels by volume or g/m^3 by mass during fires. In order to

understand the effects on the survival of fire victims it is necessary to study the effects of smoke and irritants on escape capability and the incapacitating physiological effects of asphyxiating gases during critical periods of from a few seconds to a few minutes, in order to calculate time to loss of consciousness and death. For subjects rescued alive from fires it is also important to consider the more permanent effects of these gases on cerebral and cardiovascular function, and the effects of irritants and smoke particulates on lung function and pathology (complicated by burn injuries).

Moving on to exposure periods of approximately 1-100 hours, for situations such as acute exposures to diluted smoke plumes from wildfires, the concern relates mainly to effects from smoke particulates and irritants, including nuisance odour, mild eye and respiratory tract irritation and possibly more serious acute effects on vulnerable individuals.

Long term exposure to ambient air pollutants has been shown to be associated with a significant effect on health. In this context the concentrations of interest are very low, for example in the µg/m^3 range for pollutants, such as fine particulates (PM 2.5) or formaldehyde, and in the µg/m^3 range for dibenzodioxins (e.g. 2,3,7,8 TCDD). Studies reviewed by the Committee on the Medical effects of Air Pollutants (COMEAP) in 2009 and 2010 led to the conclusion that current levels of fine particles (PM 2.5) in the UK are responsible for 29 000 attributable deaths each year. A large proportion of material monitored as PM 2.5 comes, directly or indirectly, from combustion processes. No threshold of effect for such findings has been discovered. The effects leading to an increased risk of death involve those on the cardiovascular system and on the risk of lung cancer. It is interesting that effects on the respiratory system appear to be less important. Short term increases in ambient concentrations of air pollutants are also associated with increases in deaths and hospital admissions: in this case the respiratory system is affected, in addition to the cardiovascular system. The European Commission has funded a recent review of these effects[16].

2.4- Experimental methodology to measure toxicity

It is important to note that a toxicity assessment based on lethality due to toxic gases is only part of the total fire hazard that needs to be evaluated especially when one is making choices as to the best material for a specific end use. ASTM defines "fire hazard" as the potential for harm associated with fire. The discussion that follows this definition states, "A fire may pose one or more types of hazard to people, animals or property. These hazards are associated with the environment and with a number of fire-test-response characteristics of materials, products or assemblies including (but

not limited to) ease of ignition, flame spread, rate of heat release, smoke generation and obscuration, toxicity of combustion products and ease of extinguishment." Other factors that need to be evaluated when considering a material for use in a given situation include the quantity of material needed, its configuration, the proximity of other combustibles, the volume of the compartments to which the combustion products may spread, the ventilation conditions, the ignition and combustion properties of the material and other materials present, the presence of ignition sources, the presence of fire protection systems, the number and type of occupants, and the time necessary to escape[18].

2.4.1- Fire scenario and combustion conditions

Toxic product yields depend on the interactions between the material composition and the fire conditions; particularly temperature and ventilation and whether decomposition is non-flaming or flaming. As the fire develops, the conditions change: the temperature increases and oxygen concentration decreases. The temperature and oxygen concentration vary significantly during a fire, and between different fires. Different fire scenarios are shown in Figure 12.[20]

Figure 12 : Stages of fire growth

The most important fire stages identified by the ISO, from non-flaming to well-ventilated flaming to under-ventilated flaming, have been classified in terms of heat flux, temperature, oxygen availability, and CO_2 to CO ratio, equivalence ratio and combustion efficiency (the % conversion of fuel to fully oxygenated products, such as CO2 and water).

The most significant differences in terms of toxic product yields with fire conditions arise between flaming and non-flaming combustion. Typically, non-flaming combustion produces small volumes of highly toxic, partially burnt effluent, well-ventilated fires

produce larger volumes of less toxic effluent, while developed under-ventilated fires produce large volumes of toxic effluent, and therefore represent the greatest hazard. For flaming combustion, the fuel/air ratio has the greatest effect on the yields.

Research predicting the carbon monoxide evolution from flames of simple hydrocarbons, reviewed by Pitts, has shown the importance of the equivalence ratio, Φ, for predicting the CO yield from the oxygen depletion in flaming conditions, presented below.[38]

$$\emptyset = \frac{actual\ fuel\ to\ air\ ratio}{stoichiometric\ fuel\ to\ air\ ratio}$$

Φ = 1   "Stoichiometric" combustion

Φ ≪ 1   Well-ventilated fires (fuel lean flames)

Φ > 1   Under-ventilated fires (fuel-rich flames)

Stoichiometric combustion describes burning a material in its nominal chemical oxygen requirement (Φ =1) providing just enough oxygen for full oxidation to CO_2 and H_2O. In practice, for condensed phase fuels, very little air usually results in incomplete combustion because mixing is never perfect. In well-ventilated fires, combustion is fuel lean with excess air (Φ between 0.5 and 0.75), while in the later stages of a fire, when there is not enough air available and the conditions are under-ventilated, the equivalence ratio will be typically between 1.5 and 2.5. Each fire stage has a characteristic temperature and equivalence ratio, as summarized in Table 3.[1]

ISO Fire Stage	Temperature (°C)	Equivalence ratio φ	CO_2/CO Ratio
1a. Oxidative pyrolysis	350	Not applicable	1-5
2. Well-ventilated flaming	650	Φ < 0.75	2-20
3. Under-ventilated flaming			
3a. Small fires	650	Φ > 1.5	2-20
3b. Post-flashover fires	825	Φ > 1.5	2-20

Table 3 : Classification of fire stages according to ISO 19706

Fire can also be characterized by the CO_2/CO ratio as an indicator of combustion efficiency. However, this only correlates with the equivalence ratio (and degree of ventilation) when there is no gas phase quenching for example by hydrogen halides. Therefore, this parameter also corresponds to combustion efficiency.

Ideally, all bench-scale fire effluent toxicity test methods should be capable of reproducing the conditions in each of the stages of actual fires, including incipient, growing, and fully developed fires. It is therefore essential for the assessment of toxic hazard from fire that each fire stage can be adequately replicated, and preferably the individual fire stages treated separately.

A simplified growth curve showing the transition through the stages of a fire in an enclosure is shown in Figure 13. The curve shows the slow induction period, leading to ignition, and followed by rapid growth, until limited by the access of oxygen, reaching a quasi-steady state. When the fuel is used up, the fire decays. Many bench-scale fire models can only replicate the early stages of fire development using small samples under open ventilation. In large-scale tests the greatest toxic product yields usually occur under oxygen depleted conditions, when the fire is ventilation controlled. Small scale toxicity assessment only replicates large scale fires when burning can be forced under oxygen depleted conditions.
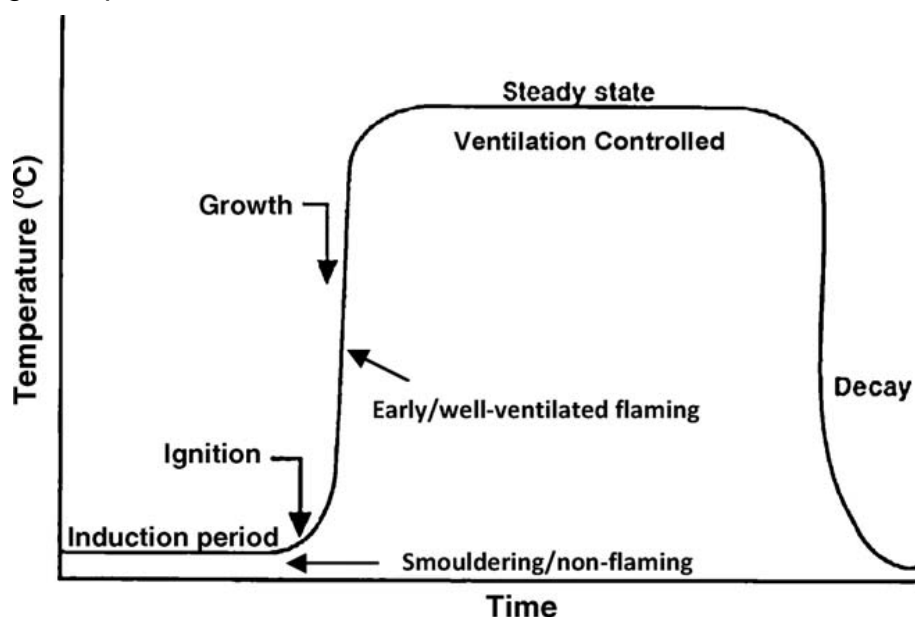
Figure 13 : Simplified fire growth curve

The question then arises as to which of the many tests available gives toxic potency values that are "right." ISO 16312-1 describes the characteristics of the ideal fire effluent toxicity test method:[40]

- The combustor (or physical fire model) replicates one or more fire stages (radiative pyrolysis, well-ventilated flaming, etc.)
- The test specimens are representative of as-used products
- The apparatus itself does not affect the results
- The apparatus is straightforward to use
- The method generates gas/smoke yields and specimen mass loss data
- The method has demonstrated accuracy relative to real-scale fires
- The results are repeatable and reproducible

2.4.2 - Evolution of testing

In the 1970s, there were essentially two experimental strategies to examine the issues raised by the field of combustion toxicology:
- the analytical chemical method
- the animal exposure approach

In the analytical chemical method, investigators thermally decomposed materials under different experimental conditions and tried to determine every combustion product that was generated. This approach generated long lists of compounds. The toxicity of most of these individual compounds was unknown, and the concept of examining the toxicity of all the various combinations of compounds was and still is considered an impossible task. An additional problem with the analytical method was that, as mentioned earlier, one could not be certain that every toxic product was detected and identified. This approach enabled one to identify many of the multiple products that were generated, but not know the toxic potency of all the identified compounds, especially when combined.[41]

In the animal exposure approach, the animals (usually rats or mice) serve as indicators of the degree of toxicity of the combustion atmospheres. The materials of concern are thermally decomposed under different combustion conditions, and the animals are exposed to the combined particulate and gaseous effluent. Multiple animal experiments (each with multiple animals) with different concentrations of material are conducted to determine an IC_{50} (incapacitation) or an LC_{50} (lethality) value for a specific set of combustion conditions. The LC_{50} is defined as the volume fraction of toxic gas in µL/L or smoke in g/m^3 statistically calculated from concentration-response data to produce lethality in 50 percent of test animals within a specified exposure and post-exposure time (before breathing fresh air). The IC_{50} is similarly defined for incapacitation.[42]

Each material would then have a particular IC_{50} or an LC_{50} value that can be used to compare the toxicities of different materials decomposed under the same conditions. The lower the EC_{50} or LC_{50}, the more toxic the combustion products from that material. In this approach, one knows the relative toxicity of a material as compared to another material, but does not know which of the toxic gases is responsible for the adverse effects.

In the 1980s, investigators began examining the possibility of combining the analytical chemical method with the animal exposure approach to develop empirical mathematical models to predict the toxicity. These predictions were based on actual experiments with animals and their response to each of the main toxic combustion gases, CO, CO_2, low O_2, HCN, NO_2, HCl, HBr and various combinations of these gases. The following are the four advantages of these predictive approaches:

1. The number of test animals is minimized by predicting the toxic potency from a limited chemical analysis of the smoke.
2. Smoke may be produced under conditions that simulate any fire scenario of concern.
3. Fewer tests are needed, thereby reducing the overall cost of the testing.
4. Information is obtained on both the toxic potency of the smoke (based on the mass of material burned) and the responsible gases (based on the primary toxic gases in the mixture). The prediction is checked with one or two animal tests to ensure that an unexpected gas or toxic combination has not formed.

The results of using these empirical mathematical models indicated that in most cases, one could predict the toxic potency of a combustion atmosphere based on the main toxic gases and did not need to worry about the effects of minor or more obscure gases.[43]

The toxic gases, vapours, particles, and irritants that are present in all types of smoke need to be considered as potential dangers. As described above, combustion products can cause both acute and delayed toxicological effects. It is the acute and extremely short-term effects that prevent escape from burning buildings by causing faulty judgment, incapacitation, and death. The irritants in the smoke can also interfere with one's ability to escape by causing severe coughing and choking and by preventing one from keeping one's eyes open long enough to find the exits. Delayed effects such as mutagenicity and carcinogenicity have been measured extensively in animals and cellular assays, especially for polycyclic aromatic hydrocarbons (PAHs). Other delayed effects, such as tissue or organ injury, teratogenicity, adverse cardiovascular events,

and reproductive dysfunction also need to be more extensively studied, since they may ultimately lead to permanent disability and post-exposure effects.

Toxicity screening tests for both the acute and delayed effects are, therefore, needed to evaluate the combustion products, including any agents that may be released from newly proposed materials and products. It is imperative that the materials and products be tested under experimental conditions that simulate realistic fire scenarios of concern (e.g., flashover conditions emanating first from smouldering and then flaming of upholstered furniture in homes or smouldering fires in concealed spaces in aircraft). The ideal tests should be simple, rapid, inexpensive, use the least amount of sample possible (since, in many cases, only small amounts of a new experimental material may be available), use a minimum number of test animals, and have a definitive toxicological end point for comparison of the multiple candidates.

While faulty judgment and incapacitation are significant causes of worry since they can prevent escape and cause death, they are extremely difficult and complex end points to define and measure in nonhuman test subjects. Death of experimental animals (e.g., rats), on the other hand, is a more definitive and easily determined end point and can be used to compare the relative toxicities of alternative materials deemed suitable for the same purpose. The assumption made here is that if the combustion products of material X are significantly more lethal than those of material Y, the combustion products of X would probably cause more incapacitation and more impairment of judgment than Y. The number of experimental animals can be significantly reduced by utilizing one of the predictive mathematical models developed for combustion toxicology such as the *N-gas model*.[1]

Although care is needed in making quantitative extrapolations from results obtained using rats to predict effects in humans, the basic mechanisms of acute toxicity from fire gases are known to be common to all mammals, including rodents and humans. For this reason it is considered that the identification of the key toxic gases and their largely additive interactions in rats apply equally to humans. For predicting effects on human escape capability, the incapacitating effects during exposure are considered more important than lethal effects, especially than the lethal lung effects developing several hours or days after exposure. This raises the issue of the extent to which additivity would be expected on incapacitation effects during exposure, which is partly due to asphyxiant effects and partly due to painful eye and respiratory tract irritation. Based upon these rat experiments and other work in primates, it is considered that inhaled irritants are likely to make some additive contribution to hypoxia, due to their impairment of lung function, while the painful effects are due to the additive effects of

the irritant acid gases and organics alone. For the rodent experiments deaths were also measured at the end of the exposure period, so it would be possible to determine additive effects on lethality from the data set during the exposure period alone. In general it is considered that the results from these lethality models and experiments are relevant to incapacitating effects, so that the same general principle of additivity applies.[41]

Many test methods for the determination of the acute toxicity of combustion products from materials and products have been developed over the past two decades and continue to be developed and/or improved. All scale-up of fire is difficult, but particularly in combustion toxicity where product yields may differ by two orders of magnitude, depending on fire scenarios. It was shown that for many common materials, the yield of toxic products such as carbon monoxide, hydrogen cyanide, organo-irritants, and smoke increases by a factor between 10 and 50 as the fire changes from well-ventilated ($0.5 < \Phi < 0.7$) to under-ventilated ($1 < \Phi < 5$).[44]

2.4.3- Direct assessment - animal exposures

The standard in combustion toxicology for quantifying the toxic potency of individual fire gases or of smoke has mostly been the LC_{50} for 30 minutes exposure of rats. It is significant that consensus among experts has been to recognize that the rat is a reasonably acceptable animal model for human exposure to smoke when the principal effects are due to inhalation of asphyxiating toxicants. Over the years, LC_{50} values have been experimentally determined for rodent (and less frequently, other laboratory animals) exposure to individual fire gases, as well as for many materials and products. Although individual fire gas toxicants may exert quite different physiological effects through different mechanisms, when present in a mixture each may result in a certain degree of compromise experienced by an exposed subject. It should not be unexpected that varying degrees of a partially compromised condition may be roughly additive in contributing to death. The extensive bank of rodent lethality data became useful in the development of a strategy for calculating smoke LC_{50} values from combustion analytical data without the need for exposure of animals. As early as 1972, Tsuchiya and Sumi proposed that a toxicity index could be constructed from the sum of terms for all the gases generated by a fire. Each term was the ratio of the actual concentration of the gas divided by the concentration fatal to a person in a 30 minute exposure[13].

Several testing methods were developed from 1980 to 2000 such as: (non-exhaustive list)

- DIN Method
- US-National Bureau of Standards (NBS) test
- U-PITT methodology (US-University of Pittsburgh)
- ASTM E 1678 – NFPA 269
- ISO 13344

Since the purpose of the review is not to focus on every single difference of the testing methods themselves, it has been decided to detail one relevant as an example: the ASTM E1678 also known as NFPA 269.

The radiant furnace test[45] uses a 0.2 m^3 box as the combustion chamber (see Figure 14 and Figure 15). The heat generator (radiant furnace) applies a fixed radiant flux to the test specimen, as shown in Figure 16. A spark source is used to ignite the fuel vapours. The test is particularly applicable to layered products, such as furniture or wall coverings. In the operation of the method, a test specimen up to 10 cm by 15 cm by 5 cm thick is exposed to a radiative flux of 50 kW/m^2 for 30 minutes. The smoke enters the box through the centre hole of a three-slot chimney. Air from the box is recirculated to the combustion zone through the two outer slots.

The rat exposures and gas analyses are the same as with the cup furnace test. In each test, six rats are held in tubular restrainers, with their heads inside the box. They inhale the smoke for 30 minutes and then are observed for the following 14 days. Successive tests are performed, with the top surface area of the specimen being varied to vary the concentration of smoke in the box. The lethal toxic potency, LC50, of the smoke from the test specimen is predicted from the combustion atmosphere chemical analytical data by first calculating the FED for the test. The 30 minute LC50 is then calculated as that specimen mass loss that would yield FED = 1 within a chamber volume of 1 m^3 from the equation:

$$LC_{50} = \frac{Specimen\ mass\ loss}{FED \times Chamber\ volume}$$

where the specimen mass loss is in grams and the chamber volume is 0.2 m^3. The resulting LC_{50} has the units of g/m^3. The predicted LC_{50} is then confirmed in limited tests using rats to ensure that the monitored toxicants account for the observed toxic effects. The referred standards also provide for a mathematical adjustment of experimental LC_{50} values in order to make them appropriate for the toxic hazard assessment of oxygen-vitiated, post flashover fires. The test results have been

compared to results from room scale post flashover fires[46]. Prior to performing the comparison, an adjustment was made to the CO yield. Following flashover, the oxygen concentration in a room drops precipitously. Were these conditions replicated in the current test, the animals would succumb to the reduced oxygen, regardless of the effects of the other gases in the smoke. A literature search indicated that post flashover fires typically generate yields of CO of about 0.2 kg CO per kg fuel consumed. This yield is substituted for the CO yield determined in the tests. For five different criteria, the bench-scale apparatus produced results consistent with the room-scale data. Accuracy to within a factor of three was established as both attainable and practical.
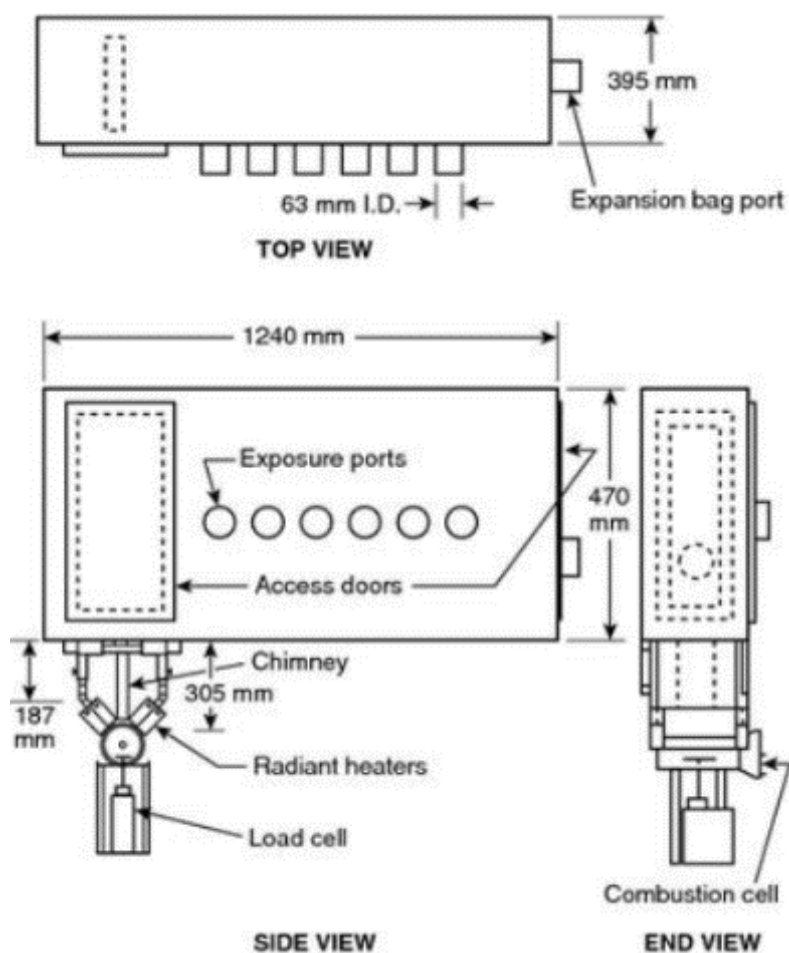
Figure 14 : Schematic of the ASTM E1678/NFPA 269 test apparatus

Figure 15 : Picture of the ASTM E1678/NFPA 269 test apparatus (Source: NIST)

Figure 16: Picture of the radiant furnace used for ASTM E1678/NFPA 269 test (Source: NIST)

2.4.4- Indirect assessment – analytical chemical methods

➢ Smoke analysis

Death or incapacitation may so be predicted by quantifying the fire effluents in different fire conditions in small-scale tests, using chemical analysis. Lethality may be predicted using equations, based on rat lethality data, presented in ISO 13344. Incapacitation (the inability to effect one's own escape) may be predicted using methodology and consensus estimate data in ISO 13571.

Toxic product data from chemical analysis may be expressed in various ways, including effluent gas concentrations, effluent gas yields, toxicity indices, Fractional Effective Dose (FED), Fractional Effective Concentration (FEC), and LC_{50} (lethal concentration to 50% of the population).

The combustion of complex formulations used in commercial products generates hundreds of different gases. The evaluation of the FED values and the nature of the combination of those FED values would have been a daunting, if not insurmountable, task. Researchers at the National Institute of Standards and Technology (NIST) proposed the *N-gas model*. This concept suggests that the toxic potency of most commercial products could be estimated from the contributions of a small number, N, of the combustion gases. The general approach in generating toxic potency data from chemical analysis is to assume additive behaviour of individual toxicants, and to express the concentration of each as its fraction of the lethal concentration for 50% of the population for a 30min exposure (LC_{50}). Thus, an FED=1 indicates that the sum of the actual/lethality concentration ratios of individual species will be lethal to 50% of the population over a 30min exposure. Since CO_2 increases the respiration rate, the Purser model, presented in Equation 1 uses a multiplication factor for CO_2 driven by hyperventilation, V_{CO2}, to increase the FED contribution from all the toxic species, and incorporates an acidosis factor A to account for toxicity of CO_2 in its own right.[47]

$$FED = \left\{ \frac{[CO]}{LC_{50,CO}} + \frac{[HCN]}{LC_{50,HCN}} + \frac{[HCl]}{LC_{50,HCl}} + \frac{[NO_2]}{LC_{50,NO_2}} + \cdots + organics \right\} \times V_{CO_2} + A$$
$$+ \frac{21 - [O_2]}{21 - 5.4}$$

$$V_{CO_2} = 1 + \frac{\exp(0.14 \times [CO_2]) - 1}{2}$$

where A is an acidosis factor equal to $[CO_2]$ x 0.05.

Equation 1 : Purser model for estimation of toxicity of fire effluents

The results of rat exposure experiments to single and mixed gases were compared with experiments in which rats were exposed to the gases generated by the combustion of a number of materials. The mean FED value corresponding to the LC50 was 1.07, using the "*N-gas*" calculation, with 95 percent confidence limits of 0.20. This provided substantial support for this concept.

This equation is related only to lethality, or "cause of death". However, many people fail to escape from fires because of the incapacitating effect of smoke (obscuring visibility) and its irritant components that cause pain, inhibiting breathing, actually being the "reason for death".

ISO 13571 considers the four major hazards from fire that may prevent escape (toxic gases, irritant gases, heat, and smoke obscuration)[48]. It includes a separate calculation for prediction of incapacitation by each of the four hazards for humans exposed to fire effluents (indicating, in a non-normative appendix that the effects of heat, smoke, and toxicants may be estimated independently). Incapacitation is commonly inferred from lethality data, since exposure doses are generally considered to be one-third to one-half of those required for lethality.

Equation 2 and Equation 3 have been taken from ISO 13571. They calculate the FED of asphyxiatings, CO and HCN, and the FEC of sensory irritants in the fire effluent that limit escape.

$$FED = \sum_{t_1}^{t_2} \frac{[CO]}{35,000} \times \Delta t + \sum_{t_1}^{t_2} \frac{\exp(\frac{[HCN]}{43})}{220} \times \Delta t$$

Equation 2 : FED model for ISO 13571

Equation 2 considers the two significant asphyxiating fire gases CO and HCN. The FED value is calculated using the exposed dose relationship (concentration-time product, C•t) for CO. The lethal C•t product corresponds to the incapacitating dose (C•t) for CO of 35 000 µl/L.min, equal to around 1170 ppm for a 30min exposure and an exponential relationship for HCN.

$$FEC = \frac{[HCl]}{IC_{50,CO}} + \frac{[HBr]}{IC_{50,HBr}} + \frac{[HF]}{IC_{50,HF}} + \frac{[SO_2]}{IC_{50,SO_2}} + \frac{[NO_2]}{IC_{50,NO_2}} + \frac{[acrolein]}{IC_{50,acrolein}}$$
$$+ \frac{[formaldehyde]}{IC_{50,formaldehyde}} + \sum \frac{[irritant]}{IC_{50,irritant}}$$

Equation 3 : FEC model from ISO 13571

Equation 3 uses the same additive of Purser's principle in ISO 13344 to estimate the combined effect of all irritant gases (IC is the concentration resulting in incapacitation of 50% of the population). ISO 13571 is a more robust methodology for ensuring the safety of potential fire victims. It is included here for completeness, to show the steps needed to avoid incapacitation, but subsequent results are presented using the simpler FED calculation of ISO 13344 (rat lethality) in order to illustrate the relative and absolute contributions of individual toxicants. The 30 minute LC_{50} values used in Equation 3 are given in Table 4.

Combustion product	30 min LC_{50} (µL/L)
CO	5700
HCN	165
HCl	3800
HBr	3800
HF	2900
SO2	1400
NO2	170
Acrolein	150
Formaldehyde	750

Table 4 : 30 Minute LC_{50} values for rats (data from ISO 13344)

In order to relate the fire effluent toxicity to a maximum permissible loading, the FED can be related to the mass of material in a unit volume, which would cause 50% lethality or incapacitation for a given fire condition; as an LC_{50}, a specimen mass M of a burning polymeric material that would yield an FED equal to one within a volume of $1m^3$ according to Equation 4.

$$LC_{50} = \frac{M}{FED \times V}$$

Equation 4 : Relation of LC50 to FED

Equation 4 is the relation of LC_{50} to FED. Here V is the total volume of diluted fire effluent in cubic meters at standard temperature and pressure (STP). Comparing the toxic potencies of different materials, the lower the LC_{50} (the smaller the amount of materials necessary to reach the toxic potency) the greater its fire toxicity. LC_{50} values should be referenced to the fire condition under which they were measured.

Several test methods have been used to generate products for the purpose of evaluating the toxic product yields from burning polymers. For example the following tests are in use nowadays:

- ISO 5659-2 + FTIR
- NF X 70-100
- ISO 13571
- FTP CODE IMO part 2
- BSS 7239
- ISO 19700

However, many of them fail to be related to a particular fire scenario[49]. In addition, although room- and larger-scale fire tests have been also conducted and the results published, only a few of these have attempted to segregate the fire stages, allowing the complexities of full-scale burning behaviour to be addressed using a bench-scale model. We consequently chose to detail one relevant test: the steady-state tube furnace, ISO 19700.

It has been developed specifically to replicate individual fire stages by decomposing materials under the full range of fire conditions from oxidative pyrolysis to fully developed, under-ventilated flaming. By controlling the fuel feed rate and air flow into a tubular furnace, steady burning can be achieved for different fuel/air ratios even forcing combustion in oxygen-depleted atmospheres[50]. The apparatus is shown in Figure 17.
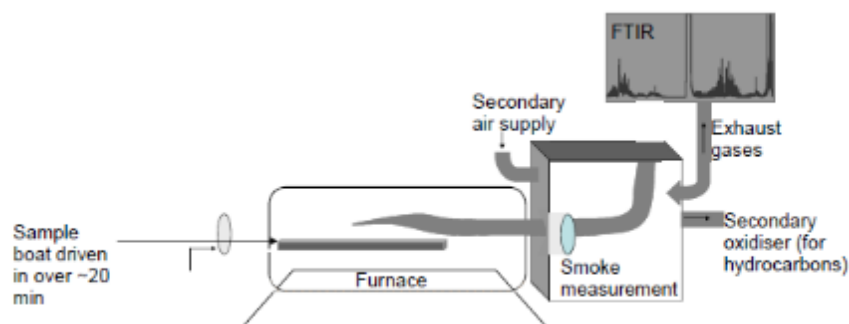
Figure 17 : Schematic of the steady-state tube furnace, ISO 19700
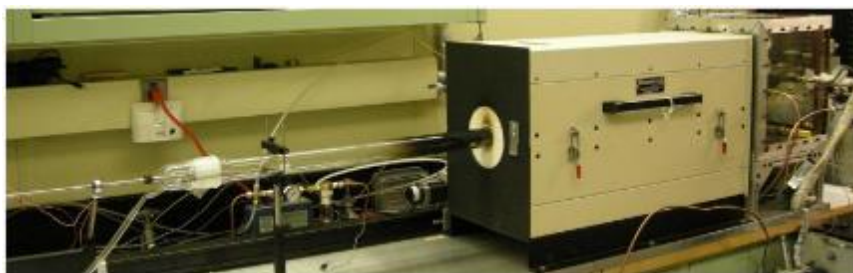
Figure 18 : Picture of the steady-state tube furnace, ISO 19700 (Source: NIST)

The apparatus typically consists of a tube furnace (600- to 800-mm heating zone) and a quartz tube (1600-1700 mm) that passes through the furnace and into a mixing and measurement chamber (27-30L capacity). The standard procedure uses around 20 g of material uniformly placed in a silica boat (800 mm) to give a linear density of 25 mg/mm. A drive mechanism pushes the specimen boat into the furnace tube at a rate of 40 mm/min to give a fuel introduction rate of 1.00 g/min.

A constant stream of primary air is provided at the furnace tube entry, and secondary air is supplied into the mixing chamber to give a total air flow through the apparatus of 50L/min. This provides a steady-state mass charge concentration of 20 mg/L (or 20 g/m^3) in the chamber. After dilution with secondary air, this effluent is equivalent to a fuel mass of 1 kg in 50 m^3 in a room. For materials that leave a residue or form a char, the residual mass is measured, and product yields based on mass loss concentrations may be also calculated. The requirement in each test run is to obtain a steady state of at least 5 min during which the concentrations of effluent gases and particulates can be measured. A light/photo cell system is used to determine smoke density across the mixing and measurement chamber. Organics (unburnt and partially burnt hydrocarbons) are determined as products of incomplete combustion using a secondary oxidizer for further oxidation at 900°C in excess air, over silica wool, as the difference between secondary CO_2 and primary CO and CO_2 measured using a nondispersive infrared analyser. The toxicity of organic species in the fire effluent may be quantified as a ratio of the actual organic yield to the organic yield of 10 mg/L resulting in incapacitation, as described by Purser[15].

The steady-state tube furnace has been shown to replicate a range of large scale fire stages or conditions, characterizing the fire behaviour of materials under controlled and well-defined laboratory conditions, in terms of the equivalence ratio (Φ) or the CO_2/CO ratio. Further, since each test run represents the burning behaviour for a particular fire stage, the results are better defined than those of a single large-scale test, where individual fire stages may coexist so the transition is indistinguishable. An example for CO from PP is presented in Figure 19.
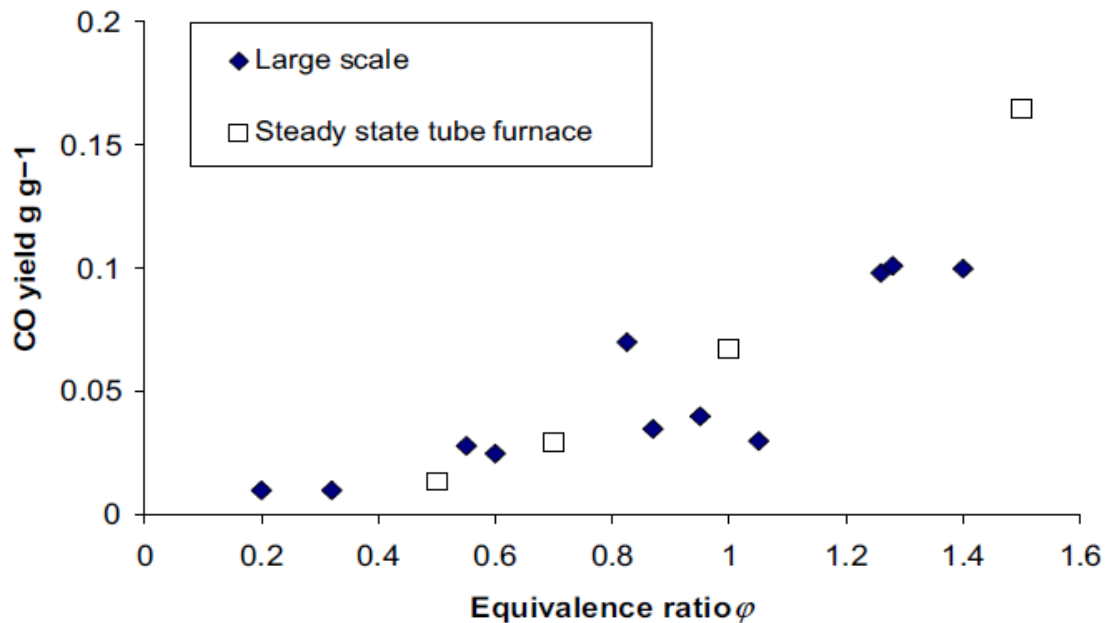
Figure 19 : Comparison of tube furnace CO yields with large scale data for polypropylene

The large-scale test data (from the ISO room corner test) show a good agreement with the steady-state tube furnace data; a significant improvement on any other toxicity test. In well-ventilated conditions, both the tube furnace and the large- scale fire give CO yields of around 0.02-0.03 g/g, then following the same rising trend to 0.1 g/g at Φ = 1.3 in the large-scale test and 0.17 g/g at Φ = 1.5 in the tube furnace and for under-ventilated flaming.[44]

➤ Soot analysis

A cascade impactor is one of the only techniques which provides a particle size distribution expressed in terms of mass (rather than number) of particles in each size range[52]. The comparisons have been made between cascade impactor and other methods. This system is generally coupled with the steady-state tube furnace ISO 19700.

Figure 20 : Cascade impactor filters

Cascade impactors measure aerodynamic particle size directly, as physiological effects are a function of size distribution based on mass. This is the most relevant parameter for predicting particle transport and deposition within the respiratory tract. Airborne particles pass through the apparatus and no impaction occurs when streamlines (straight arrows in Figure 20) bend as air flows bypass a solid object (i.e., a collection plate). Particles larger than the cut off-size (Table 5) of each impactor plate will slip across the streamlines and impact upon the filter while smaller particles will be carried by the streamlines and pass through the impactor stage to be separated on subsequent filters.

Filter cut off	Approximate maximum aerodynamic diameter	Position in the human respiratory tract
21.3 μm	21.5 μm	Nasal cavity
14.8 μm	15 μm	Oral cavity
9.8 μm	10 μm	Larynx
6.0 μm	6.5 μm	Trachea
3.5 μm	4 μm	Bronchi
1.55 μm	2 μm	Bronchioles
0.93 μm	1 μm	Bronchioles
0.52 μm	0.5 μm	Alveoli

Table 5 : Filter size and corresponding deposition point within the human respiratory tract
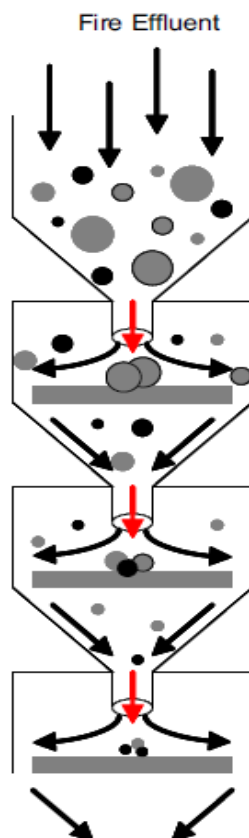
Figure 21 : Cascade impactor

The cascade impactor was attached to the mixing chamber of the Purser Furnace. Fire effluent was drawn through at a flowrate of 2.0 L.min^{-1} for a period of 5 min during the steady state stage and aerosol mass distributions were determined and collected for further analysis (i.e., the chemical composition). Each test, and the cascade impactor analysis is generally carried out in triplicates (Figure 21).

DLPI (Dekati® Low Pressure Impactor - Figure 22) is a 13-stage cascade low pressure impactor to determine particle gravimetric mass size distribution. This second system to assess the particles size and the quantity of soot, can be coupled with cone calorimeter test. The size classification in DLPI is made from 30 nm up to 10 µm with evenly distributed impactor stages and can be extended down to 30 nm with an additional back-up filter. In each size fraction the particles are collected on 25 mm collection substrates that are weighed before and after the measurement to obtain gravimetric size distribution of the particles. A chemical analysis of the size classified particles can also be performed.
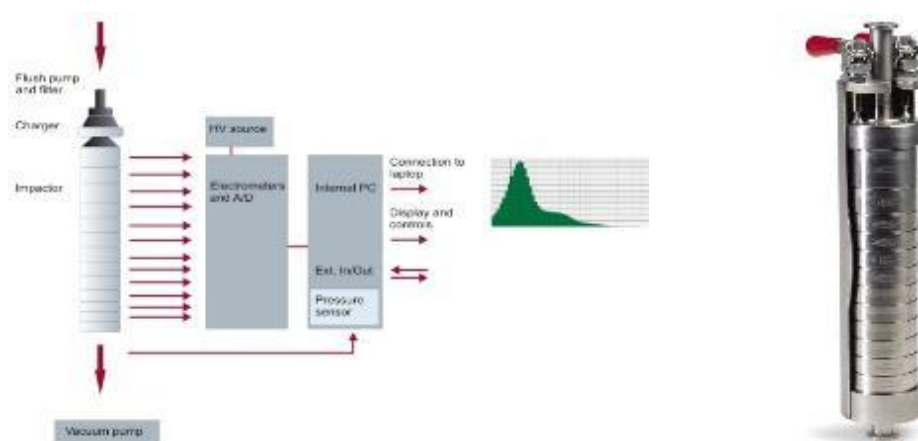
Figure 22 : DEKATI low pressure impactor

2.4.5- Indirect assessment on large scale/ real fires

As discussed earlier, the highest difficulty in assessing the toxicity at bench-scale is to replicate the different stages of a fire. Moreover, we saw that mainly the methods used focus on a particular stage in the growth of the fire thus putting into question in which the degradation pathway is affected by the fact that the material is not submitted to the real fire spread and growth. As a consequence, three main methods have been already successfully used to get rid of the scale up problem.

1. Real fire is reproduced at full scale in a representative room with products and materials subjected to the investigation
2. Gas and soot samples are trapped in canisters during real fires. Due to the high risk level implied only firefighter can carry out the sample collection.
3. Post-fire soot and particulates picking up can also be done.

It is worth noted that those methods are not standardized like bench scale ones thus the comparison between them is barely not possible. Anyhow, the few studies dealing with real fires scenario allow this review to draw the best mapping of the state of the art of smoke characterisation.

The first method[51] uses an experimental facility such as the one presented in Figure 23. This one comprises a burn room equipped with a burner of sufficient power to start the fire, connected to one end of a corridor and a target room at the opposite end. Exhausts from the fire are collected in a hood which is connected to the gas and soot analysis line. Set up of the test items is adequately chosen to allow proper flame spread and gathering significant data.
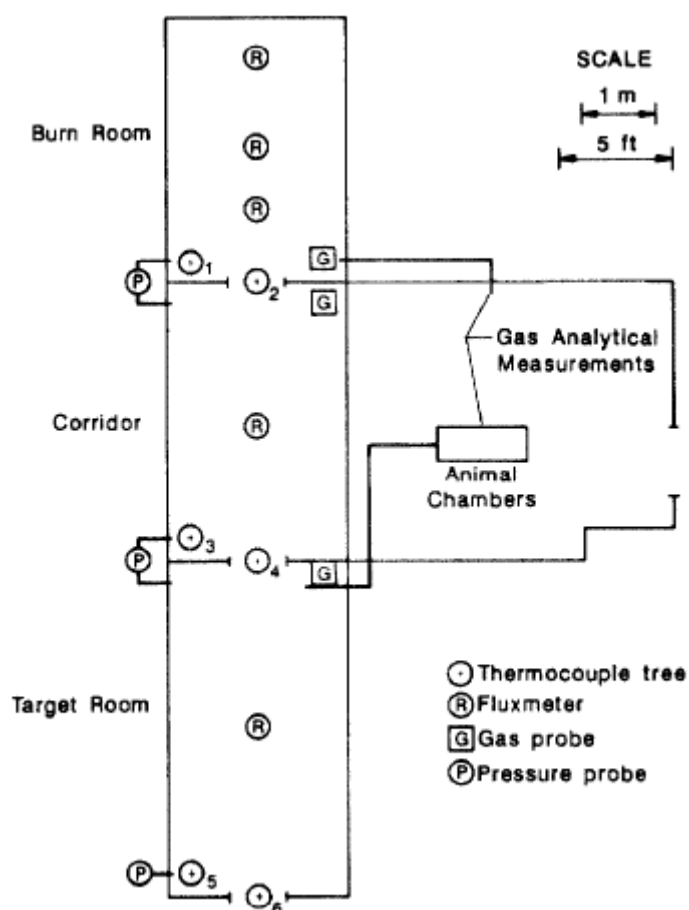

Figure 23 : Plan view of large scale test arrangement

Other instrumentation such as thermocouples, pressure probes, flux meters or animal exposure chambers can be also used to assess various relevant parameters allowing a global comprehension of the fire growth, tested items degradation and contribution to flame spread or smoke opacity and toxicity.

The second method than can be helpful in real fires toxicity assessment consists in collecting VOCs in canisters during real fires[37]. Firefighters inside burning buildings collect the air into evacuated Summa electro-polished stainless-steel canisters. Samples are collected at mixed occupancy fires, such as electronics industry fire, or structural fires that smouldering for a certain time. Samples are collected without regard to location. Firefighters can receive special instructions e.g., collecting samples when they judged that at least some firefighters might remove their self-contained breathing apparatus (SCBA) masks. This sample collection allows nonpolar VOCs present in the air and smoke to be identified and quantified. Classical post treatment consists in using cryogenic pre-concentration followed by gas chromatography (GC) mass spectrometry (MS) analysis. Then, identification of the major compounds is made by comparison of the mass spectrum obtained with appropriate reference spectra found in appropriate databases. The probability that a correct match is found is required to be greater than 90% for example. Quantitative analysis can also be performed thanks to internal standard method for example.

As realized in a study led by Hewitt, F and al[53], condensed particulate samples can be collected on microscope slides and Whatman GF/A microfiber glass filters (37 mm diameter). Three microscope slides and three filters were attached above the door frame at each location of a determined room (see Figure 24). The slides and filters were attached above the door frame outside bedroom one for sampling from the stairway, as this bedroom was located immediately at the top of the stairs. These were in place before the fire was started and were collected after the fire was extinguished and the house was ventilated. Condensed particulate sampling was performed only at the stairway for kitchen experiments, while in all other experiments sampling inside the bedrooms also occurred. The photographs in Figure 3 show this set-up for sample collection.
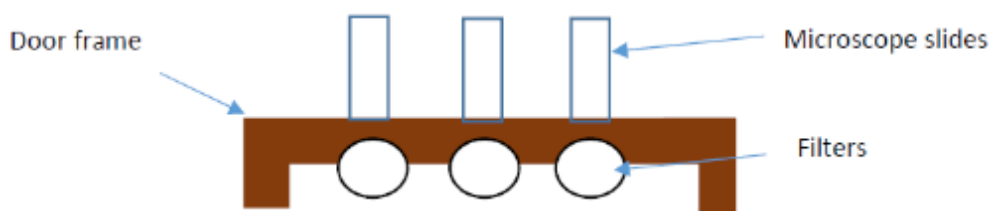
Figure 24 : Schematic set-up for condensed phase sampling

Aerosolised soot in the gaseous effluent was collected remotely on filters using stainless steel sampling lines. The filters were removed from their cassettes and placed in 7 mL sample vials. The solvent (3 mL hexane-acetone mixture in a 3:1 ratio) was added and the vial was sealed, wrapped with Parafilm and then aluminium foil. This

procedure was optimised in the laboratory, prior to the fire experiments, where the use of filters and impingers, and varying types and concentrations of the solvent mixtures were compared. These optimisation studies used bench scale methods of generating fire effluent (NFX-70-100 and the Steady State Tube Furnace (ISO TS 19700)). The samples were sonicated in water for 30 min then stored in an ice box for transportation prior to laboratory analysis.

All sonicated samples were removed from the ice box, warmed to room temperature and transferred to 1.5 mL Eppendorf tubes where they were centrifuged (Progen Genfuge, 24D) at 13,000 revolutions per minute (rpm) for 5 min. The supernatant was then transferred to GC-MS vials. The samples were analysed by GC-MS using the same parameters as used for the standard solution. Mass spectrometry was run in positive ion mode with the ion source at 250 °C. Data analysis was performed using the XCalibur software provided by Thermo.

3- Gas toxicity studies

Although it has long been demonstrated that the smoke toxicity of combustion products is a key factor in fire hazard; it has also been shown that it is relatively rare for multiple fire fatalities to occur in fires that have remained small. The reason for these paradoxical facts is that the inherent toxic potency of smoke resulting from burning most combustible materials is very similar and appears to fall within a narrow range. Moreover, it has also been shown that the key fire property that governs the loss of human tenability in a fire atmosphere is the heat release[54] rate of the burning materials, which can drastically vary for common combustibles (while, as just stated, the toxic potency of most combustibles is very similar). Thus, toxic hazard is often a direct function of heat release rate rather than of toxic potency, provided the comparison involves materials that have significant differences in fire performance.[55]

Hence, heat release rate both governs the intensity of a fire, and the survivability in a fire scenario. Table 6 illustrates this fact, by determining survival time (through computer modelling) in a standard room, with a common chair. When the chair is made of a material with half the time to ignition, the survival time does not change. Similarly, if the toxic potency of the chair materials is doubled, it has very little effect on survival time, while doubling the rate of heat release immediately decreases survival time, by a factor greater than 3.

Product	Survival time
Primary chair	>10min
Double ignitability	>10min
Double toxic potency	>10min
Double heat release rate	3min

Table 6 : Effects of different fire properties on survival time

This is a very important fact to keep in mind since it starts putting into perspective the importance (or lack of it) of smoke toxic potency data in terms of fire hazard assessment, or simply of fire safety. It must also be kept in mind that fire fatalities tends to occur in fires that become very large[33], hence the importance to consider real fires data in addition to bench scale study.

As it has already been discussed, estimation of fire toxicity is mostly limited to the toxic products considered most significant in causing incapacitation and death in fire victims. These consist mainly of asphyxiating gases (CO, HCN, CO_2 and lowered oxygen) and

irritants, including acid gases (HBr, HCl, NOx). The following paragraphs are then dedicated to draw an objective overview of some representative studies dealing with acute toxicity measurement of the gases emitted during the combustion of some polymers, either neat or fire retarded. As already seen, a lot of different factors impact the thermal degradation of a material thus leading to various toxic gases mixings being specifically related to a fire test scenario. As a consequence, the comparison of the results is non-sense and the reader is then invited to consult the cited papers for further information.

3.1- Toxicity without FR

3.1.1- Stec, A. A. 2008 [56]

The purpose of this first study is to show the importance of the equivalence ratio Φ on the toxicity. Actually, it presents the combustion product yields generated using a small-scale fire model (The Purser Furnace apparatus ISO 19700). Identification and quantification of combustion gases and particularly their toxic components from different fire scenarios were assessed by continuous Fourier transform infrared spectroscopy. The relationship between type of the fire particularly the temperature and ventilation conditions and the toxic product yields for four bulk polymers is reported:

1. Low-density polyethylene (LDPE)
2. Polystyrene (PS)
3. Nylon 6.6 (PA 6.6)
4. Polyvinyl chloride (PVC)

For all the polymers tested, excepted PVC, there is a dramatic increase in the yield of products of incomplete combustion (CO and hydrocarbons) with increase in equivalence ratio, as might be expected. For PVC, there is a consistently high level of products of incomplete combustion arising both from flame inhibition by HCl and oxygen depletion. There is a low sensitivity to furnace temperature over the range 650–850°C, except that at 650°C PS shows an unexpectedly high yield of CO under well-ventilated conditions and PVC shows a slightly higher hydrocarbon yield. This demonstrates the dependence of toxic product yields on the equivalence ratio, and the lack of dependence on furnace temperature, within this range.
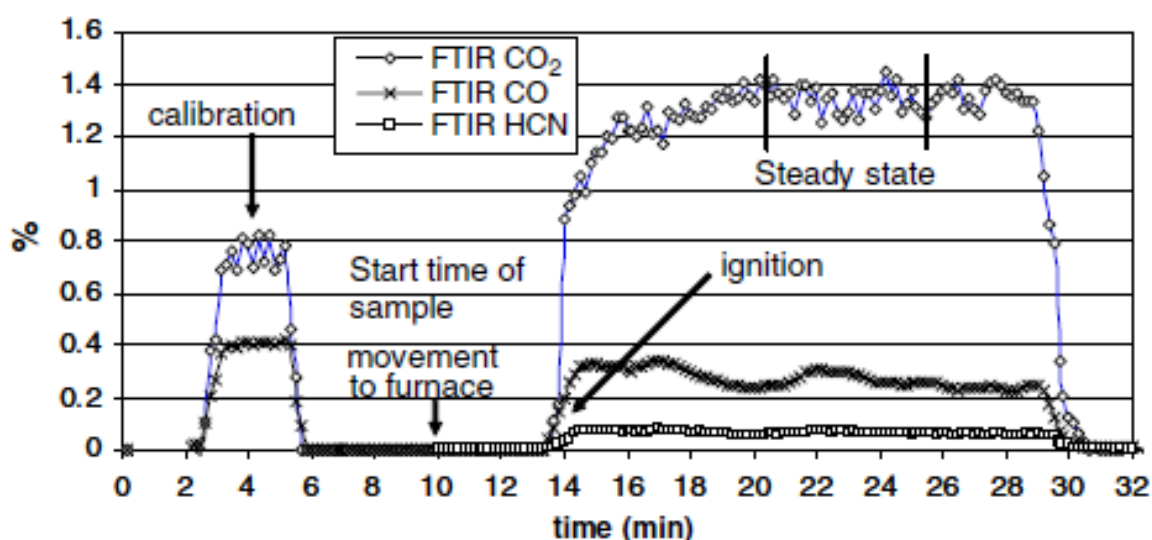
Figure 25 : Steady state in the Purser furnace (PA 6.6)

3.1.2- Purser, D. 2012 [41]

Here is another interesting work that illustrates the extent to which different toxic species contribute to the overall toxic potency of different non-flame retarded materials for the main different fire types according to the equivalence ration already introduced. The contributions from different chemical species are calculated using the Purser LC50 FED model. The chemical atmosphere composition data are from the NBS cup furnace, NIST radiant and mainly from ISO 19700 tube furnace.

Figure 26.a shows the results for non-flaming oxidative thermal decomposition. The data are plotted as toxic potency ($1/LC_{50}$), so that the higher the bar the greater the toxicity. The shading then illustrates the contribution to the overall toxic potency from each atmosphere component. Under non-flaming oxidative thermal decomposition conditions toxic potencies are relatively high. The main toxic components are HCN, with a small contribution from NO_2 (for nitrogen-containing polymers), CO, organic irritants for most materials, and HCl (for PVC).

For well-ventilated flaming (Figure 26.b) the yields of toxic products are low, so that toxic potencies are generally low. The results are therefore plotted at a scale five times higher than that for non-flaming decomposition. A variety of different components contribute to the overall potencies, but for well-ventilated combustion CO_2 is always important as a cause of hyperventilation. In this sense it is not directly toxic itself, but magnifies the toxicity of the other components by increasing their rate of uptake. For nitrogen-containing materials HCN is important, but NO_2 also makes a contribution, since the yields of nitrogen oxides are highest under well-ventilated combustion

conditions. CO is also important for some materials, and for materials containing chlorine, both CO and HCl are significant components of the overall toxicity (due to inefficient combustion resulting from the gas phase effect of chlorine). Hypoxia and organic irritants also make a contribution at high mass loss concentrations.

For under-ventilated combustion (Figure 26.c), the overall toxic potencies are considerably higher than for well-ventilated combustion conditions. Carbon monoxide is a significant toxic component in all cases, with a contribution from CO_2 and organic irritants. For nitrogen containing materials the toxicity is dominated by HCN, with a small contribution from NO_2, and for PVC, HCl and CO are the main toxic components with a small contribution from organic irritants. Polystyrene toxicity is heavily influenced by organic irritants.

At higher temperatures, representing post-flashover under-ventilated combustion conditions (Figure 26.d), the toxic potencies and patterns are similar to those under pre-flashover under-ventilated combustion conditions, but yields of CO and HCN can be somewhat higher.

Those results demonstrate that, in general, the toxic potencies are lower under well-ventilated combustion conditions, and higher under non-flaming, and under-ventilated conditions. Flaming combustion conditions in compartment fires begin by being well-ventilated and then gradually become more vitiated as the fire grows and the ventilation becomes limited. Individual materials in fires are therefore first decomposed in well-ventilated conditions at low equivalence ratios, and the equivalence ratio increases as combustion becomes under-ventilated. Most materials show a considerable increase in toxic product yields and overall toxic potency as the equivalence ratio increases.
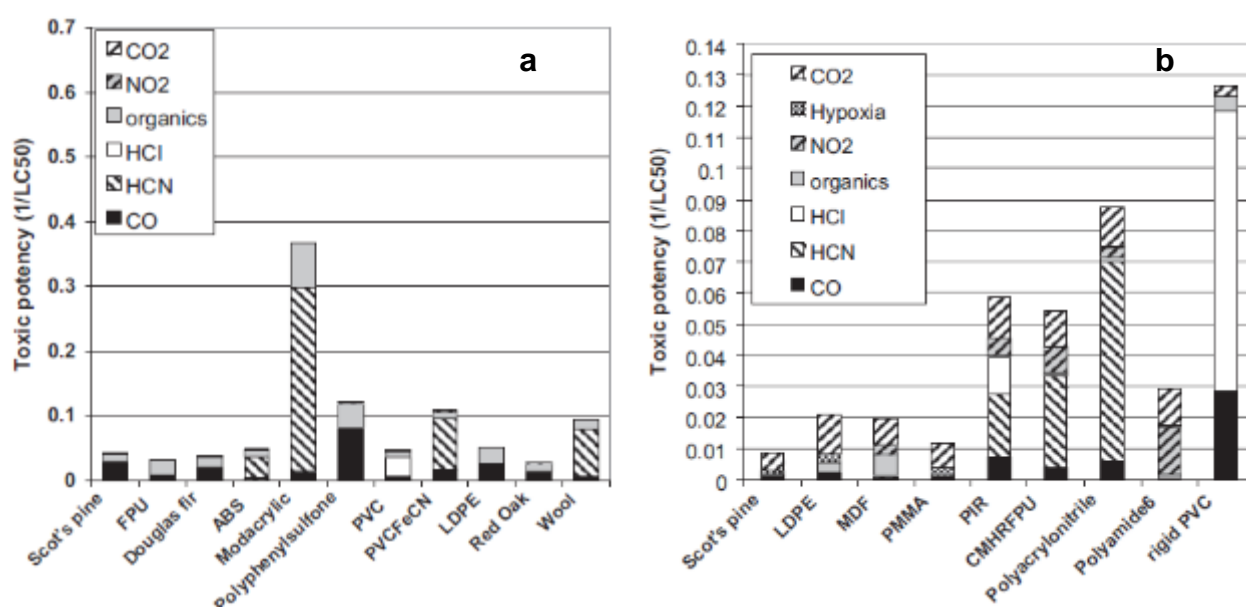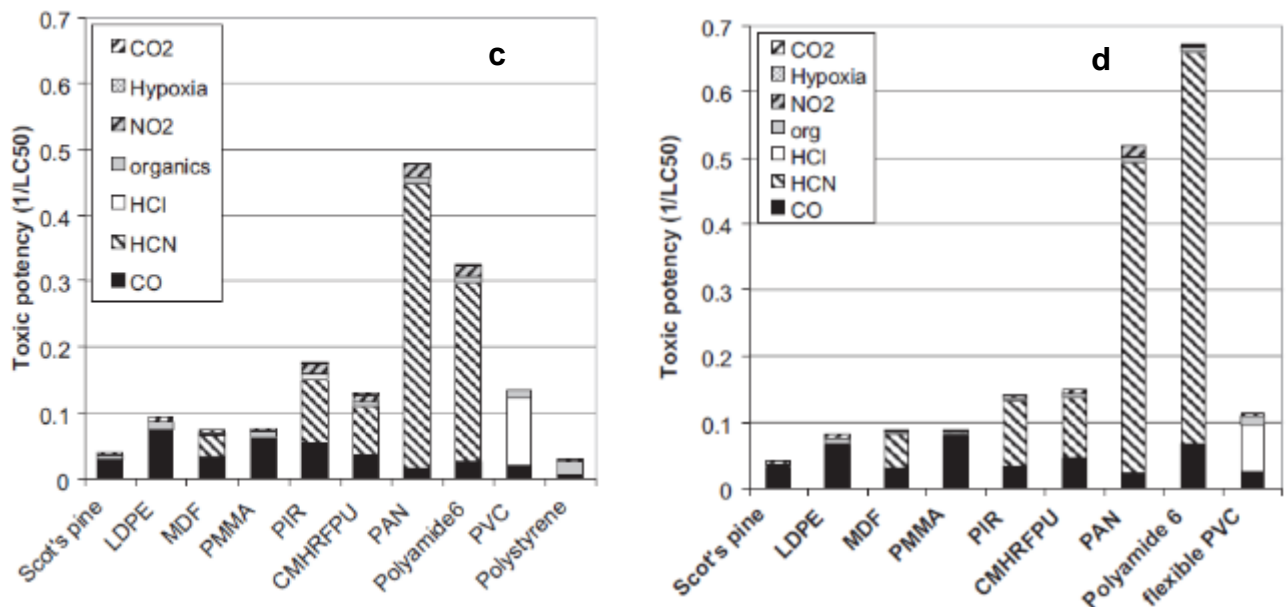
Figure 26 : Toxic potencies (1/LC$_{50}$) for (a) non-flaming oxidative decomposition conditions (b) well-ventilated flaming conditons (c) under-ventilated flaming conditions (d) post flash-over under-ventilated flaming conditions

3.1.3- Stec, A. A. 2011 [1]

This work reviews the investigations led on the fire toxicity of six insulation materials (glass wool, stone wool, expanded polystyrene foam, phenolic foam, polyurethane foam and polyisocyanurate foam) under various fire conditions. Two of the materials, stone wool and glass wool failed to ignite and gave consistently low yields of all of the toxic products. The toxicities of the effluents, showing the contribution of individual toxic components, are compared using FED (Figure 27).

As the toxic products of some materials vary as a function of ventilation condition, it is necessary to perform assessments of fire toxicity under the more dangerous, but most likely under-ventilated burning conditions. The ISO TS 19700 steady state tube furnace is a suitable tool for undertaking such assessments.

Earlier studies showed an increase in fire toxicity from glass wool and stone wool to polyurethane foam. This work shows lower carbon monoxide yields for all materials under well-ventilated conditions, compared to under-ventilated conditions, although the presence of halogens (presumably present as flame retardants) increases the CO yield in well-ventilated conditions. For the two nitrogen containing materials, PUR and PIR, the yields of hydrogen cyanide also increases with decrease in ventilation. When these yields are expressed in terms of the fire toxicity this shows a dramatic decrease in toxicity for the most common and most toxic under-ventilated condition: PIR > PUR > PHF > EPS. For the well-ventilated condition the order is similar: PIR > PUR > EPS > PHF.
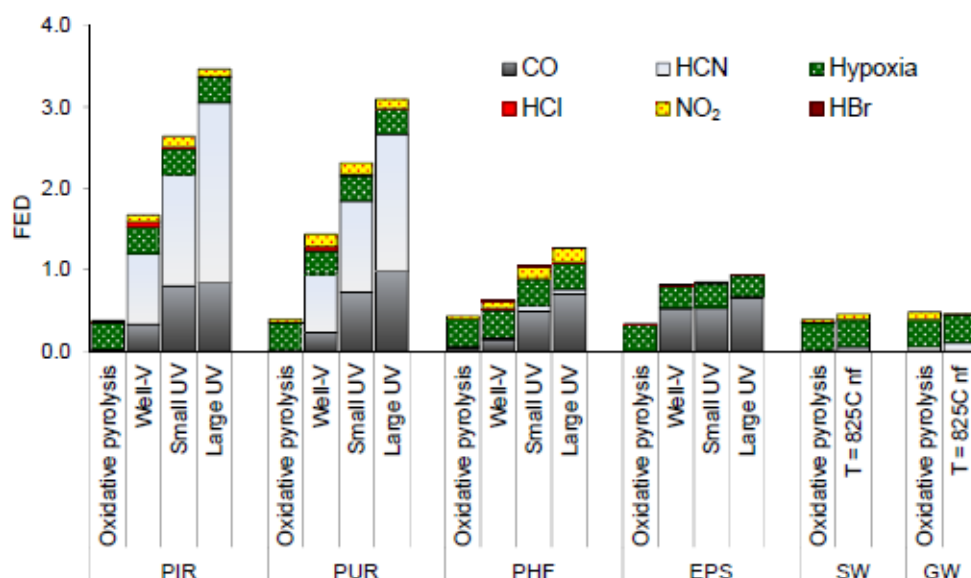
Figure 27 : Fractional effective dose (FED) for insulation materials (for oxidative pyrolysis and flaming conditions, except stone wool (SW) and glass wool (GW) non-flaming (nf))

Since neither GW nor SW undergo flaming combustion, while they can be tested under conditions which would represent well-ventilated or under-ventilated flaming, the data cannot properly be described as either. However, it is evident from the data presented here and that of other studies that the contribution to the fire toxicity for either glass wool or stone wool is negligible compared to that from any of the foam products. These results also indicate that fire toxicity of expanded polystyrene foam is lower that of PUR, PIR or even phenolic foam. That study gives a first insight on the fact that there is no need to add any PIN FR in a material to end up with a toxicity high enough to lead to death in case of fire.

3.1.4- Austin, C. C. 2001 [36]

Unlike the previous studies in this review, this work has not been performed with bench-scale thermal tools but somehow in real fire conditions. The global objective also was a little bit different than previously, since it was not to characterize the immediate lethal or incapacitating toxic potency of the fire effluents with the traditional *N-Gas model* but to characterize the presence of volatile organic compound (VOC) combustion products in fire smoke. That allows to feed the discussions about a certain long term exposure toxicity especially addressed to people repeatedly exposed to fires: firefighters.

Practically, air samples from experimental fires burning various materials commonly found at structural fires were collected into evacuated Summa canisters and analysed for 144 target VOCs using cryogenic pre-concentration and gas chromatography coupled with mass spectroscopy (GC/MSD) methodology. The data for this study were

obtained from 15 experimental fires burned in one corner of an enclosed, concrete basement (9 x 9 x 2.2 m) of an abandoned, two-story brick house using different combustible materials including spruce wood, cardboard, plywood, a bed mattress, a foam sofa, gasoline, varsol, and solid white foam insulation.

The resulting chromatograms were characterized by a small number of predominant peaks, with 14 substances (propene, benzene, xylenes, 1-butene/2-methylpropene, toluene, propane, 1,2-butadiene, 2-methylbutane, ethylbenzene, naphthalene, styrene, cyclopentene, 1-methylcyclopentene, isopropylbenzene) being found in proportionately higher concentrations in all experimental fires and accounting for 65% (standard deviation = ±12%) by mass of total measured VOCs. Benzene, toluene, 1,3-butadiene, naphthalene, and styrene were found at higher concentrations than most other VOCs and increased with the time of combustion together with increasing levels of carbon monoxide. Benzene was found in the highest concentrations, with peak levels ranging from 0.6 ppm to 65 ppm, while the levels of 1,3-butadiene, styrene, and naphthalene peaked at 0.1, 0.4, and 3 ppm, respectively . This study revealed that there were no new or novel toxic non-polar VOCs resulting from the burning of common building materials. This is important in view of the studies that have found associations between firefighting and various forms of cancer.

3.2- Toxicity with PIN-FR

3.2.1- Hörold, S. 2004 [57]

In this work, properties of compounds containing the flame retardant based on a phosphinate (Exolit OP 1312) are compared with non-flame retarded PA 66-GF, a typical halogen-containing formulation (based on Saytex HP-7010 BrPS, antimony trioxide and PTFE) and a formulation based on red phosphorus Exolit RP695 from Clariant (see Table 7).

	PA 66-GF	PA 66-GF + BrPS	PA 66-GF + red phosphorus	PA 66-GF + phosphinate
	wt%	*wt%*	*wt%*	*wt%*
PA 66	*70*	*43.6*	*56*	*52*
Glass fibers	*30*	*30*	*30*	*30*
BrPS	-	*20*	-	-
Antimony trioxide (80% in PA 6)	-	*6.0*	-	-
PTFE	-	*0.4*	-	-
Red Phosphorus (50% in PA 6)	-	-	*14*	-
Exolit OP1312	-	-	-	*18*
	-	-	-	-
UL 94-V (0.8 mm)	No rating	V-0	V-0	V-0

Table 7 : Formulations of PA 66-GF compounds

The approach of the work is really interesting since the FR additives loading rates have been chosen so that the three formulations pass UL 94 V-0 at the thinnest thickness requested. Nevertheless, a look at the optical smoke density (c.f. smoke density graphs according to ASTM E 662 in Figure 28) shows different behaviour: whereas the formulation with red phosphorus shows the same high smoke density as the formulation with brominated polystyrene, the new formulation with Exolit OP 1312 M1 (TP) gives a significant reduction in optical smoke density.
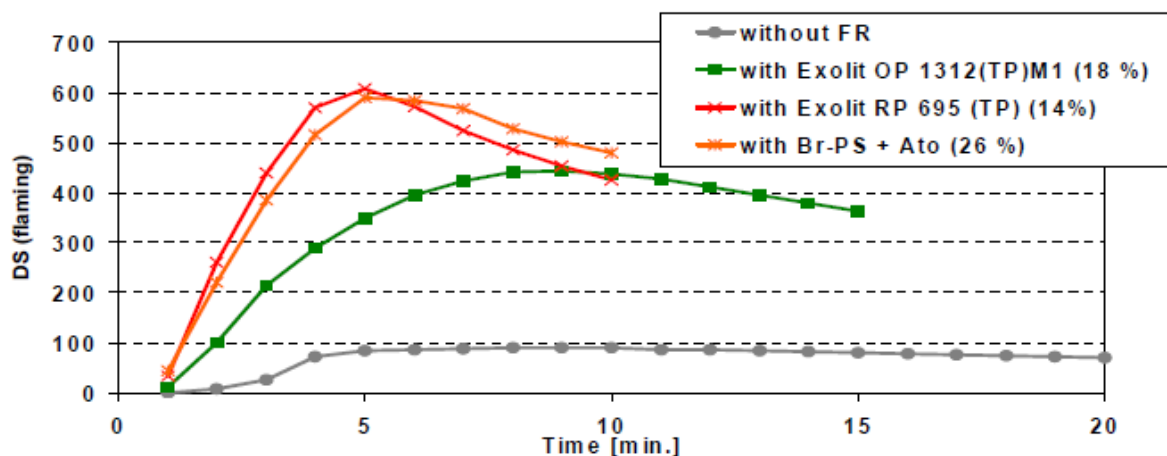
Figure 28 : Smoke density of burning PA 66 30% GF (ASTM E662)

Those results point out that even though low flammability and good burning behaviour are achievable thanks to different FR technologies, the effect on optical smoke density can be dramatically different. Indeed, it is well known that a deleterious effect of the

use of halogenated FR and antimony oxide is the increase in smoke. Red phosphorous tends to suffer from the same drawback. As a consequence the phosphinate based FR represents a very good alternative to reach the flammability requirement while having a reduced impact on the smoke density.

3.2.2- Hauk, A. 1995 [58]

Similarly to the study presented above, here the focus was made on E&E polymers but dedicated to printed circuit board and chip housing applications. The purpose of the work is to characterize the hazard potential of gaseous combustion products of phosphonate derivatives flame retardant in glycidyl-ether based polymers using analytical methods. They were actually degraded in ventilated controlled oven at 200, 400, 600 and 800°C. The gases emitted were compared with data from the combustion of polystyrene and beech wood. It appeared first that at 200°C, the volatile products detected were way below the threshold analytical value. Then the materials investigated showed no unusual thermochemical behaviour. Regarding the volatile fraction containing CO_2, CO and HCN at temperature between 400 and 800°C are typical of such polymers, independently of the flame retardants added. Actually, the phosphorus containing flame retardant component formed no detectable volatile organic combustion products meaning that all the initial phosphorus added to the matrices remained in the residue. As a consequence, the acute toxicity seems not badly impacted by the flame retardant and values at different temperature were similar to combusted polystyrene and beech-wood samples.

> ➢ Curry, B. 'Comparison of Flame, Smoke and Toxicity in a Halogen-Free and a Halogenated Reinforced Composite'. Journal of Advanced Materials 37, no. 4 (1 October 2005): 36–39.

3.2.3- Curry, B. 2005 [59]

Another alternative from halogenated FR derivatives is the use of metal hydroxides to achieve a required fire performance. This publication describes the benefit of using Alumina Trihydrate (ATH) to reduce the smoke and toxic components released from fiberglass composites compared to a halogenated formulation. To that purpose, a detailed comparison of a halogenated and a non-halogenated ATH filled polyester was made. Analyses were run according to ASTM E 662 optical smoke density, and BSS 7239 toxic gas test. In both cases, a blend of styrene/MMA was used as the monomer. Results follow the same trend whatever the test considered. The smoke density values

(Figure 29) according to the ASTM E 662 were lower for the non-halogenated composite over the halogenated composite by a significant margin. Based on the BSS 7239 test results (Figure 30), the toxic gases given off from the halogenated composite were much higher than those released by the non-halogenated composite. Even though there is no chlorine in the halogen free resin, the HCL found in the gas during the BSS 7239 testing may be due to the filler or the glass. HBr would be expected to be given off from the halogenated resin. However the BSS 7239 test does not aim to analyse bromine, HBr was then analyzed as HCl. Regarding those results, it is easy to conclude that the overall smoke density and toxicity of the halogenated resin is significantly higher than the ATH based resin. When the regulation targeted requires low smoke and toxicity, the inorganic flame retardant must be chosen over the halogen based flame retardant.

TEST	RESULTS	
	FIREPEL® K133-AAA-00	H2
NON FLAMING EXPOSURE		
Maximum smoke density	40	93
% Standard deviation	17	28
Smoke density after 1.5 minutes	0.2	0.06
% Standard deviation	60	67
Smoke density after 4.0 minutes	2.0	4.7
% Standard deviation	40	74
FLAMING EXPOSURE		
Maximum smoke density	61	192
% Standard deviation	28	17
Smoke density after 1.5 minutes	1.3	2.8
% Standard deviation	18	61
Smoke density after 4.0 minutes	16	81
% Standard deviation	41	35

Figure 29 : ASTM E 662 results – specific optical density of smoke

TEST	RESULTS			
	FIREPEL K133-AAA-00		H2	
	Flaming Mode	Non-Flaming Mode	Flaming Mode	Non-Flaming Mode
Hydrogen Cyanide (HCN), ppm	<2	<2	2	2
Carbon Monoxide, (CO), ppm	67	<10	225	300
Nitrous Oxides, (NOx), ppm	<2	<2	1	1
Sulfur Dioxide, (SO2), ppm	<1	<1	<1	<1
Hydrogen Fluoride (HF), ppm	<1.5	<1.5	<1.5	<1.5
Hydrogen Chloride (HCL), ppm	4	2	15	16

Figure 30 : BSS 7239 results - toxicity of gases

3.2.4- Stec, A.A. 2014 [20]

This comprehensive review examines the effects of the main parameters determining product yields of toxic gases, illustrated with data for various common polymeric materials obtained using the ISO 19700 tube furnace, which is now well known to provide an excellent method for exploring the relationship between combustion conditions and product yields. For a particular material in a fire, it is possible to estimate the impact on lethality or incapacitation from a knowledge of the composition of the fire effluent produced under different fire conditions. The yields have been translated into their predicted toxic effects. The materials include low-density polyethylene, polymethylmethacrylate, polystyrene, polyvinyl chloride, ethylene-vinyl acetate copolymer, polyamide 6, etc., used alone, and in the presence of fire retardants and nanofillers (synergistic agents).

NEAT POLYMERS

The yields of toxicants from polymethylmethacrylate (PMMA), low-density polyethylene (LDPE), polyvinyl chloride (PVC), polyamide 6.6 (PA 6.6), and polystyrene (PS) are presented in Figure 31 as a function of equivalence ratio, Φ.

For PMMA, very efficient combustion at equivalence ratios below 1 is observed, with high CO_2 yields and very low yields of other carbon-containing products. In under-ventilated combustion conditions, there is a large increase in yields of organic gases and CO with increasing Φ. For under-ventilated combustion, the yields of organics and CO are both high compared to well-ventilated flaming.

A similar pattern of product yields for LDPE is observed. The theoretical yield (100% conversion of fuel carbon to CO_2) for LDPE is 3.14 g/g under well-ventilated conditions. It can be seen that almost all the fuel carbon is converted to CO_2. The CO_2 yield follows an almost linear decrease as the ventilation is decreased, while the CO yield increases with decrease in ventilation from $\Phi = 0.5$ to $\Phi = 1.5$ then starts to decrease slowly, presumably due to limited oxygen availability. At an equivalence ratio of 1.6, the results show some increases in yields of hydrocarbons.

PS has a similar carbon content to that of LDPE, but a higher carbon/hydrogen ratio. The combustion product yield pattern is similar to that of LDPE, but with less sensitivity to the ventilation conditions. It shows a high CO_2 yield at low equivalence ratios, decreasing as $\Phi > 1$, but there is a greater propensity to form carbon-rich soot throughout the Φ range and especially at high equivalence ratios. The relatively high CO yields in well-ventilated combustion conditions and low CO yields in under-ventilated conditions suggest the presence of stable aromatic molecules, and low hydrogen ratio, resulting in inefficient oxidation. The higher CO yield and correspondingly higher soot yield for aromatics and unsaturated fuels burning in well-ventilated conditions is well known; the lower CO yield under fuel-rich conditions is more interesting; the CO yield of 0.11 g/g for toluene under fuel-rich conditions, and attributed it to the thermal stability of the molecule. This results in a further reduction in combustion efficiency as the aromatic hydrocarbons are not converted to CO. Since the main product of decomposition of PS is the monomer, with smaller quantities of dimer, trimer, and tetramer, these are also likely to show similar enhancements in thermal stability, limiting the availability of $OH^\bullet$ radicals, responsible for converting CO to CO_2.

PA 6.6 shows a similar trend to PP and PMMA. Combustion is efficient at low equivalence ratios with low yields of CO and organics, all of which increase at equivalence ratios > 1. The efficiency of conversion of fuel carbon to CO is lower than that for PMMA, which may be related to the lower oxygen content of the polymer. The yields for CO and HCN show an increase with increase in Φ. In well-ventilated combustion conditions, the yield was low, but increased steeply to a maximum of 0.44 g/g at $\Phi = 2.5$. Under well-ventilated combustion conditions, the main toxic species

produced was NO at a maximum yield of 0.012 g/g at $\Phi = 0.5$, decreasing as Φ increased to a yield of 0.0026 g/g in under-ventilated combustion conditions. The yield of NO_2 was approximately a factor of 10 lower than that of NO.

PVC burns with a low heat release rate, because the halogen atoms in the structure are released as HCl, accounting for almost 60% of its mass, which then inhibits the conversion of CO to CO_2 and combustion is inefficient, even under well-ventilated conditions. The yield pattern is very different from that of all the other polymers described, in that the yields of all products are relatively similar across the whole Φ range from 0.5 to 2.5. Combustion is very inefficient across the range, with relatively low CO_2 yields and high yields of CO, and organics. The CO yields in the steady-state tube furnace, are almost constant with increase in Φ. The theoretical yield of HCl is 0.585 g/g, and it can be seen that most of the chlorine is released as HCl.
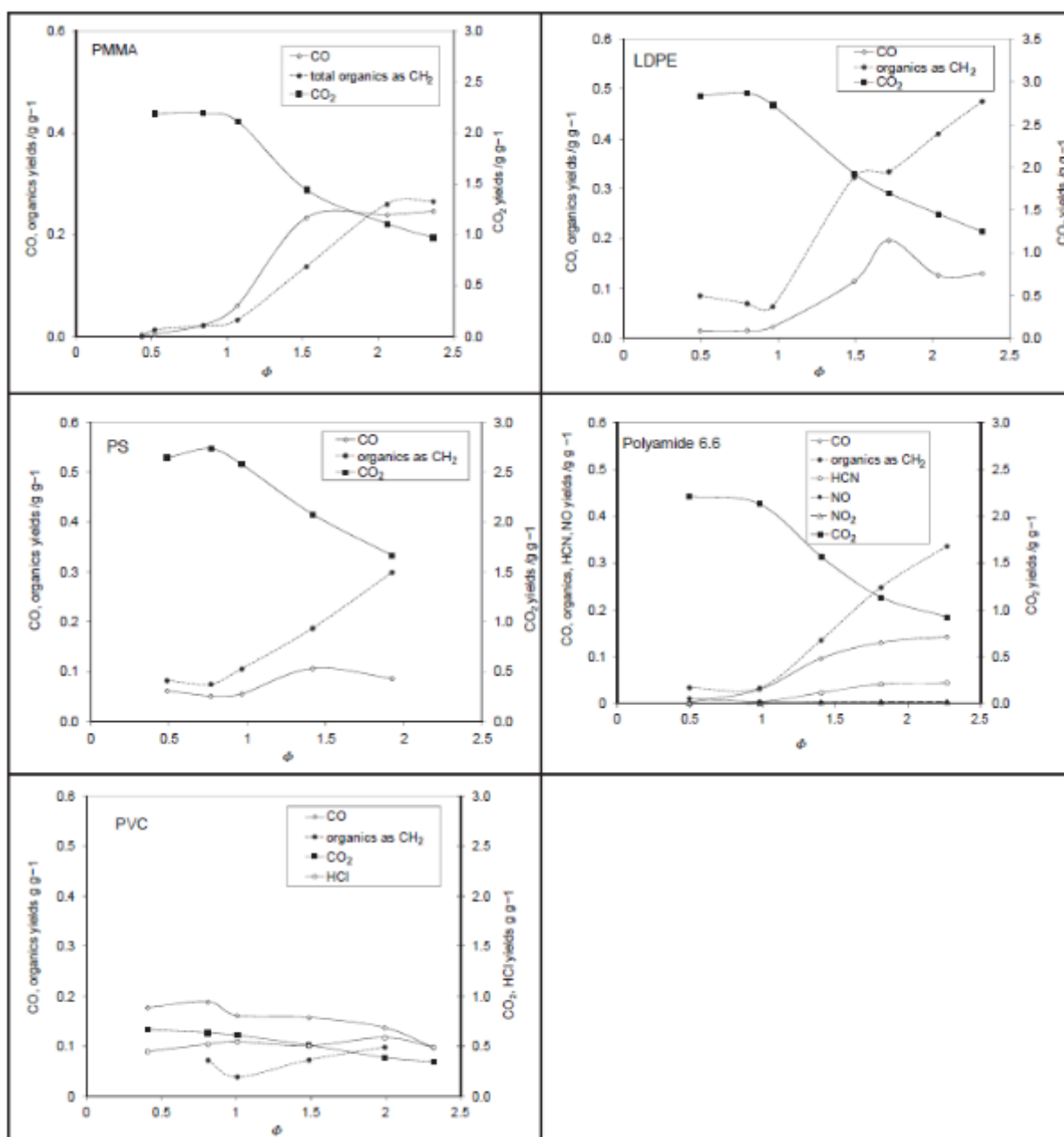
Figure 31 : Fire effluent yields from polymethylmethacrylate (PMMA), low density polyethylene (LDPE), polystyrene (PS), polyamide (PA) 6.6, and polyvinyl chloride (PVC)

The major LDPE, PMMA, PS, PA 6.6, and PVC product yields, obtained from the steady-state tube furnace, have been translated into an overall estimation of the fire effluent toxicity, using the methods described in ISO 13344 indicating the contribution of each toxicant towards the overall fire hazard. Hypoxia is presented here as a decrease in oxygen supplied to, or utilized by, body tissue. The toxicity is expressed as FED for a fuel mass charge concentration of 20 g/m^3.

Most polymers without heteroatoms follow the trend shown by LDPE and PMMA of fire toxicity increasing from a very low value in well-ventilated conditions, to a much higher value in under-ventilated flaming. As can be seen from Figure 32 , there is a large

variation in FED values for materials containing chlorine or nitrogen. For well-ventilated tests, the largest FED value is for PVC. The FED is >1, indicating the lethality of the diluted fire atmosphere over 30 min. PVC is one of the few materials to show a predicted combustion toxicity that is almost independent of the equivalence ratio, showing unusually high toxicity under well-ventilated conditions. As an irritant gas, HCl will have the greatest effect of any toxic species.

For under-ventilated fires, HCN from PA 6.6 makes the most significant contribution to the toxicity, and a high dependency on fire conditions is observed. HCN generated during small and large under-ventilated flaming tests makes the most significant contribution to the toxicity. For PA 6.6 in under-ventilated conditions, and for PVC, HCN, and HCl make the greatest contribution to the final FED, showing the importance of two toxicants other than CO. PMMA, LDPE, and PS are hydrocarbons without any halogens or nitrogen, and this is reflected in FED values well below 1 for the well-ventilated fire scenario. The fire effluent from PS has a relatively low toxicity, and shows a characteristically low dependence on fire conditions. The toxic contribution of CO under fuel-rich conditions is remarkably similar to those generated under fuel lean conditions.
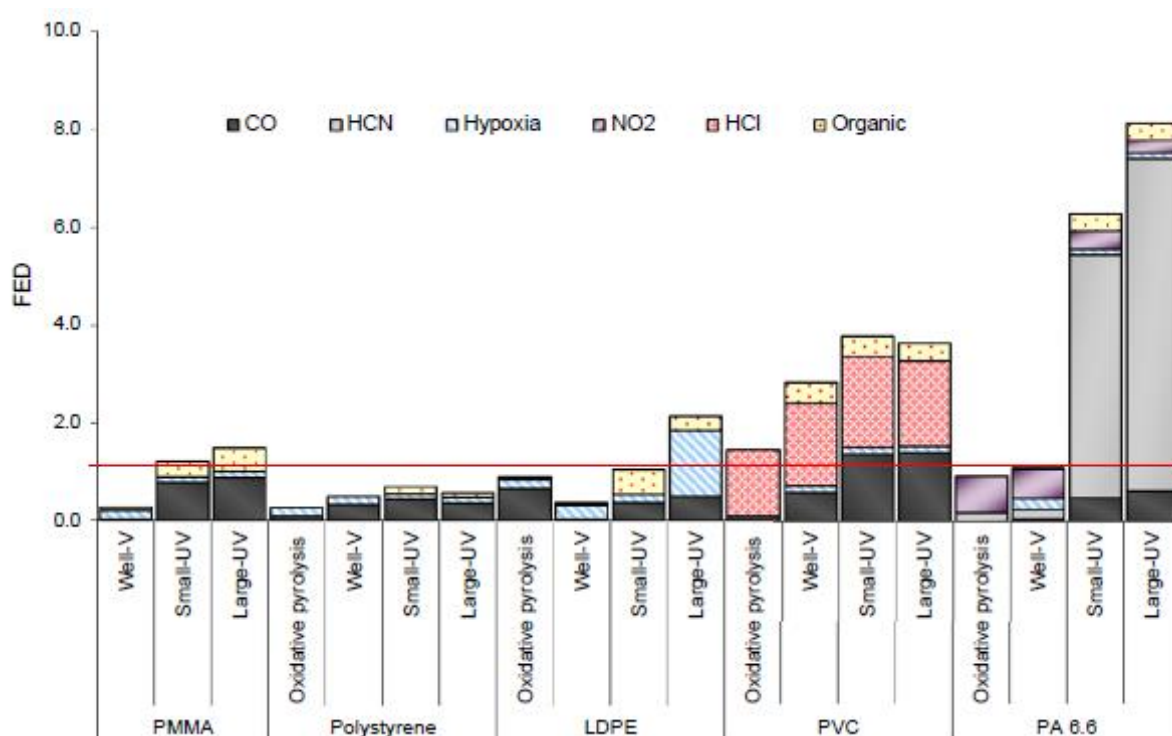
Figure 32 : Fractional effective dose (FED) for common polymers

POLYPROPYLENE (PP)

Samples of PP containing 5% PP grafted with maleic anhydride, to allow dispersion of nanoclay (NC), were compounded with 30% ammonium polyphosphate fire retardant and/or 5% Cloisite 20A (NC). The toxicity of the PP materials is much lower than that for the PA samples in under-ventilated conditions (Figure 33). Again there is a progressive increase in the toxicity from small under-ventilated to large under-ventilated, which is shown consistently across the samples. Although the addition of either fire retardant (FR) or NC has no significant effect on the CO yield, it appears that the combination of both NC and FR results in higher CO yields for under-ventilated flaming[63].
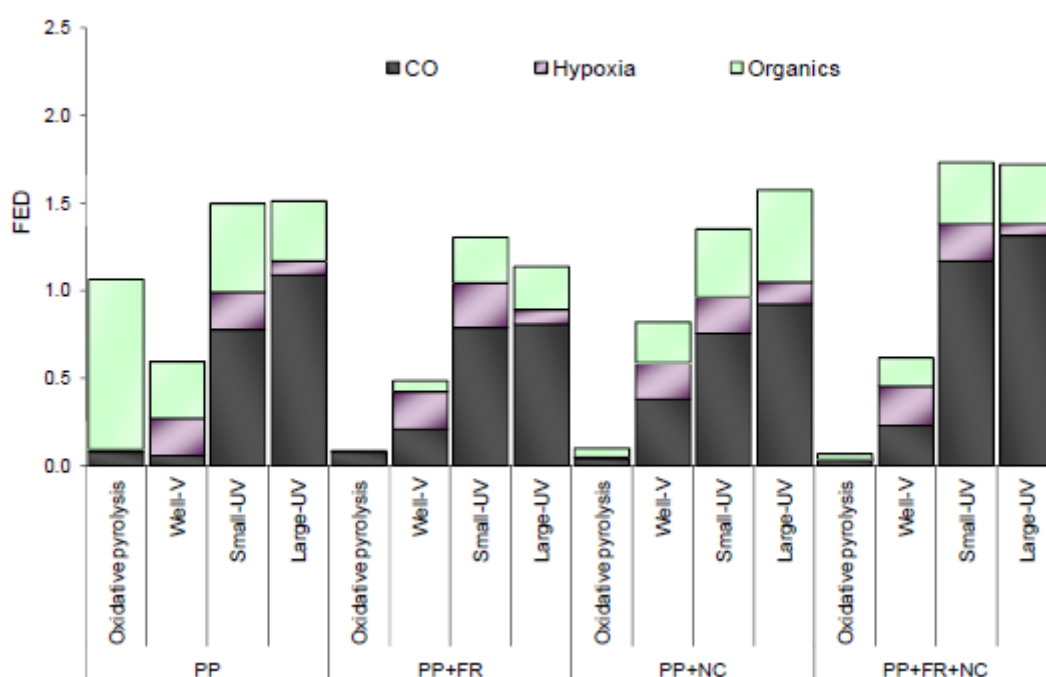
Figure 33 : Fractional effective dose (FED) for polypropylene (PP) with the fire retardants and nanoclays (NCs)

ETHYLENE-VINYL ACETATE COPOLYMER (EVA)

EVA is widely used with mineral fillers in the cable industry, as a material for avoiding the toxic, smoky, corrosive effluent of PVC-sheathed cables. EVA containing 27% vinyl acetate was compounded into low smoke and fume formulation. Fire retarded composites were formulated with 30% by weight of the EVA and 70% aluminium hydroxide (ATH) or 65% ATH and either 5% zinc hydroxystannate (ZS) ($ZnSn(OH)_6$), 5% magnesium borate (MgB) ($MgO (B_2O_3)2 H_2O$), or 5% zinc borate (ZB) ($2ZnO.3B_2O_3.3.5H_2O$)[64].

The contributions to FED, shown in Figure 34, indicate that except as a diluent filler, ATH and ATH with MgB or ZS have only a modest effect on fire toxicity, increasing the

CO contribution during under-ventilated burning compared with EVA alone. In contrast, ATH with ZB has a dramatic effect on reducing the carbon monoxide contribution to fire toxicity especially in under-ventilated conditions. It is thought that ZB forms a glass, which destroys the char oxidizing catalytic properties of the freshly formed alumina, leaving more of the carbonaceous residue in the condensed phase[65].
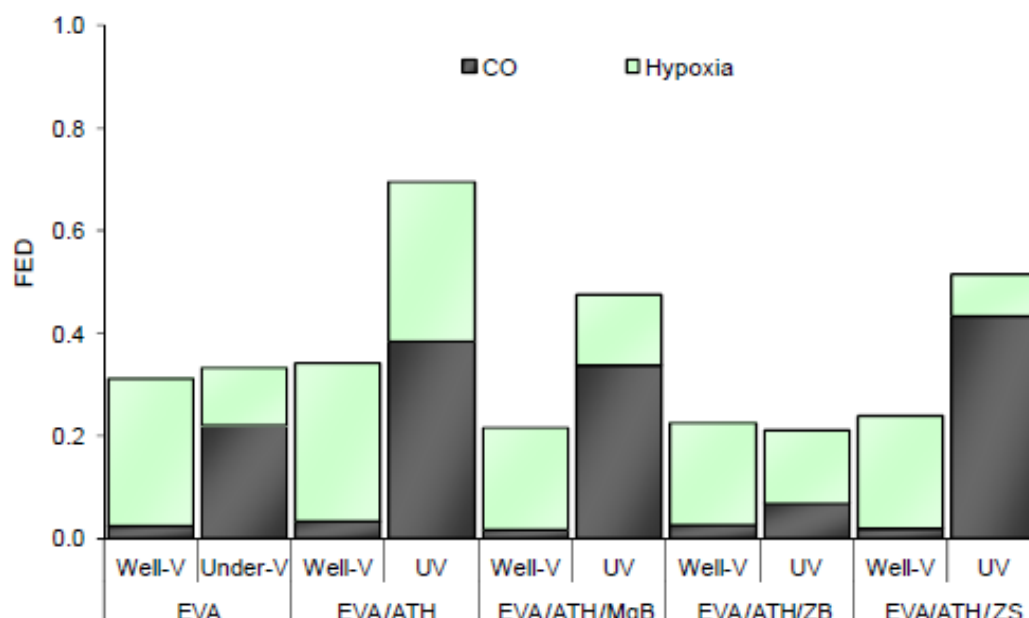
Figure 34 : Contribution of each component to toxicity at different ventilation conditions for EVA fire retarded composites

POLYBUTYLENE TEREPHTHALATE (PBT)

PBT was fire retarded with 18% aluminium phosphinate Exolit OP1240 and/or 5% of Cloisite 30B or Sepiolite NC.

Figure 35 shows the consistently higher toxicity from burning PBT under different fire conditions and the additional increase in toxicity resulting from the use of fire retardant presumably through gas phase inhibition. It is interesting to see this effect disappear on incorporation of either sepiolite or Cloisite. A slight increase in CO yield from well-ventilated to under-ventilated conditions for PBT and PBT with sepiolite, and PBT FR combinations is observed. As aluminium phosphinate is a gas phase flame retardant, the increase with FR would be expected, but this effect seems to diminish in the presence of the NCs. The NC alone has little effect on the CO yield[63].
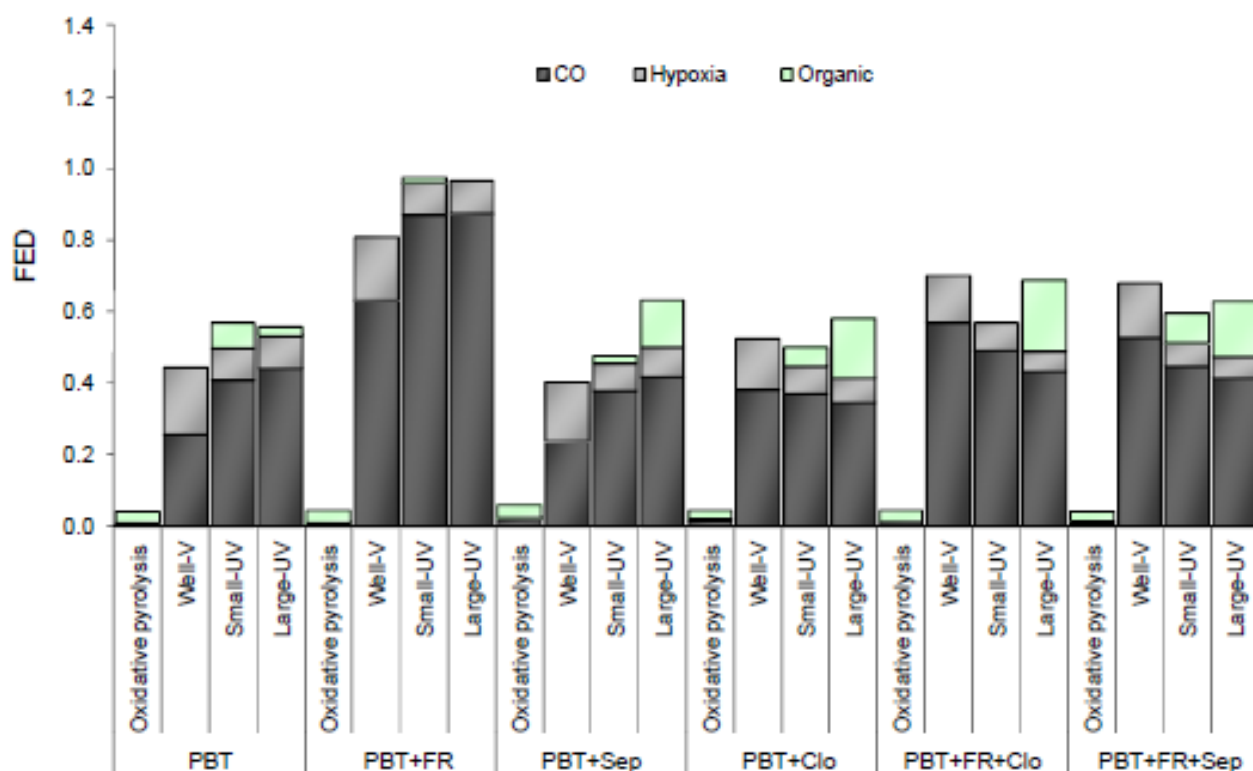
Figure 35 : Contributions to FED for PBT with fire retardant and nanoclays

CABLES

Ten commercial cables (Figure 36) were investigated for fire toxicity using the conditions specified in the precursor International Electrotechnical Commission (IEC) standard, IEC 60695-7-50, which uses the steady-state tube furnace, but a simplistic methodology for ensuring the setting up of the tube furnace ventilation condition to obtain a particular fire stage.

For each cable, the FED is shown for each of three fire stages. In most cases (8/10), oxidative pyrolysis is the least toxic, presumably due to the low mass loss of the polyolefin polymers at 350°C[66]. However, this temperature is high enough to release HCl from PVC in two cases. In general, the FED, based on the limited range of gases analyzed, increases from oxidative pyrolysis, to well-ventilated, to developed flaming. In common with most materials, the most hazardous fire condition is confirmed to be the under-ventilated fully developed fire. The two major toxicants are seen to be CO and HCl. However, it is notable that the CO yield the PVC fires is greater than that in halogen-free fires, and it is also noted that the CO yield in PVC fires increases with under-ventilation, whereas for pure PVC, the yield is almost independent of ventilation.
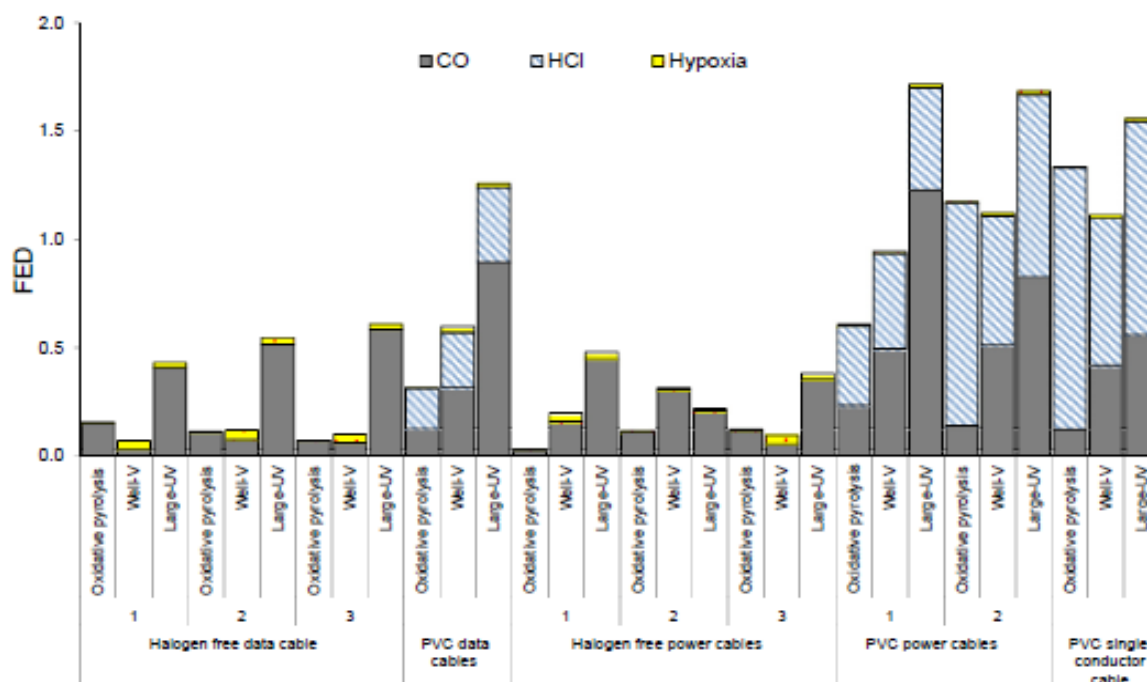
Figure 36 : Contribution of individual gases to toxicity from burning cables

3.2.5- Molyneux,S. 2013 [60]

This work is complementary from the one above. It is especially dedicated to standard industry formulations of flame retarded aliphatic polyamides, meeting UL 94 V-0 that have been burnt under controlled conditions with the steady state furnace apparatus (ISO 19700), and the yields of the major asphyxiants, carbon monoxide (CO) and hydrogen cyanide (HCN) have been quantified.

Polyamides are often chosen for electrical connectors and switch housings because of their toughness and rigidity. They are frequently reinforced with glass fibres to enhance their strength and dimensional stability.

The FED equation seen earlier in this report can be applied to toxic product yields, such as those shown in Graph 1, in order to predict the toxicity of the effluent. This shows that for polyamide 6, the effluent toxicity and particularly the contribution of HCN grows significantly with under-ventilation, and increasing severity of fire. FED values of 6 or 8 may be interpreted as a polymer loading of 167 g or 125 g, respectively, burning in a 50 m^3 room, under the specified conditions, will be lethal to 50% of the occupying population in 30 min exposure. The contribution of each toxic species to the FED has been calculated, and is presented in Figure 37. This shows that in well-ventilated conditions, ($\Phi \ll 1.0$) the toxicity is low. For under-ventilated conditions ($\Phi > 1.0$), the most significant contribution to the toxicity comes from HCN.
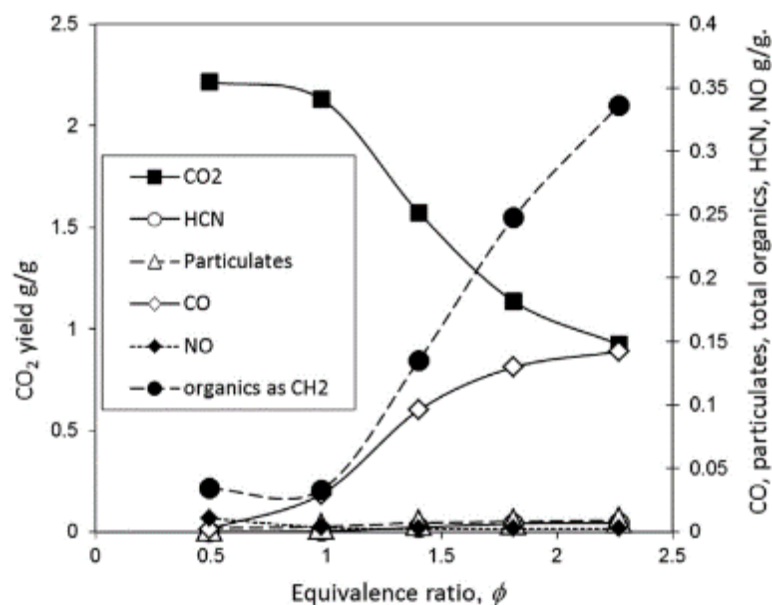
Graph 1 : Yields of toxicants from burning polyamide 6, over the temperature rans 650-825 °C
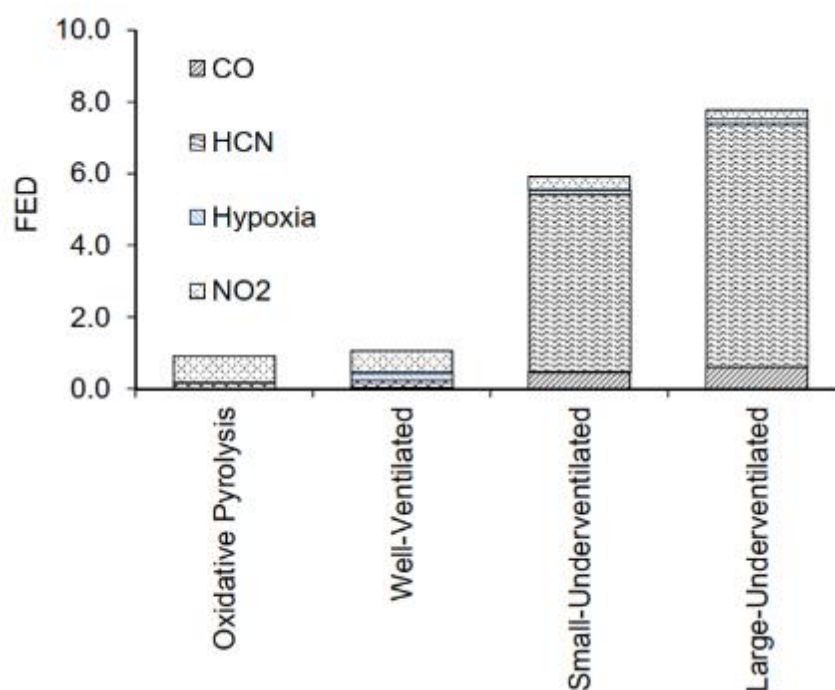
Figure 37 : The contribution to toxicity of individual effluent components from polyamide 6 in different fire conditions

Flame retardants added to meet demanding requirements such as the UL-94 V0 classification must not adversely affect the physical properties, or the durability of electrical components. Glass fibre reinforced polyamide 6 and 6.6 can be effectively flame retarded with halogenated flame retardants, such as brominated polystyrene, often used in combination with a synergist of antimony oxide, or with salts of organic phosphinic acids. The efficiency of dialkyl phosphinic acids as flame retardants in

polyamides has been improved by synergism with melamine polyphosphate (MPP), achieving UL94 V-0 in glass filled polyamides. The combination of diethyl aluminium phosphinate and MPP (AlPiM) allows the loading in PA 6.6 to be reduced from 30% (for AlPi alone) to around 15-20%, and still meet regulatory requirements, such as UL94 V-0 at thicknesses as low as 0.8 mm. Halogenated flame retardants have a significant share of the market in reinforced polyamide mouldings, although competition from commercially available mixtures of the aluminium salt of diethyl phosphinate with melamine polyphosphate is growing.
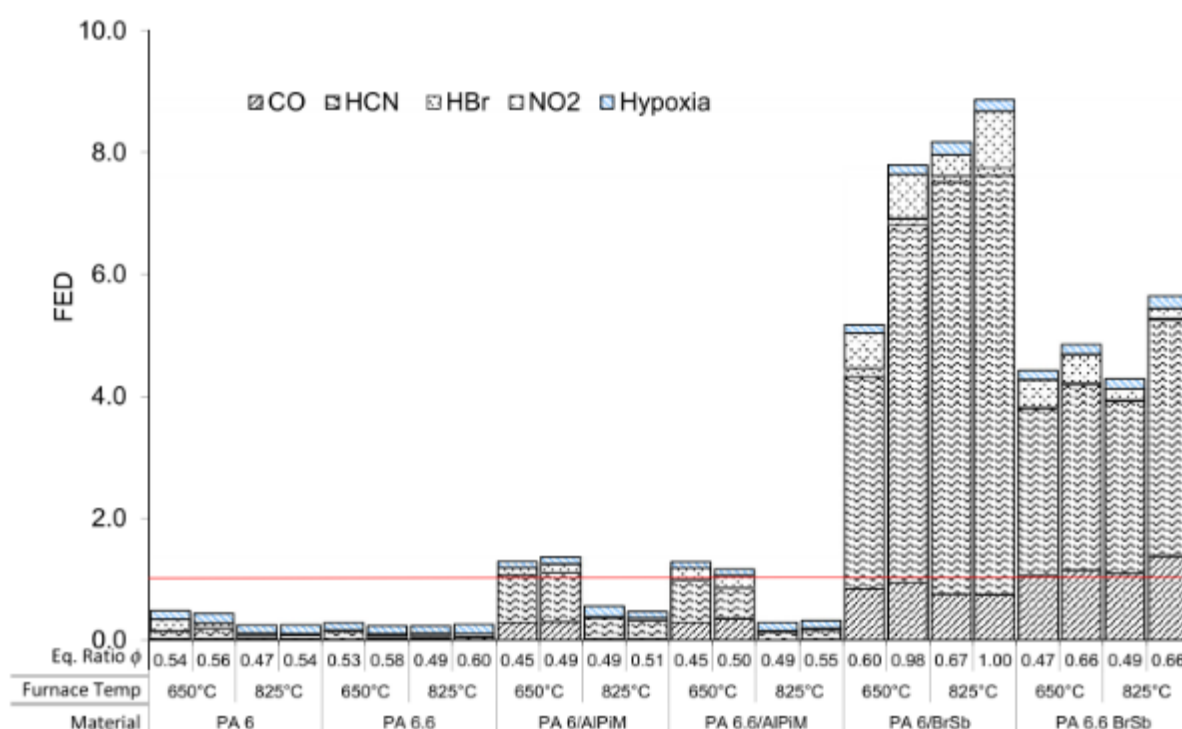
Figure 38 : Contributions to effluent toxicity from PA6 and PA6,6 based materials

Figure 38 shows how the individual yields may be translated into estimates of toxicity expressed as fractional effective dose (FED), (at an arbitrary loading of 1 kg of material in 50 m^3). Even at this high loading, many of the material/conditions show FEDs well below the critical value of 1 (representing lethality to 50% of the population during a 30 min exposure). The two exceptions are the materials containing AlPiM, when burning at the lower furnace temperature of 650°C, and the materials containing BrSb at both furnace temperatures. In each case, where the FEDs exceed one, the major contribution to the toxicity comes from hydrogen cyanide, with smaller contribution from carbon monoxide at about one fifth of the HCN level. There is also a minor contribution from NO_2 from all materials, in all fire conditions. It is notable that the fire toxicity of the PA 6/BrSb materials is a factor of 10 larger than that of PA 6 and a factor of 5 larger

than the AlPiM material at 650°C; at 825°C it is a factor of 30 larger than the PA 6, and 17 larger than the AlPiM material. The BrSb materials all show high fire toxicity under the normally least toxic, well-ventilated fire conditions. The lower fire toxicity of the AlPiM materials at higher temperatures suggest a reduction in fire hazard. It is well known that under more severe conditions than a small flame ignition test, flame retarded materials will burn, and frequently produce more toxic effluents as a result of quenching of the gas phase flame reactions. It appears that the AlPiM system switches off this flame quenching process as the fire becomes more severe, reducing the toxicity of the effluent. These estimates of toxicity can be expressed in terms of fire safe limits on combustible loadings in enclosures. The LC50 concept may also be applied to materials burning under specified conditions following the equation seen before.

Table 3

LC_{50} for each material and furnace temperature (the mass required to generate a lethal effluent in grams per cubic metre).

Sample	Furnace temperature/°C	
	650	825
PA 6	44	83
PA 6/AlPiM	15	40
PA 6/BrSb	3.3	2.4
PA 6.6	80	84
PA 6.6/AlPiM	16	66
PA 6.6/BrSb	4.3	4.1

Table 8 : LC50 for each material and furnace temperature (the mass required to generate a lethal effluent in grams per cubic metre).

Thus for the base polymers with glass fibre reinforcement, and for the four flame retarded samples, an LC50 may be calculated (Table 8).

The LC50 is inversely proportional to the toxicity (higher values indicate lower toxicity). If the mass of material equal to the LC50 is burnt in well-ventilated conditions, this would be fatal to 50% of the occupying population. Therefore, if a 1 kg fuse box made of glass reinforced polyamide 6, flame retarded to UL94 V-0 with brominated polystyrene and antimony oxide, was to burn completely in conditions corresponding to a small, well-ventilated fire (650°C) it would generate a volume of lethal effluent of 300 m^3 (for 30 min exposure), whereas if it were flame retarded with AlPiM it would only generate a volume of lethal effluent of 67 m^3 under the same conditions. Fire safety engineers would generally apply a safety margin, for example that the FED could

not exceed 0.3, to ensure that the fire effluent would not be lethal to the occupying population.

This work clearly shows that HCN is the major contributor to the toxicity for fire retarded PA materials, even in well-ventilated conditions, although the contribution from CO from the BrSb materials is also significant. It shows that when comparing two formulations of comparable flammability, the one with the flame retardant containing bromine and antimony causes a significant increase in the fire toxicity, compared to the material flame retarded by the aluminium phosphinate/melamine polyphosphate blend. It demonstrates, how hydrogen cyanide yields from aliphatic polyamides increase tenfold in the presence of a brominated flame retardant and antimony oxide, but only modestly, around twofold, in the presence of AlPiM. This has clear implications for fire safety: a fire of a 1 kg PA 6 fuse box flame retarded with the BrSb combination would produce a lethal effluent in a 10 m x 10 m x 3 m enclosure, where the same fuse box fire retarded with AlPiM would only produce a lethal volume of effluent for a 4.5 m x 5 m x 3 m enclosure. Thus while both fire retardant combinations reduce the risk of fire, if a fire does occur, the use of BrSb increases the hazard by increasing the fire toxicity much more than the AlPiM.

3.2.6- Baxter C. S. 2001 [13]

Inorganic materials can also act as toxicant suppressant, since it has already been demonstrated that the addition of copper compounds to flexible polyurethane foam significantly reduced the generation of hydrogen cyanide (HCN) as well as the toxicity of the combustion products when the foam was thermally decomposed. The experiments in this paper were designed to simulate the non-flaming and the flaming stages of a chair ignited by a cigarette (a two-phase heating system that simulates the fire scenario that results in the most fire deaths in the United States). Hydrogen cyanide concentrations in the thermal decomposition products from a flexible polyurethane foam were reduced approximately 85% when the foam was treated with Cu_2O. Regarding the use of melamine-treated foamed PU; small-scale tests indicated that a melamine-treated FPU generated six times more HCN than an equal amount of a non-melamine treated foam. The presence of Cu_2O reduced HCN from the melamine foam by 90%.

3.2.7- Wang, B. 2016 [61]

Zinc hydroxystannate (ZnHS) was employed to reduce toxicity and fire hazards of thermoplastic polyurethane (TPU) composites using ammonium polyphosphate (APP) as a flame retardant agent (Table 9). Smoke suppression properties and synergistic flame retardant effect of ZnHS on flame retardant TPU composites were intensively investigated by smoke density test, cone calorimeter test, and thermogravimetric analysis. Thermogravimetric analysis/infrared spectrometry and tube furnace were employed to evaluate the toxic gases (CO, NOx and HCN) of TPU formulations.

Sample	TPU	APP	ZHS	LOI	T1	T2	Dropping	UL-94
TPU	100			21.5	>30	–	Yes	NR
TPU1	85	15		26.5	3.2	4.5	No	V-0
TPU2	85	14.5	0.5	27.5	1.9	3.1	No	V-0
TPU3	85	14	1	28.5	1.0	1.2	No	V-0
TPU4	85	13.5	1.5	28.5	0.9	1.5	No	V-0
TPU5	85	13	2	28	1.3	1.8	No	V-0
TPU6	85	12	3	27.5	1.1	1.9	No	V-0

Table 9 : Formulations of flame retarded TPU composites
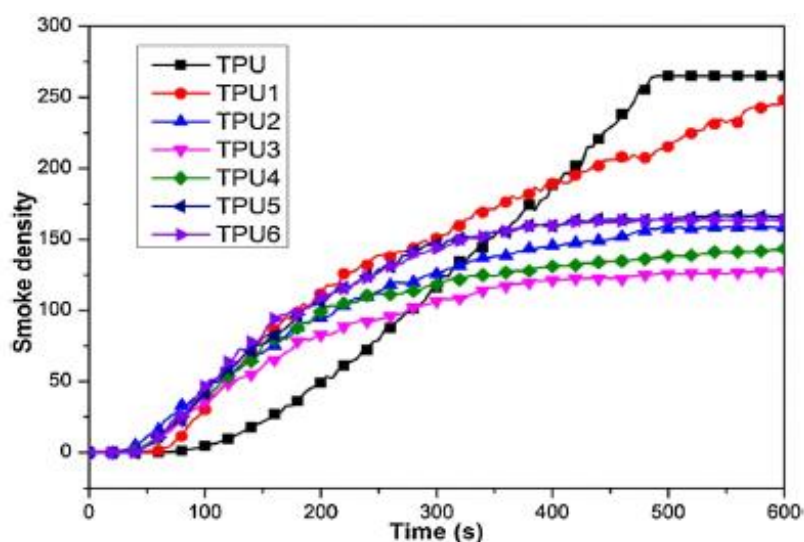
Graph 2 : Smoke density results of TPU composites tested at 25 kW/m² with pilot flame

It has been first found out (Graph 2) that there is a synergistic effect between ZnHS and APP in decreasing the smoke density of TPU with an optimal loading rate of 1 wt% of ZnHS. Actually, ZnHS can improve the structure of char residue for TPU composites. It reacts with polyphosphoric acid from the decomposition of APP thus generating

bridges which results in a stabilization of the char. This could reduce smoke in terms of particles and VOC and protect the TPU from the heat radiation.

Formulation	FR%		Product				Residue(%)
	APP%	ZHS%	CO_2(mg)	CO(mg)	NO_x(mg)	HCN(mg)	
TPU	0	0	2232.8	267.72	0.284	3.03	0
TPU1	15	0	1781.0	234.78	0.286	2.97	16.3
TPU2	14.5	0.5	1805.7	220.74	0.267	2.77	17.1
TPU3	14	1	1888.7	214.74	0.239	2.47	19.6
TPU4	13.5	1.5	1834.6	217.39	0.24	2.48	19.3
TPU5	13	2	1917.6	224.53	0.243	2.67	18.7
TPU6	12	3	2026.0	213.84	0.256	2.58	19.4

Table 10 : Quantitative analysis of gaseous products of degradation using tubular furnace at 600°C

Analysis of gaseous products of degradation at 600°C using the tubular furnace methode highlighted interesting trends (Table 10). Indeed, the introduction of APP (TPU1) inhibits the generation of CO while it has no effect on reducing NOx and HCN. Moreover, the addition of ZnHS in the formulations exhibits some positive effects on the reduction of the whole toxicants analyzed, especially regarding 1 to 1.5 wt% of ZnHS. As for smoke density reduction, this phenomenon can be explained by the enhanced charring effect of ZnHS leading to the generation of a protective shield slowing down the heat transfer and so the thermal decomposition. As a conclusion it is worth noting once again that the use of PIN FR helps reducing the opacity of the smoke and the formation of toxic gases in case of fire.

3.2.8- Gupta, R. C. 2011 [62]

Unlike all the other scientific publications presented in the frame of this work, the paper herein is focused on the neurogenic toxicity induced by phosphorus FR by putting into questions the rats and mice traditional model used and *N-Gas* calculation arising from it. The problem is whether, when materials containing these substances are decomposed thermally, they might produce neurotoxic phosphorus esters in significant quantities in the thermal decomposition product atmosphere. It has already been proposed that considerable toxicological problems may exist in the decomposition products of some flame retardants. This concern is not hypothetical, but there is very little information on the chemistry and toxicology of the decomposition products from the majority of other phosphorus-containing fire retardants.

Phosphorus-containing fire retardants are non-reactive (fabric furnishes, surface coatings and fillers in resin) or reactive, combining with polymeric structure during

processing. Figure 39 and Figure 40 show typical examples of phosphorus containing fire retardant.

Non-intumescent coatings:

Phosphonitrilic chloride
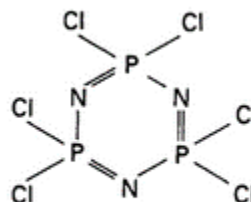
Intumescent coatings:

Ammonium polyphosphate
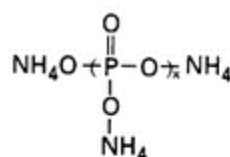
Bicyclic phosphate intermediate formed with pentaerythrotol
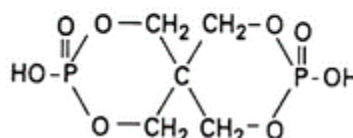
Figure 39 : Examples of phosphorus-containing additive fire retardants

Bis(2-chloroethyl) vinylphosphonate $CH_2=CH-P-(OCH_2CH_2Cl)_2$
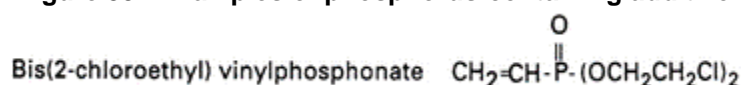
Figure 40 : Example of phosphorus containing reactive fire retardant used for copolymerization

These substances act in a number of different ways to impede combustion in both the solid and gas phases. The wide variety of chemical structures and reactions involved can therefore lead to a wide variety of phosphorus containing products. In some cases the phosphorus may remain largely in the char (in intumescent coatings for example), in which case the formation of phosphorus—containing volatiles may be low, while in other cases (where the major reactions are in the gas phase), it is possible that a variety of potentially toxic phosphorus-containing products may be formed. On the other hand, fire retardants reduce the efficiency of combustion, which can increase the yield of the normal toxic products. Also, the decomposing fire retardant may itself, or in combination with other fire products, form toxic organophosphates. As we know, acute combustion toxicity tests on rats and mice are not specifically designed to detect neurotoxicity, so that it may be missed among the general narcotic and irritant effects of combustion product atmospheres. Also, the problem of potential delayed neurotoxicity is not covered because the young rodents used in these tests are usually unaffected. While delayed neurotoxicity does occur in humans, chickens and cats.

The effects of pyrolytic and oxidative thermal decomposition on trialkyl phosphates (trimethyl (TMP) and triethyl (TEP)) and also a tryaryl phosphate (triphenyl (TPP)) were examined. All phosphorus was recovered as phosphoric acid (resulting from hydrolysis of phosphorus pentoxide), with small amounts of red phosphorus being formed under pyrolysis. Although the authors did not analyse for organophosphates, which might have been present in small amounts. The work established that phosphate esters are easily destroyed by heat to release inorganic phosphorus oxides and acid. The main expected toxic hazard would therefore be from the irritant effects of inhaled phosphorus pentoxide (1h LC_{50} of 1.217 mg/L) adding to the general irritant effects of the smoke. In these studies the phosphorus flame retardants compounds were decomposed alone. When fire retardants are added to materials the inorganic phosphate may be released to combine with other substances such as alcohols in the solid or vapour phase to form new phosphate esters, which may survive in the cooling smoke or char. An example of such a mechanism in the solid phase occurs in char formation in intumescent coatings containing ammonium polyphosphate and pentaerythritol [27]. The bicyclic phosphate (Figure 39) generated may be neurotoxic however when rats are exposed to the thermal decomposition products of lubricants containing pentaerythritol and tricresyl phosphate, no sign of neurotoxicity was observed.

Several combustion toxicology studies have been carried out to investigate the toxicological patterns of some fire retarded materials such as PU foam and polyester fibres and films. The general findings of these experiments is that by reducing the combustion efficiency, generally the yields of common toxic products is increased thus leading to greater toxic potency. However no evidence for unusual toxicity or exotic phosphorus containing products was brought.

3.2.9- *Babrauskas V. 1988* [52]

An extensive study was led by Babrauskas and al. to investigate to which extent the use of fire retardant products to manufacture building and furnishing materials gives a net safety benefit compared to the relatively unknown impact on the smoke toxicity. To that purpose, five representatives of commonly used plastic products were manufactured in non-fire retarded and fire retarded version:

- Polystyrene (PS) television cabinet
- Polyphenylene oxide (PPO) business machine housing
- Polyurethane (PU) foam-padded upholstered chair
- Electrical cable with polyethylene (PE) wire insulation and rubber jacketing
- Fiberglass reinforced polyester (FRP) electric circuit board

The test program covered bench-scale tests as well as large-scale tests (presented in section 2.4.5- Indirect assessment on large scale/ real fires) in order to gather every single significant data thus being able to draw detailed conclusions.

Regarding small-scale tests, cone calorimeter and NBS cup furnace combustion apparatus were performed. The first one to measure the rate of heat release, ignitability and rate of smoke production and the second one to assess the toxicity of gaseous effluents. The results showed that none of the test specimens produced smoke of extreme toxicity. Smoke given off from FR and NFR samples was similar in toxic potency and comparable to the smoke produced from common building materials.

Entire products were then tested in furniture calorimeter which allows the same measurements as cone calorimeter but at full-scale. That study generally confirmed the small-scale heat and toxicity results, especially the fraction accounted for by CO was very similar in both testing scales.

Finally, testing was carried out in a large-scale burn room/corridor facility where an arrangement of all the products picked up for the study (NFR and FR) had been used. The idea was to examine the impact of FR materials on the survivability of the building occupants, through two concepts:

1. Comparing the time to tenability in the burning room: judged by the time available to the occupants before the earlier of room flashover and/or untenability of toxic gas production occurs.
2. Comparing the total production of heat, toxic gases, and smoke from the fire.

The most interesting results were those from those full scale fire tests, which also helped to identify the importance of heat release rate as the most important physical variable in these tests which is a predictor of the fire hazard. Table 6 shows the most important results of the burns. During the first burn carried out with the flame retarded products under the same conditions as the non-flame retarded products (a single 50 kW burner) very little combustion took place. Thus, all successive tests with the flame retarded products also included an additional 120 kW burner, which allowed all the products to burn.

It has been then demonstrated for FR products that significantly enhanced fire performance can be obtained, in that:

1. The average available escape time was more than 15-fold greater for the FR products in the room burn tests.
2. The amount of material consumed in tests of the FR produce was less than half the loss in the NFR tests.
3. FR products, on the average, gave 1/4 the heat release of NFR products.

4. The total quantities of toxic gas, expressed as CO-equivalents released by the FR products was 1/3 of that for the NFR products.

5. The production of smoke was not significantly different in room fire tests between FR and NFR products.

Consequently, the FR additives did decrease the overall fire hazard compared to the neat materials. The same kind of trend than the other studies presented in this review is found out, since it can be concluded that the proper selection of fire retardants can improve fire and life safety. This is a clear indication that considerable improvements in toxicity are obtained by decreasing the heat release rate of the materials/products considered, almost irrespective of the actual toxic potency of the materials/ products involved. Thus, toxic hazard is a direct function of heat release rate, provided there has been proper flame retardancy.

Products	Peak temperature (°C)	Smoke toxicity (kg CO)	Tenability time in burn room (s)	Tenability time in target room (s)	CO yield (kg/kg)	Pk HRR (MW)
Non-FR	>600	21	110	200	0.22	1.59
Non-FR	>600	17	112	215	0.18	1.54
Non-FR	>600	16	116	226	0.14	1.79
FR 1B	185	2.6	NA	NA	0.22	0.22
FR	273	5.5	1939	NA	0.23	0.37
FR	285	6.1	2288	NA	0.23	0.35
FR	334	5.6	1140	1013	0.23	0.45

Peak temperature: maximum temperature in burn room;
Smoke toxicity: level of toxicity, calculated in equivalent mass of carbon monoxide;
Tenability time in room: time to reach untenable conditions in burn room or target room (via smoke toxicity or by having reached flashover, i.e. temperatures over 600°C);
CO yield: mass of carbon monoxide (CO) formed per mass of fuel burnt;
Pk HRR: maximum heat release rate in room; non-FR: non fire-retarded;
Non-FR: non-flame retarded products;
FR: flame retarded products; and
FR 1 B: flame retarded products tested without an auxiliary burner.

Table 11 : Effect of flame retardants on smoke toxicity

3.2.10- Hirschler, M.M. 2013 [32]

In contrast to the previous statement, in at least one other study no improvement in toxic hazard was found following the use of materials (upholstered furniture) containing flame retardants. An analysis of the materials involved indicates that the so-called flame retarded materials simply contained very low levels of flame retardants, insufficient to make a substantial difference to the heat release rate of the final product. Thus, no real improvement in fire performance occurred, resulting in no improvement in toxic hazard.

Material	Heat flux (kW/m²)	Non-FR Pk HRR (kW/m²)	FR Pk HRR (kW/m²)	NFR/FR ratio —	Test method —
ABS (+ FR1)	20	614	224	2.7	Cone
ABS (+ FR1)	40	944	402	2.3	Cone
ABS (+ FR1)	70	1311	409	3.2	Cone
ABS (+ FR2)	20	614	224	2.7	Cone
ABS (+ FR2)	40	944	291	3.2	Cone
ABS (+ FR2)	70	1311	419	3.1	Cone
EVA (Cross-linked)	30	463	110	4.2	Cone
EVA (Thermoplastic)	30	574	83	6.9	Cone
HDPE	30	1803	114	15.8	Cone
HDPE # 2	50	1167	476	2.5	Cone
LDPE	20	913	88	10.3	Cone
LDPE	40	1408	192	7.3	Cone
LDPE	70	2735	268	10.2	Cone
Polypropylene	30	1555	174	8.9	Cone
PVC rigid	20	102	25	4	Cone
PVC rigid	40	183	84	2.2	Cone
PVC rigid	70	190	93	2.1	Cone
PVC rigid # 2	30	98	42	2.3	Cone
PVC rigid # 3	30	118	56	2.1	Cone
PVC wire and cable	20	116	9	12.8	Cone
PVC wire and cable	40	167	64	2.6	Cone
PVC wire and cable	70	232	100	2.3	Cone
PVC wire and cable # 2	20	116	72	1.6	Cone
PVC wire and cable # 2	40	167	92	1.8	Cone
PVC wire and cable # 2	70	232	134	1.7	Cone
Particle board	25	151	66	2.3	OSU
Particle board B (+FR 1)	25	160	70	2.3	Cone
Particle board B (+FR 1)	50	227	141	1.6	Cone
Particle board B (+FR 2)	50	227	52	4.4	Cone
Plywood	25	114	43	2.7	Cone
Plywood	50	150	75	2	Cone
Polyester	30	186	95	2	Cone
Polystyrene	20	723	277	2.6	Cone
Polystyrene	40	1101	334	3.3	Cone
Polystyrene	70	1555	445	3.5	Cone

Cone: ASTM E1354 (Cone calorimeter) and
OSU: ASTM E906 (Ohio State University heat release rate calorimeter).

Table 12 : Comparison of heat release rate date for FR and non-FR materials

Table 12 is a compilation of a few of the data available wherein the same basic material was tested, using the same technique before and after the addition of flame retardants. The data indicate that, in fact, considerable improvements in rate of heat release are commonplace, including increases of over ten fold. The range of materials presented in the table is also very broad, including thermoplastics, cross-linked materials, thermosets, and cellulosics. This is crucial data, because it indicates that the effect of fire retardants can, indeed, lead to great improvements in smoke toxicity. In order to

understand its further implications with respect to smoke toxicity, it is essential to investigate toxic potency ranges for different materials.

The data above shows that fire hazard is primarily a function of the rate of heat release of the materials or products involved and the importance of heat release rate vastly exceeds that of smoke toxic potency. Heat release rate can be decreased by factors of 10 or more by using flame retardants. Therefore, adequate flame retardant considerably decreases fire hazard, by decreasing heat release rates and improving time to escape.

Note that all the analysis in this section has dealt with the immediate acute effects of smoke, which is always toxic. The key conclusion to be drawn from this analysis is that, in order to minimize smoke toxicity, it is essential to do everything possible to minimize fires and, failing that, to strive to lower heat release rate.

3.2.11- Austin, C. C. 2001 [37]

Along with the acute toxicity, one subject of interest related to smoke composition patterns of fires deals with the potential long term effect of repeated exposure to such exhaust fumes. It is easy to understand that this is of particular concern for firefighter, routinely exposed to fires and smoke given off. As already discussed carcinogenic chemicals which could be responsible for such long term toxicity represent a broader family than acute toxic gases, called Volatile Organic Compounds (VOC). This means that investigations performed to measure those VOC are different from the previous discussed studies, involving mainly sampling during real fires and generally by firefighters themselves.

The objective of this study was to characterize volatile organic compounds (VOCs) found at 9 municipal structural fires in order to identify sources of long-term health risks to firefighters, which may be contributing factors in heart disease and cancer. It sounds quite logical to assume that firefighters are exposed to several different substances from one fire to another. However, similarity in the nature of the combustion products from a variety of sources, demonstrated by the characteristic prevalence of benzene, toluene, and naphthalene found in air at experimental fires, suggested that similar patterns might be found in municipal structural fires (Austin et al., 2001a). Although it is true that fires emit a myriad of combustion products, the same predominant substances (benzene, toluene, 1,3-butadiene, naphthalene, and styrene) were prevalent also at municipal structural fires. Similar "fingerprints" of the same 14 substances identified at fires burning various solid combustible materials were also found at municipal structural fires, accounting for 76.8% of the total VOCs measured.

Five of them (benzene, toluene, 1,3-butadiene, naphthalene, and styrene) account for 31.1% of the total VOC concentrations. Benzene and 1,3 butadiene are known human carcinogens (Group 1) with OSHA established 15 minute short term exposure limit values of 5 ppm while toluene, naphthalene, and styrene are possible human carcinogens (Group 2B) with respective OSHA 8 hour time weighted average values of 200 ppm, 10 ppm, and 100 ppm.

Although it could be argued that the positive associations between firefighting and certain forms of cancer identified in these studies are not relevant since modern firefighter use today self-contained breathing apparatus (SCBA), it should also be considered that in previous decades, firefighters did not wear respiratory protection. Moreover, the samples were taken at times during which the firefighters thought that some co-workers might remove their SCBA masks. It is not clear, then, to what extent their true exposures are different particularly in view of the fact that firefighters today do not, in fact, wear their SCBAs all of the time.

It has also been suggested that modern-day building materials (polymers) might give rise to new supertoxicants, either during the phase of rapid combustion (knockdown) or during the smouldering conditions following extinction of the fire (overhaul). Neither this study of municipal structural fires, nor the previous one by Austin et al. (2001a) of experimental fires burning various combustible materials, found any such new toxic nonpolar VOCs that would have not been present in the past. The results of the present study also suggest that the lower combustion temperatures characteristic of the latter stages of a fire do not result in higher levels of toxic combustion products. Furthermore, the spectra of combustion products were similar at mixed-occupancy, municipal structural fires, an electronics industry fire and, a 9-d smouldering fire. The presence and concentration of contaminants, such as benzene, styrene, and 1,3-butadiene having known long-term effects may not have been less in previous decades (where wood, cotton, and wool were predominant in the fire surroundings) than in modern fires where there is a prevalence of polymers. Those VOCs likely to be responsible for many of the long term toxic effects of smoke do not appear to be new, they appear to be relatively few in number, their levels are considerably higher than the remaining numerous combustion products, and they appear also in the combustion of wood, a traditional building material. Given the toxicity/carcinogenicity of those VOCs that were found in the highest concentrations, particularly benzene, 1,3-butadiene, and styrene, investigation of time-integrated personal exposures of firefighters to VOCs is warranted.

3.2.12- Hewitt, F. 2016 [53]

In line with the previous study, qualitative results are presented from analysis of volatile and semi-volatile organic compounds (VOCs/SVOCs) obtained through sampling of gaseous effluent and condensed particulates during a series of experimental house fires conducted in a real house[53]. The fire source was initially either cooking oil or a sofa, burnt both alone and in a furnished environment in different ventilation conditions. Phosphorus based compounds including flame retardant have been detected notably in the gaseous effluents from sofa and other upholstered furniture. It was also shown that those FR were volatilised in their original form. However no quantitative analysis has been carried out; consequently it is impossible to evaluate to which extent the exposition to those VOC could exacerbate the acute toxicity of the fire or any delayed effect. PAHs and particulates have also been examined, this will be dealt in the next part.

4- Soot/PAHs/Dioxins/Furans toxicity studies

4.1- Toxicity without FR

Several studies have been led to assess the composition of soot and the quantity of it during the combustion of common material used in the building sector. Analysis have been performed at small scale (analytical methods: cone calorimeter or steady-state tube furnace) and on real fires after the extinguishment by firefighters. This part of this report relates the conclusions of 6 relevant and concrete studies.

4.1.1- Reisen, F. 2014 [67]

A series of experimental small-scale fire tests using a cone calorimeter were conducted by F. Reisen & al[67]. The objective of the tests was to provide a comparative assessment of particle and volatile organic compound emissions from the combustion of 10 commonly used types of building and furnishing materials relative to radiate pine, a dominant construction material. The materials tested included wood-based products (particle board, particle board with melamine surface finishes, medium-density fibreboard, painted pine), wool/nylon carpet, polyester insulation, two types of polyurethane (PUR) foams, high density polystyrene with cladding material and plasterboard.

Materials	Thickness (mm)	Weight (g)	Elemental composition (%)[a]						
			C	H	O	N	S	Cl	Ash
Radiata Pine	20	123.5 ± 1.7	53	6	41			0.02	0.18
Painted pine (100% acrylic self priming exterior white paint)	20	127.8 ± 2.6	51	6	40	0.01	0.01	0.01	4.1
Particle board (PB)	16	104.7 ± 2.0	50	6	41	2.6	0.04	0.01	0.34
Particle board w/ melamine	16	108.7 ± 3.6	50	6	41	2.6	0.03	0.01	1.0
Medium density fibreboard (MDF)	15	111.5 ± 1.6	50	6	40	3.8	0.01	0.02	0.31
Carpet (wool/nylon blend)	12	18.6 ± 0.7	50	7	19	5.4	0.17	0.01	19.2
Polyester insulation	35–40	6.2 ± 1.3	62	4	33		0.02	0.02	0.37
PUR foam 23/130	30	4.9 ± 0.1	62	8	22	6.7	0.02	0.08	1.8
PUR Foam 36/130 CM[b]	30–32	11.0 ± 0.3	56	8	29	3.6	0.02	0.05	3.2
Polystyrene (high density) with cladding	30	35.0 ± 0.9	91	8	0.7	0.3	0.10	0.07	0.17
Plasterboard	10	67.6 ± 0.5	4	0.1	< 5		19	0.02	91

Table 14: Elemental composition of materials tested in the experimental burns

Tests were run at two irradiance levels with a cone calorimeter apparatus, 25kW/m^2 and 50kW/m^2 under well-ventilated conditions. Samples were collected for analysis of gravimetric mass, particulate organic and elemental carbon, polycyclic aromatic hydrocarbons (PAHs), carbonyls and volatile organic compounds along with continuous measurements of carbon monoxide (CO), carbon dioxide (CO2) and fine particles (PM2.5).
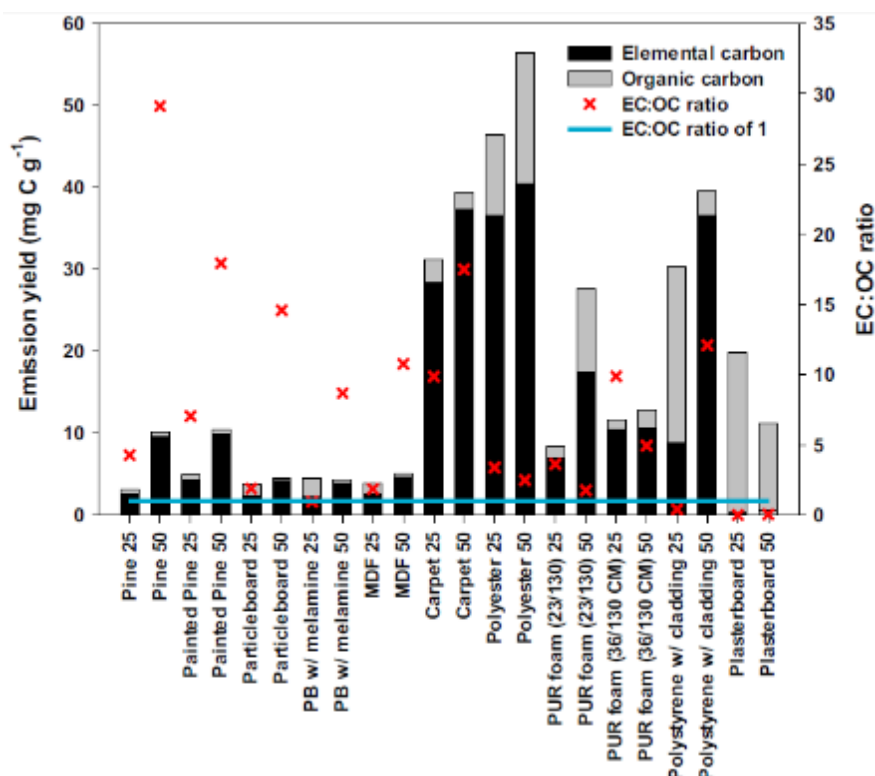
Figure 41: Elemental and organic carbon emitted during combustion of materials at irradiance levels of 25kW/m² and 50kW/m²

Sedimentation, diffusion and thermophoresis are the main processes that can lead to losses of particle concentration during transport. The transport efficiency for gravitational deposition was calculated to be 0.92, 0.98 and 1.0 for particle sizes of 2.5, 1.0 and 0.1µm respectively. No particle losses by diffusion were observed for particles larger than 0.01µm. For particles smaller than 0.01µm, the transport efficiency with diffusive particle loss decreased to 0.92. No particle loss due to thermophoretic deposition was observed in the exhaust duct. Potential particle losses of up to 25% may have occurred for submicron particles in the sampling line which had a temperature gradient of approximately 300K. Particle losses were minimised by the short residence time (<1 s). At 25 kW/m² highest particle emission yields were measured for polyester and polystyrene, both materials emitting about 20 times more particles compared to pine. This is likely linked to the aromatic rings in their structure which has been shown to increase particle production. Wood-based products had the lowest PM$_{2.5}$ yields ranging from 3.2 to 4.0 g/kg, with no statistically significant differences between the various wood-based materials. These emission yields were similar to those measured in a previous study. Particle emission yields from the combustion of carpet and plasterboard were approximately 10 times higher than those measured for wood-based products. At 50 kW/m², PM emission yields from the

combustion of wood-based materials were 1.2 to 3.6 times higher, with a more significant increase observed for pine compared to manufactured wood products. No significant increases in PM emission yields were observed for carpet, polyester, polystyrene and combustion modified PUR foam. The elemental and organic carbon composition of particles is shown in Fig41. Wood-based materials had the lowest carbon emission yields (3–5 g C/kg), while polyester, carpet and polystyrene had the highest carbon emission yields (30–62 g C/kg). Most of the particle mass (>70%) was carbonaceous. In general there was a larger fraction of EC compared to OC, with the exception of plasterboard and polystyrene where we observed a significant OC fraction (70–98%). At 50kW/m^2, the EC fraction was significantly higher than the OC fraction, except for polyester. We also observed some significant differences between the wood-based materials. At 25kW/m^2, pine had an EC:OC ratio of approximately 4, while both particle board and MDF had a lower EC:OC ratio of approximately 2.The differences are likely due to the presence of glues and resins in manufactured wood products, which increases the organic fraction of particles. Adding melamine reduced the EC:OC ratio to approximately 1. While in the small-scale tests in this study EC dominates, studies on residential wood combustion and biomass burning emissions have shown a larger contribution of OC compared to EC. For combustion of pine in residential wood heaters EC to OC ratios varied from 0.025 to 0.25, while EC to OC ratios measured during emissions of biomass burning ranged from 0.06 to 0.29. The higher EC:OC ratios measured in this study were attributed to the higher temperatures of a flaming combustion which is known to produce more EC. Under the tested conditions of flaming combustion of 11 materials, the highest pollutant concentrations per mass of specimen burnt resulted from the combustion of polyester insulation, polystyrene with cladding material, PUR foam and a wool/nylon carpet. Among wood-based materials, medium-density fibre board and particle board with melamine surface ranked highest in emissions, with pine ranking lowest. However, wood-based products make up the majority of mass in building structures so that emissions from wood-based products may contribute more significantly to total emissions and hence to exposures than emissions from the polymeric materials.

4.1.2- Hertzberg, T [24]

A second study led by SP Institute (Swedish National Testing and Research Institute) has allowed assessing the capacity of generation of particles from the combustion of 24 different building materials or products. The main aim of this project has been to obtain a picture of the potential capacity for particle generation from different materials

commonly found in buildings. Additionally, some cable materials have been tested in the small-scale experimental set-up since they are an important part of the overall fire hazard in buildings. A piece of upholstered furniture (a sofa) was tested in the room-corner test to get an idea of particle levels in a full-scale fire, and a composite material (laminates of carbon fibre and vinyl ester resin) were tested in various fire scenarios. The main reason for including the latter material was to investigate if asbestos-like fibres could be generated from burning this material. In Table 15 the products used in this series of tests are listed.

Material	Comment	usage
Glass fibre	insulation wool	building insulation
Mineral fibre	insulation wool	building insulation
Wood	Deal board	building construction
Bitumen	waterproofing membrane	building construction
Polystyrene	expanded polystyrene (EPS)	packaging, insulation, etc
Nitrile rubber	insulating material	tubing insulation
PVC	flooring material	surface lining
Fluoropolymer	pure pellet material	cable base material
Polyethylene	halogen free, fire retarded pellets	cable base material
FR4 laminate	brominated laminate	printed circuit board base material
Melamine	laminate	building construction
Wool	92 % wool, 8 % polyamide	lining, clothes
Particle board	laminate	building base material
PUR	flexible foam	furniture upholstering
PUR	rigid foam	building insulation
PIR	rigid foam- polyisocyanurate (modified PUR)	building insulation
Plywood	laminate	room surface lining
Carbon fibre laminate	composite material, small and intermediate scale experiments	high performance vehicles, airplanes, etc
Cable products:		
Polyethylene cable	halogen free, fire retarded cable	data cable
PVC cable	fire retarded cable	data cable
Fluoropolymer cable	high performance cable	data cable
PVC+fluoropolymer cables	50% of each material	data cable
Optical cable	uses urethane acrylate based polymer	optical signal transport
Real-scale products:		
Sofa	PUR upholstering; full scale experiment	furniture
Mattress	PUR; large scale experiment	furniture

Table 15: Materials and products investigated within the test program

The amount of particles were obtained using a DEKATI low pressure impactor that collects particles in the size range of 30 nm to 10 μm. A sub-flow of the smoke gases was led to the impactor from the horizontal duct of the Cone calorimeter at a position 61.5 cm from the centre of the sample. This sub-flow had a flow rate of 10 l.min^{-1}, which together with the 10 mm diameter nozzle of the sampling probe (positioned in the centre of the duct and pointed in the direction towards the gas stream) resulted in iso-kinetic sampling conditions. The low pressure impactor measures airborne particles, size distribution in the size range 0.03 – 10 μm, with 13 channels by the means of pre-

weighed impactor plates. Airborne particles are size classified according to their aerodynamic diameter in the cascade low pressure impactor. The sampled mass distribution within the 13 size ranges was determined gravimetrically after each test. The gravimetric determination was made using a calibrated analytical balance with a mass error less than 4 µg. The impactor plates were stored in a desiccator before weighing.

The particles were collected using a low-pressure impactor where the amount of material is obtained gravimetrically. In Figure 42 the mass distribution of particles obtained in all experiments is shown.

mass size distribution
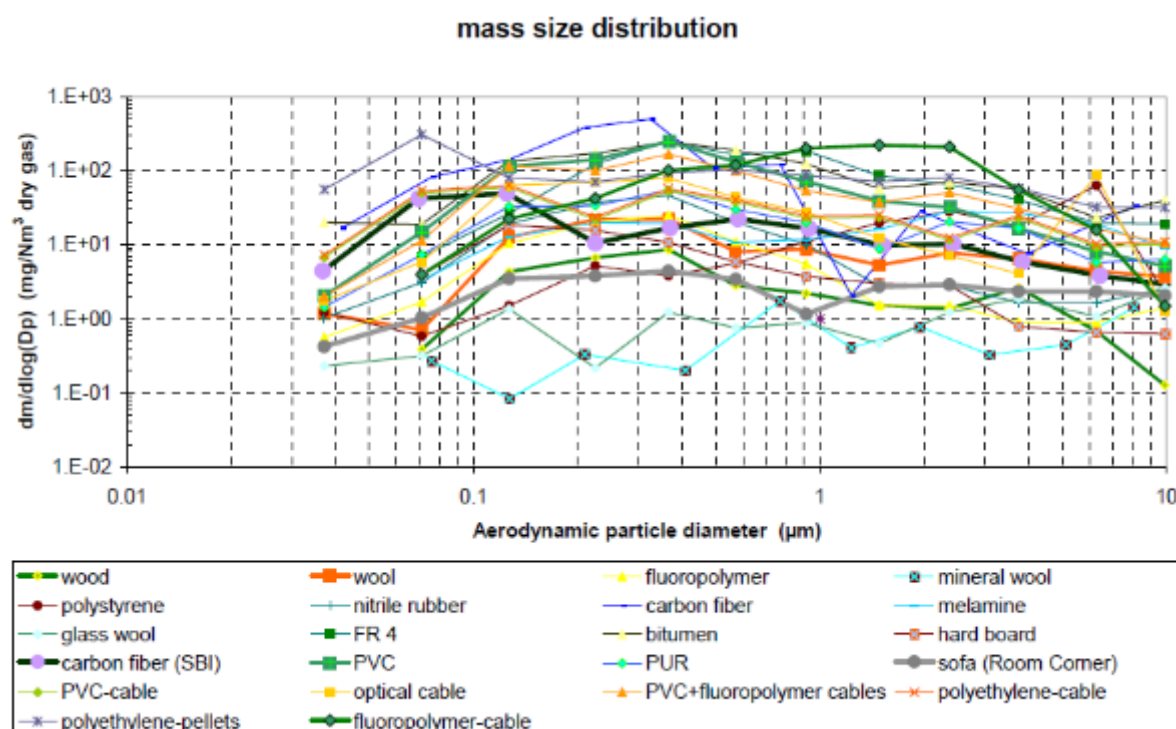
Figure 42: Particulate mass size distributions; logarithmic axes

All cone calorimeter experiments, except when the carbon fibre material was used, were based on the ISO 5660-1 standard. When the carbon fibre laminate was tested, the samples were submitted to a reduced oxygen content (16%) in order to obtain vitiated pyrolysis conditions. This should, in theory, produce higher amounts of soot than a well-ventilated scenario. Figure 42 resolved into four different mass concentration classes and it can be observed that the highest particle concentration is indeed obtained for the carbon fibre experiment. However, the high carbon content of the laminate in itself indicates the possibility of a high soot and particle production even with a normal oxygen atmosphere present. This is also seen from the SBI carbon fibre experiment (Figure 42). Bitumen is another 'efficient' particle producer with high carbon/asphalt content that also belongs to the 'top' group. The rest of this group

consists of flame retarded material (Polyethylene, PVC, FR4) or samples that mainly were pyrolyzed in the Cone calorimeter test (fluoropolymer based cable), i.e. no ignition took place.

To get a picture on the number of particles obtained in Figure 42, an assumed density must be used together with the assumed particle shape. Using the density on which the aerodynamic particle diameter is based ($1g/cm^3$) and assuming sphericity of the particles, the number-mapping of the mass distributions shown in Figure 42 is given by Figure 43.
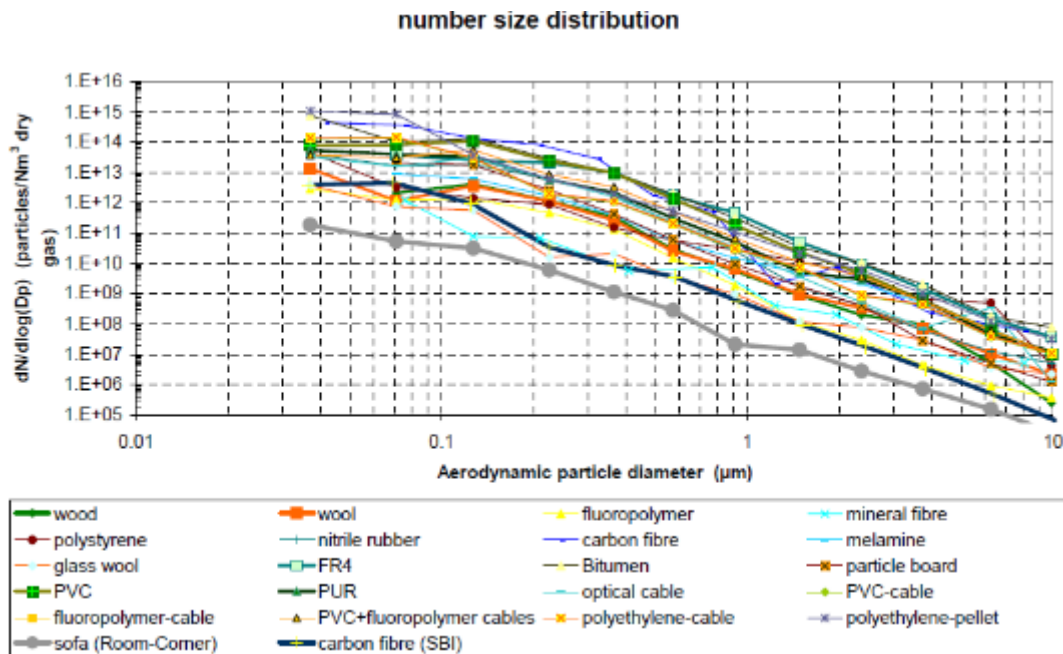
Figure 43: Number size distribution obtained by 'mapping' of particulate mass measurements.

Obviously, the density will vary depending on the particulate material but also depending on the particle size since the size relates to the shape. The smaller particles are more likely to be spherical while the larger ones might be very irregular as they often consist of an agglomeration of smaller particles. A correct density is therefore in reality not easily found for the entire spectrum of particle sizes. However, even if the real densities were several tens of percent different from the assumed value, the number distributions shown in Figure 43 would still be a relevant measure of the quantity of particles generated, as the main cause for the large number concentration is related to the smallness of the particles and not so much to their densities.

Another way to visualize the potency for particle generation from different materials, is to calculate the particulate 'yield', i.e. to relate the mass of the particulate phase in the smoke plume to the total mass loss of the experimental sample. The results from such relations are shown in Figure 44.

Particulate yield in Cone calorimeter tests
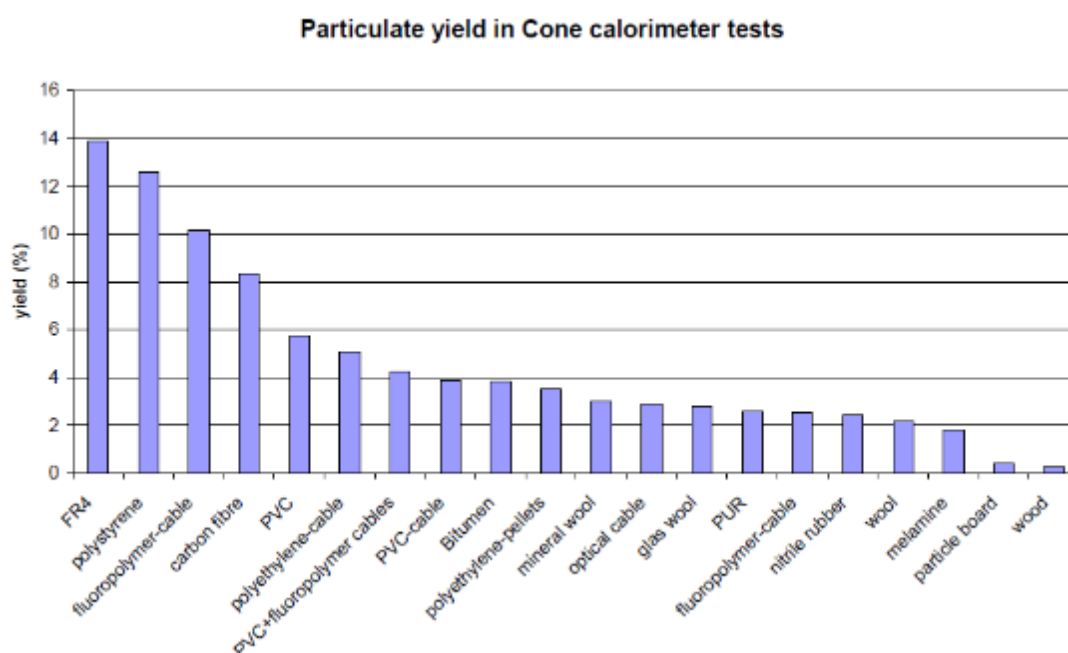
Figure 44: Yield obtained from Impactor and sample mass loss measurements

Total particulate mass in the cone calorimeter exhaust duct is calculated based on the impactor mass measurement and the measured sample weight loss during the experiment. It can be seen when comparing to other investigations that the yields shown in Figure 44 are of the same order of magnitude as the reported ones. The polyethylene ('Casico') material has previously been reported to provide ~3% particulate yield in the cone calorimeter (3.5% in Figure 44) and the yield for wood given in Figure 44, ~0.25%, might be compared to the amount reported for particulate material exhausted from an open fire place, ~0.6-1.6 % (the min/max depends on the wood-type). It is reasonable that burning of a dry ideal piece of wood under well-ventilated conditions in a cone calorimeter may provide somewhat better burning conditions, i.e. somewhat less particulate yield than would an open fire place.

Maximum particulate yield is obtained for the materials that do not burn well because of flame retardants. The polystyrene used is an exception to this as it is not flame retarded but did produce a large amount of particulate material. This is due to the presence of the styrene molecule (an aromatic species) in the polymer backbone. When polystyrene pyrolysis large amounts of aromatic molecules are produced providing the building blocks for soot formation and the basis for particle formation. Lowest yields are obtained for the materials that burn well, such as wood and particle board.

4.1.3- Savolainen, H. 1997 [68]

Another paper sums up and compares the effects of smoke from insulating materials such as mineral fibres, rigid polyurethane, polystyrene and cellulose fibres.

EFFECTS OF SMOKE FROM TECHNICAL MINERAL FIBRES

Contamination of air with mineral fibres occurs in case of fire in buildings where the technical products have been used as construction material. Glass and rock wool fibres melt in the temperature range of 1,000 to 1,500°C so that in high-temperature fires they begin to lose their fibrous structure. Otherwise, the uptake of the fibres by the lungs follows the same rules as for fibres released in the air by other means. In the fire situation, the mineral fibres are included in analysis of the particulate fraction (Table 16) whereas systematic studies for fibre counts in house fires have not been published in the literature. The possibility of inhalation exposure to mineral fibres occurs after the fire in the demolition or rebuilding of the remains.

Contaminant	Concentration (ppm)		IDLH (ppm)
	Mean	Maximum	
Acrolein	1.9	98	5
Benzene	4.7 - 56	250	3,000
CO	246-1,450	27,000	1,500
HC1	0.8-13	280	100
HCN	0.14-5.0	75	50
NO_2	0.04-0.7	9.5	50
SO_2	23	42	100
Particulates*	232	15,000	n.a.

*Particulates are given as mg/m3. IDLH stands for a concentration defined as "immediately dangerous for life and health". Data taken from Burgess and Crutchfield (1995). n.a. = not available.

Table 16: Common combustion product concentrations in residential fires

As mineral fibres do not burn, the toxicity of off-gases from the technical products results most probably from binders, covers or vapour barriers (Table 17). Thus, the use of layers of fibrous minerals rather limits than adds to the toxicity of fire smoke as calculated by dose or by exposure time (Table 17). It seems that e.g. the glass wool can be classified as one the safest construction materials in this respect.

Material	LC_{50} (g)	LT_{50} (min)	CO (%)	HCN (ppm)	Remarks
EPS	5.8	11	1.95	--	Fluorocarbon blown, no flame retardant
PUR	7.5	17	1.20	130	
Cellulose	11.5	21	4.0	--	Blown fibres for insulation
Glass fibres	35.7	25	n.a.	--	4.4 cm building insulation pane with paper and vapour barrier

Table 17: Common combustion product concentrations in residential fires

LC50 indicates the amount of material to cause smoke concentration that is fatal to 50% of rats when burnt at 822°C. LT50 shows the time until death of the rats under same conditions. 1% equals to 10,000 ppm (part per million, vol./vol.). EPS denotes to expanded polystyrene and PUR stands for rigid polyurethane. Addition of a flame retardant prolongs the LT50 for EPS and PUR.

EFFECTS OF SMOKE FROM RIGID POLYURETHANE

Rigid polyurethane begins to degrade already at 250°C. The degradation products include the isocyanate monomer (MDI, or methylene diphenyl isocyanate), the corresponding amine (MDA, or methylene dianiline), CO and HCN. The release of CO and cyanide is degradation temperature-dependent. The co-exposure to HCN and CO show synergistic rather than additive effect in the toxicity of the smoke in a rat model. If the experimental polyurethane samples were proofed with flame retardants, the toxicity of smoke was slightly diminished or remained unchanged. The fire smoke from rigid polyurethane contains much aerosol. Most of this is liquid droplets which contain remaining polyols and most likely short oligomeric chains of the original polymer. Accidental exposure to pyrolysis products from rigid polyurethane has caused respiratory irritation and fever and constrictive pulmonary disease. Mice experimentally exposed to smoke from polyurethane showed extensive changes in the lung surfactant metabolism;

As only polyurethane of the examined construction materials released HCN (Table 17) it is probable that it and other nitrogen-containing polymers have caused the HCN concentrations in the fire atmospheres (Table 16) and sometimes fatal cyanide doses in fire victims. It should be remembered in this context that almost invariably the victims have also been exposed to CO and have an important amount of soot in the lungs. This necessitates special treatment facilities and strategies. Long-lasting branchial hyperactivity may result from exposure to fire smoke.

EFFECTS OF SMOKE FROM POLYSTYRENE

Thermal degradation of polystyrene causes temperature dependent emission of CO and aerosol. Free styrene and benzaldehyde are also released. The aerosol contains e. g. oligomeric polystyrene chains. Styrene is moderately neurotoxic in animal models. The off-gases of thermally degraded polystyrene caused a decrease of isolated liver cell glutathione content in an in vitro experiment. Based on this, it is probable that the most important aspect of polystyrene smoke toxicity is its aerosol and CO content. Burning polystyrene causes a dense black smoke which impairs visibility and may

hinder rescue work. The health effects of smoke particles from polystyrene are not known to the detail while in a comparative study they were assessed to be less harmful than smoke from wood, cork, leather or rubber. The toxicity of polystyrene smoke is most clearly associated with the concomitant CO exposure. The authors raise also the question as to the potentiation of CO effects by a simultaneous co-exposure to CO_2. A synergistic toxic effect has been shown also in earlier independent studies. One of the mechanisms seems to include changes in the haemoglobin oxygen-binding capacity. In conclusion, the fire smoke toxicity from polystyrene seems mainly to be determined by the CO given out from the material. Its toxicity in terms of the smoke lethality is comparable to that of polyurethane (Table 17).

EFFECTS OF SMOKE FROM CELLULOSE FIBERS

Cellulose is a polysaccharide and therefore its oxygen content is higher than of that of polyurethane or of polystyrene. The cellulose polymer begins to decompose at 250°C. The initial products include various glucose and furan products with further formation of acrolein and other respiratory irritants. Acrolein is very toxic to lungs. The furans are also toxic, and a model furan derivative, furfural alcohol, shows dose dependent neurotoxicity in an inhalation exposure model. There are no data on the roles of toxicity of furan derivatives in the fire victims. The aerosol of the cellulose smoke contains free oxygen related radical species. Depending on their stability, they probably add to the toxicity of soot particles deposited in the lung. This might provide one of the synergistic toxicological mechanisms for the interaction of acrolein and carbon particles. The flame retardants in the cellulose decrease the yield of smoke CO content in a dose-dependent fashion. Whether they also facilitate the extinguishing of smouldering cellulose fire remains an open question.

Of the evaluated materials, the mineral fibres show less toxicity in case of fire than the other polymers. As mineral fibres do not burn the toxic smoke yield from the burning technical construction materials comes from resin, vapour barriers and covers attached. As to the other evaluated materials their fire smoke toxicity is grossly comparable to each other, while the mechanisms and proximal toxicants vary very considerably.

4.1.4- Stec, A.A. 2014 [20]

Another commercial material that has been investigated is PVC carpet, commonly found in domestic buildings. The PVC carpet had a thickness of 2.0 mm, and contained almost as much plasticizer and mineral fillers as PVC polymer. The contribution of carbon monoxide and hydrogen chloride to FED is shown in Figure 45. For all fire conditions, HCl makes the greatest contribution to the toxicity. In common with the other halogenated materials investigated, increased yields for CO are observed. The HCl yields found from well-ventilated and under-ventilated combustion were close to the theoretical maximum. This supports an earlier study where the HCl yields are independent of fire stages and temperature effects.
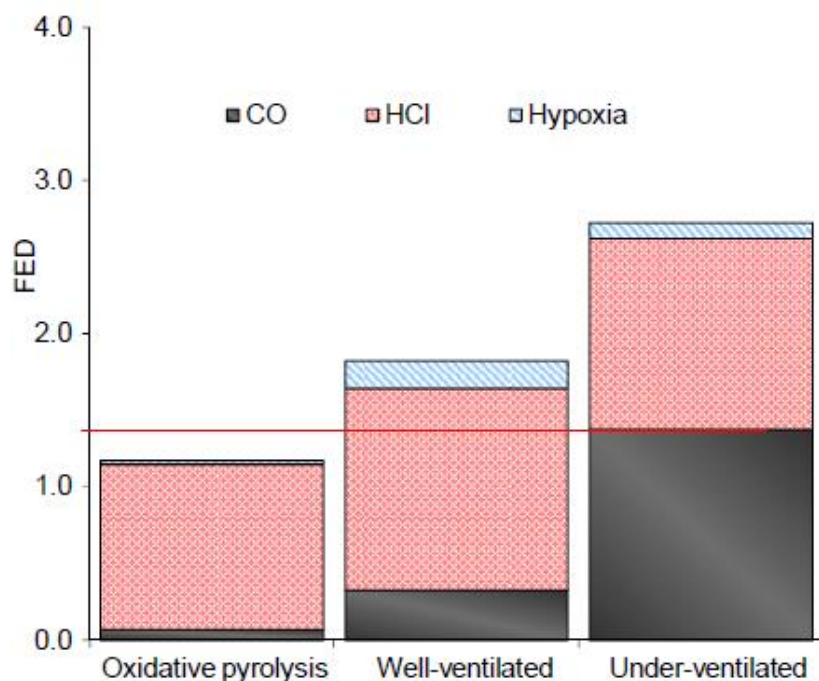

Figure 45: Contributions to Fractional effective dose (FED) for polyvinyl chloride (PVC) carpet

The PVC carpet was subjected to an in-depth study to look for other noxious substances in addition to the eight standard ISO fire gases. It was found that in well-ventilated and under-ventilated tests on PVC carpet both large and small particles are generated (of the order of 1e4 mm), whereas in oxidative pyrolysis, only a narrow distribution of large particle sizes was found. Compared to well-ventilated tests, greater quantities of smaller, more dangerous particle sizes were found for the under-ventilated fire scenario. As small particles have a higher proportion of surface area per mass than do larger particles, it is possible that more toxic substances may be adsorbed onto smaller particles.

Although some chlorine will always appear as HCl, other chlorine containing gas or vapour species will be produced while, in some formulations, some chlorine may remain in the residue. A number of chlorine-containing species have been identified from large-scale fires burning a high proportion of PVC, including monochlorobenzene and dichlorobenzene and other chloroaromatic and chloroaliphatic hydrocarbons. Evidence exists to show that, depending on the fire situation, as much as 20% of the chlorine may exist in an organic form. It was also found that the amount of chlorine from HCl could be very high in soot, even though the major part of the HCl produced was shown to be present in the gas phase. In this case, for the PVC carpet, it is reported that the chlorine content adsorbed on the soot was in the range between 0.5 and 2.5 wt%, while in non-flaming fire conditions around approximately 18-20 wt% of chlorine is present in residue, compared to 10 wt% for flaming conditions which favour polychlorodibenzo-furan and dioxin formation. These highly toxic materials are usually qualified by their toxic equivalence to 2,3,7,8-tetrachlorodibenzodioxin as toxic equivalency (TEQ). Total amounts of PCDD/F in the residue from PVC carpet shown in Figure 46 varies for different fire scenarios between 11 and 394 pg International toxic equivalents per gram (ITEQ/g) of burned material, corresponding to 41-1170 pg ITEQ/g residue.
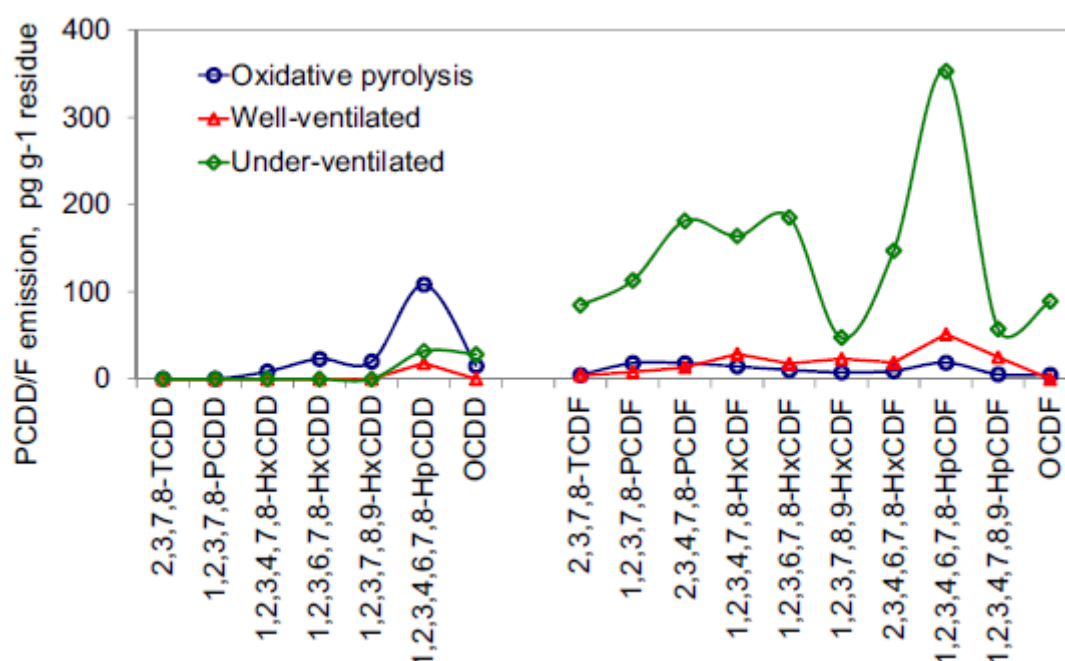
Figure 46: Concentration of polychloro- and polybromo-dibenzo-dioxins and furans (PCDD/F) in polyvinyl chloride (PVC) carpet residues under different fire conditions.

From the studies, it is interesting to note that both well-ventilated and under-ventilated combustion of the PVC carpet produced the complete range of PAHs. In the pyrolysis tests, however, only volatile and semi-volatile PAHs were produced. For both well-ventilated and under-ventilated conditions, the toxicity weighted yields for the associated particle PAHs increased and generally dominated over the volatile species. The toxicity weighted yields for the under-ventilated tests were orders of magnitude higher than the yields from the well-ventilated tests, whereas for oxidative pyrolysis conditions, it is observed that the volatile part dominated the toxicity.

4.1.5- Wobst, M. 1999[69]

A another realistic study was led by M. Wobst & al to determine the surface contaminations with polycyclic aromatic sulphur heterocycles (PASH), as representatives of a substance class, not investigated in this context, by now, polycyclic aromatic hydrocarbons (PAH) and polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F). Surface samples were taken from two private residences after real fire accidents.

Fire 1 occurred in the kitchen of a flat, causing a damage of 17,000 US-Dollars. The oxygen supply in the 10 m 2 kitchen was comparatively low. The share of plastics in the fire load was small and the degree of destruction of the inventory was low. In this configuration, the quantities of PASH, PAH and PCDD/F assessed by the GC/MS analytical method are the following:

samples from:	Σ PASH[1] $[\mu g/m^2]$	Σ PAH (EPA) $[\mu g/m^2]$	Σ PCDD/F $[ng/m^2]$
1.1 door frame (top)	27.1	4,430	605
1.2 refrigerator side wall	3.1	326	49.1
1.3 window pane	1.7	34	4.4
1.4 window pane	1.7	44	106
1.5 ceiling	4.0	96	162
1.6 wallpaper	8.9	5,060	1,300
1.7 door frame (side)	28.7	4,690	550

Table 18: Surface contaminations with PASH, PAH and PCDD/F after the first fire accident

Fire 2 resulted in a complete destruction of a flat, causing a damage of 170,000 US-Dollars. Because of broken windows the oxygen supply was sufficient, so that high temperatures up to 1,000 °C could be achieved. The inventory of the apartment, containing an average share of plastics, was almost completely destroyed. In this configuration, the quantities of PASH, PAH and PCDD/F assessed also by the GC/MS analytical method are the following:

samples from:	Σ PASH[1) Σ PASH $[\mu g/m^2]$	Σ PAH (EPA) $[\mu g/m^2]$	Σ PCDD/F $[ng/m^2]$
2.1 corridor window	5.7	1,610	4.2
2.2 corridor floor	6.5	858	3.0
2.3 corridor ceiling	13.6	2,410	25.0
2.4 corridor wall	23.8	4,270	30.5
2.5 wall above backup box	20.0	2,230	< 2.4
2.6 bathrobe (cotton)	49.3	5,620	12.9
2.7 flat hall ceiling	14.7	2,000	14.7
2.8 bathroom tiles	4.4	899	9.0
2.9 living room wallpaper	465	58,800	88.6
2.10 wall above living room window	14.6	4,780	13.5
2.11 kitchen wallpaper	23.0	6,720	42.7

Table 19: Surface contaminations with PASH, PAH and PCDD/F after the second fire accident

Both fires were comparatively small, and the share of plastics burned were below average concerning fire 1 and average for fire 2. Hazardous materials, known to cause severe pollution in case of fire, were not present in relevant amounts in the fire loads. Under these conditions surface contaminations with PASH were between 1.70 and 49.3 $\mu g/m^2$. The results for PAH (EPA) ranged from 34.3 to 6,720 $\mu g/m^2$. Sample 2.9 indicates, that contamination can locally be significantly higher than the average (danger of hot spots). As listed in table 19, this sample contained 465 $\mu g/m^2$ PASH and 58,800 $\mu g/m^2$ PAH (EPA). The average surface contaminations with PASH and PAH were found to be higher in the destroyed flat after fire 2.

In contrast to that, the PCDD/F contamination was slightly higher after fire 1. Samples were contaminated with PCDD/F in the range of 4.15 and 1,300 ng/m^2. The huge range of analytical results, measured for each substance class is caused by locally differing combustion parameters, an uneven distribution of the pollutants within turbulences, and the structure of the surfaces examined, specifying their capacity as passive samplers. Furthermore, it can be deduced from the analytical results that there is a coherence of the contaminations with the different substance classes. Samples with high PASH concentrations also contained comparatively high amounts of PAH and PCDD/F.

In contradiction to literature, the results of this study indicate that PASH were likely formed in significant amounts during the fires examined with no fossil fuels present in the fire loads. To conclude this study, in case of these two comparatively small fire accidents, the PAH were proved as being the most problematic pollution that has been identified.

Regarding the chronic toxicity of pollutants, in two well documented German fire catastrophes, the Lengerich (1922) and Dusseldorf (1996) airport fires, it was found that the cancer risk from polycyclic aromatic hydrocarbons is up to 500 times higher than that of polyhalogenated dioxins and furans. As both pollutants are strongly bound to soot and therefore of low bioavailability, no chronic toxicity effects were reported from the general population or people professionally involved in fires. The hazard from dioxins and furans in fires is highly overestimated. The chronic toxicity of polybrominated dioxins and furans from the flame retardants involved in these two fires is negligible.

Furthermore, this study reminds the risk comparison of different pollutants. A possibility to compare different pollutants is given by the "Unit Risk" model. For some carcinogenic substances "Unit Risk Factors" have been derived from epidemiological studies. These data show how many people, when exposed to the same quantity of the substances (inhalation of 1 μg pollutant per m3 of air) over their lifetime, would contract cancer. The "Unit-Risk Factors" for some carcinogenic air pollutants are summarized in table 20.

Pollutant	Unit-Risk-Factor [$1/(\mu g/m^3)$]
Arsenic	$4 \cdot 10^{-3}$
Asbestos	$2 \cdot 10^{-5}$
Benzene	$9 \cdot 10^{-6}$
Cadmium	$1.2 \cdot 10^{-2}$
Diesel soot particles	$7 \cdot 10^{-5}$
Benzo(a)pyrene (BaP)	$7 \cdot 10^{-2}$
2,3,7,8-TCDD	1.4

Table 20: Unit-Risk Factors for selected carcinogenic air pollutants

When comparing 2,3,7,8-TCDD (1.4) to BaP (0.07), it comes out that 2,3,7,8-TCDD is 250 times more carcinogenic than the latter. The Unit-Risk-Factor is multiplied by the actual measured concentration of the relevant substance to obtain the lifetime risk from carcinogenic pollutants in the air. The results showed that the risk from BaP is 10,000 times higher than from 2,3,7,8-TCDD. If a comparison between all carcinogenic PAHs and PCDD/Fs is made, factors of 2,000 and more remain. Therefore, compared to PAHs, the impact of dioxins on our health can be neglected in this fields.

4.2- Toxicity with PIN-FR

4.2.1- Rhodes, J. 2011 [51]

Polyamide 6 (PA 6) and polypropylene (PP) containing fire retardants, nanofillers or a combination of both additives have been investigated using the steady state tube furnace (ISO TS 19700).

Material	Polymer %	Fire Retardant %		Nanoclay %
		AP	OP	
Polypropylene (PP) (all samples contain 5% PPgMA)	100			
PP + FR	70	30		
PP + NC	95			5
PP + FR + NC	65	30		5
Polyamide 6 (PA 6)	100			
PA 6 + FR	82		18	
PA 6 + NC	95			5
PA 6 + FR + NC	77		18	5

Table 21: Loadings of the samples tested

The compositions of the samples tested are shown in Table 21. The virgin polymers used for the preparation of nanocomposites were commercial polypropylene (PP) grafted with maleic anhydride used as a compatibiliser (Moplen HP500N-Basell blended with 5% PPgMA Polybond 3200 by Crompton as a masterbatch), and polyamide 6 (PA6 S27 from Radici Plastics). The fire retardant (FR) for PP was Exolit AP 760 (based on ammonium polyphosphate), for PA6 was OP 1311 an organic aluminium phosphinate combined with melamine polyphosphate, all supplied by Clariant. The nanoclay (NC) was Cloisite 20A for PP and Cloisite 30B for PA6 supplied by Southern Clay Products.

The samples were tested under three different fire conditions, to determine the effect of additives on the soot production or toxic product yields.

Fire Stage	Max Temp/°C		Equivalence ratio ϕ	CO/CO_2 ratio
	Fuel	Smoke		
Non-flaming				
1a. Self sustained smouldering	450–800	25–85	–	0.1–1
Well-ventilated flaming				
2. Well-ventilated flaming	350–650	50–500	<0.75	<0.05
Under-ventilated flaming				
3a. Low vent room fire	300–600	50–500	>1.50	0.2–0.4
3b. Post flashover	350–650	>600	>1.50	0.1–0.4

*Table 22: ISO Classification of fire stages*

Most fires progress through several different stages (detailed in Table 22) from ignition to decay. The generalised stages in the development of a fire are used to classify fire growth in terms of equivalence ratio ϕ (as described in part 2.4.1 of this report), and have been successfully replicated by using the steady state tube furnace, ISO TS 19700. This is probably the best method for replicating individual fire stages on a bench scale.

The particle size distribution of the soot was investigated with a cascade impactor, and the separated soot fractions examined by SEM. A cascade impactor is one of the only techniques which provides a particle size distribution expressed in terms of mass (rather than number) of particles in each size range. Cascade impactors measure aerodynamic particle size directly, as physiological effects are a function of size distribution based on mass. This is the most relevant parameter for predicting particle transport and deposition within the respiratory tract.

Filter cut off	Approximate maximum aerodynamic diameter	Position in the human respiratory tract
21.3 μm	21.5 μm	Nasal cavity
14.8 μm	15 μm	Oral cavity
9.8 μm	10 μm	Larynx
6.0 μm	6.5 μm	Trachea
3.5 μm	4 μm	Bronchi
1.55 μm	2 μm	Bronchioles
0.93 μm	1 μm	Bronchioles
0.52 μm	0.5 μm	Alveoli

Table 23: Filter size and corresponding deposition point within the human respiratory tract

The predicted deposition based on aerodynamic size of particulates in the human respiratory tract shows clear differences between the pure polymer and its additive counterparts. If we take the case of the combustion of formulations in PA6 matrix and PP matrix in small under-ventilated conditions, the conclusions of tests are totally different.
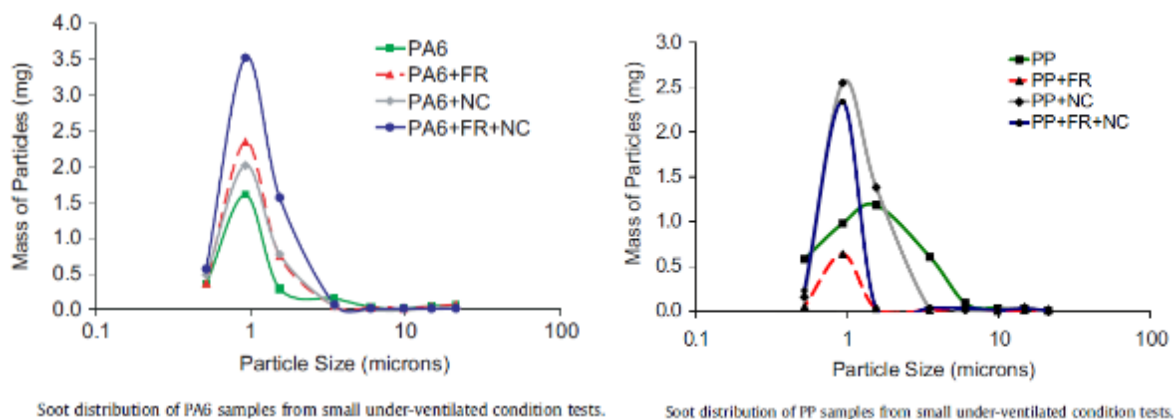
Figure 47: Soot distribution of PA6 and PP samples in small under-ventilated conditions
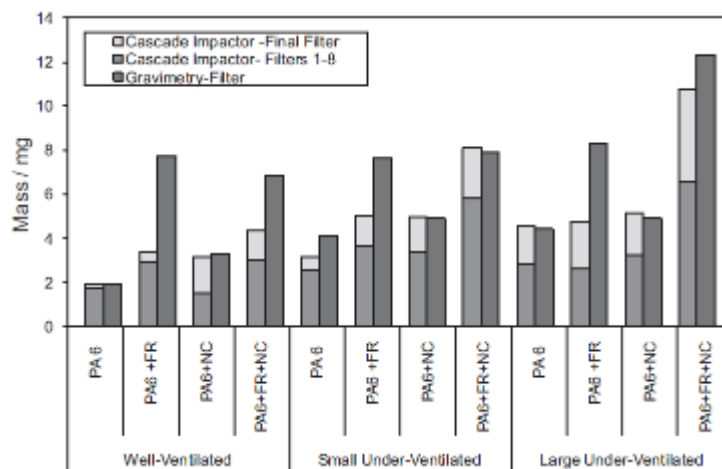
Figure 48: Total mass of soot collected in the cascade impactor and on the filter for PA6 polymers

The results appear to show that the particle size and distribution is unaffected by the ventilation condition and the sample composition for PA6 materials. Experiments on PA6 samples show that in all ventilation conditions the unaltered polymer produces the least amount of soot, indicating that the additives used increase the amount of soot produced. In addition, in all ventilation conditions, PA6 + FR + NC with both additives present, produces the most amount of soot, closely followed by the samples of PA6 + FR. The majority of the soot produced from the PA6 experiments was around 1 μm aerodynamic diameter, this trend was most noticeable in the small under-ventilated condition, but also mirrored in the large under-ventilated condition. The well-ventilated condition supported the production of a range of particle sizes for the unchanged polymer and the PA6 + NC sample, but again the PA6 + FR and PA6 + FR + NC followed the trend of the other conditions.
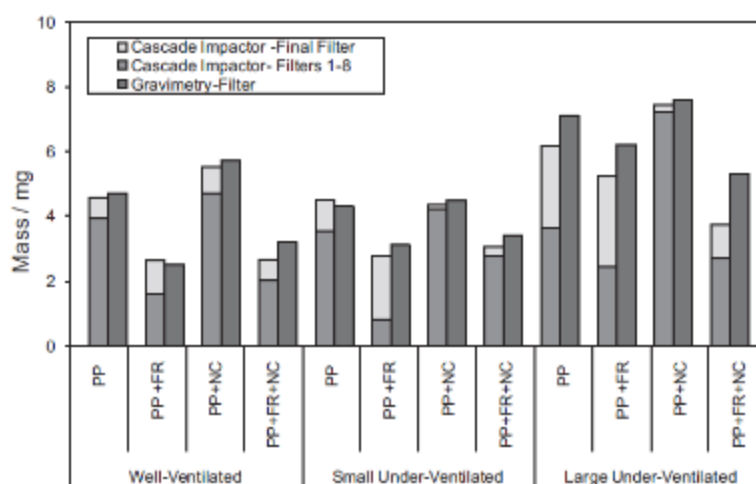
Figure 49: Total mass of soot collected in the cascade impactor and on the filter for PP polymers

Contrary to PA6 formulations, experiments on PP samples show that in all ventilation conditions the PP+30%AP760 sample produces less soot than virgin PP. In addition, in all ventilation conditions, PP + FR + NC with both additives present, produces also less soot than virgin PP.

This study demonstrates that in terms of the choice of PIN-FR in a defined polymer matrix, the material can generate more or less soot. This means that according to the chemical nature and the mode of action of PIN-FRs, combustion products can be different (yield and size of particles).

4.2.2- Hewitt, F. 2016 [53]

A study has been led by F. Hewitt and al, to obtain qualitative results from analysis of volatile and semi-volatile organic compounds (VOCs/SVOCs) through sampling of gaseous effluent and condensed particulates during a series of experimental house fires conducted in a real house. The initial fuel packages were either cooking oil or a single sofa; these were burned both alone, and in furnished surroundings.

Several of the phosphorus based compounds detected in both the gaseous effluents and condensed particulate samples are known for their use as fire retardants: 2-Propanol, 1-chloro-,2,2',2''- phosphate (TCIPP, previously known as TCPP), Phosphoric acid, triphenyl ester (TPHP), Ethanol, 2- butoxy-,1,1',1''-phosphate (TBOEP, previously known as TBEP), Phosphoric acid, tris(methylphenyl) ester (TMPP, previously known as TCP)and also Phosphoric acid, triethyl ester (TEP). These compounds were only detected in fires where the fuel included a sofa and shows that they are volatilised in their original form. Flexible polyurethane foams, used in upholstered furniture, are frequently fire retarded with TCIPP or TCEP, since the other

fire retardants have been restricted due to toxicity concerns. The toxicity and environmental occurrence of many phosphorus flame retardants (PFRs) has already been reviewed and it has been pointed out some toxicity issues when inhaled as it. The organo-phosphorus based compounds were most likely released from the polyurethane foam filling inside the sofas. This has been corroborated by similar analysis from insulation materials pyrolyzed and combusted in the laboratory using the French Railway test (NFX-70-100) and the steady state tube furnace (ISO TS 19700). Phosphorus compounds, including TCIPP, were also detected from the fire effluent of fire retarded sofas burning during large-scale experiments carried out in containers. However, that investigation does not enable to estimate the level of soot toxicity generated by phosphorus flame retardant because the quantity of detected phosphorus species has not been measured. This study must be completed with quantitative results to express relevant conclusions on the toxicity of emitted soot.

5- Discussion and conclusion

Smoke is the result of the pyrolysis and combustion of an organic substance, and it consists of two major parts: gas and soot.

Fire gases contain a mixture of fully oxidized products, such as CO_2, partially oxidized products, such as CO and aldehydes, fuel, or fuel degradation products, including aliphatic or aromatic hydrocarbons, and other stable gas molecules, such as nitrogen and hydrogen halides. As far as soot is concerned, it consists in a complex mixture of particles of different natures, resulting mainly from unburnt residue and condensed PAHs, dioxins and furans.

Acute toxicity from the inhalation of toxic gases is one parameter accountable for fire deaths, though the incapacitating effects of smoke and irritant gases also play an important role. For many materials (such as CH- and CHO- containing polymers), the yield of the main toxicant, CO, has been shown to depend only on fire conditions, not on the nature of the polymer. Once a fire has reached flashover, roughly 20 percent of the mass lost from the combination of any material has been converted into carbon monoxide CO. It is therefore essential to the assessment of fire gas toxicity that these different fire stages can be adequately replicated. Concerning soot emissions during fires, depending on the temperatures and oxygen regimes, the presence of unburnt carbon particles in the post-combustion zone significantly increases the yield of PAHs and PCDD/Fs.

For most natural and synthetic polymers, the yields of toxic products such as CO are very low under well-ventilated combustion conditions, but increase sharply in under-ventilated combustion conditions as the equivalence ratio Φ increases above 1. This results in a sigmoidal relationship between equivalence ratio and yield, so that the yields of products of incomplete combustion can increase by factors of approximately 50 between well-ventilated flaming conditions (Φ≈0.7), and fuel-rich conditions (Φ≈1.5). The increase in products such as CO, HCN, organic irritants, with Φ is matched by a corresponding decrease in the products of more complete combustion-principally CO_2, H_2O, N_2, and NO_x.

During the 1970'S and 1980's there was a belief that burning plastic materials produced smoke that was far more toxic than smoke from burning natural products such as wood, wool, or cotton. A number of studies have been done to compare the amount of carbon dioxide, carbon monoxide, and hydrogen cyanide produced by natural and synthetic materials under flaming and non-flaming conditions in order to model smoke toxicity. In summary, it has since become clear that the smoke toxicity of virtually all materials is almost identical, within the margin of error. In addition, most

modern plastics generally produce the same types and levels of carcinogenic volatile organic carbons (VOCs) than do wood products in fires.

Assessment of fire gas toxicity is still considered today as an important component of fire hazard analysis. The toxicities of the effluents, showing the contribution of individual toxic components, are compared using the fractional effective dose (FED) model. The predicted toxicities show variations of up to two orders of magnitude with change in fire scenario. They also show changes of at least one order of magnitude for different materials in the same fire scenario. Finally, they show that in many cases CO, which is often assumed to be the most, or even the only toxicologically significant fire gas, is of less importance than HCl or HCN when chlorine or nitrogen is present in the compound. However, studies show that CO concentrations regularly exceed its LC50, while those of HCl and HCN rarely exceed a small fraction of their LC50 and those of acrolein rarely exceed its LC50. In other words, there is so much more CO than anything else in fire atmospheres that CO is the big toxic killer in smoke.

The CO concentration associated with the smoke of almost all commercial polymers are within a factor of 3, which is relatively close in relation the influence of the fire scenario. However, the addition of gas phase active flame retardants can increase the amount of smoke significantly, whereas the addition of other kind of flame retardants or specific smoke suppressants can reduce it. Therefore, in high risk environments like airplanes and trains, the toxicity of emitted smoke is regulated. The use of PIN FRs and the evaluation of its related impact on the smoke composition is then becoming more and more pregnant. One important composition-related effect is the residue formation in some natural and synthetic polymers, and in PIN FRs containing products acting in the solid phase (such as phosphates), which leads to reduced yields of airborne products and partly traps carbon particulates from the fuel. Other important yield modifiers are PIN FRs acting in the gas phase (such as phosphinates), resulting in increased yields of incomplete combustion products, especially carbon monoxide and hydrogen cyanide regardless of the equivalence ratios. On another point of view, the presence of PIN FRs and the incorporation of synergists reduce the flammability, the heat release rate and for many PIN FRs, there is no significant adverse effect of these additives on the toxicity of the material studied under most fire conditions. This fact is related in the study led by Hewitt, F. 2016 [53]. In function of polymer matrix and the right choice of PIN FR, the yield of soot generated during the combustion can be decreased. Undoubtedly not all flame retardants ever developed or about to be developed are safe from all points of view, but the use of appropriate scientific knowledge and the regulatory environment can effectively ensure that unsafe materials

are kept away from consumers. It is consequently very clear that the use of flame retardants presents a benefit to society and the environment, providing improved fire safety via lowering the probability of ignition, the heat released and the amounts of smoke, combustion products, and dangerous environmental toxicants. There is an excellent correlation between blood CO concentration in fire victims and related deaths; thus the toxic effects of other combustion products (e.g. PIN FR combustion products) are negligible. Fire hazard and life safety are best served by ensuring that fires remain small, meaning that they need to exhibit heat release rates as small as possible which has been demonstrated to be achievable thanks to the use of PIN FRs. Regarding long term exposure effects, it is undoubtedly true that regarding gas inhalation added to repeated exposure to the great variety of VOCs could significantly affect the health. Firefighters have special concerns because the rates of many chronic diseases, including cancers, are higher among them than among the general population. However, there is no evidence that this is associated with any PIN FR used in materials. Finally, modern firefighters own today SCBAs mask (Self Contained Breathing Apparatus) limiting them to be exposed to high concentrations of carcinogenic chemicals and soot from smoke.

Throughout this scientific review on the characterization of gas and soot emissions of materials either non-fire retarded or containing PIN-FRs, we noticed a certain lack of interest in some topics. The first example deals with metal hydrates that have been quite forgotten by the scientific community and most of the attention has been conducted to the phosphorus and nitrogen derivatives toxicity. Indeed, there are no toxicity problems presumed with either ATH or MDH and this should be the main reason that the topic is not treated by scientific researches. Secondly, the assessment of soot particles emitted from PIN FRs containing materials is up to now a topic largely under documented by the scientific community, although their use in synthetic polymers and other materials is growing each year. Also, chemicals that are expressly used as smoke suppressants are not within the scope of this report. Last but not least, we also have to point out the shortage of data coming from real scale and accidental fire situations. This review illustrates that remark since less than 30% of the papers (6 out of 22) deal with real fires investigations. Of course, we can easily assume that those kinds of experiments are very difficult to set up and, time and money consuming. Nevertheless, as we saw before, the chemical and physical composition of the smoke are very dependent on the fire conditions. Unfortunately, we already discussed how difficult it is to extrapolate data from different small-scale fire test methods to real fires, since it is almost impossible to reproduce the fire growth and decline sequence at the

bench. Moreover, among the few accidental fire measurements already carried out, they barely contain quantitative data, but only qualitative detection of chemical species, which is not sufficient to determine the toxicity of the smoke. Appropriate quantitative data come mainly from simulations involving small-scale physical fire models. As a consequence, to rule on the toxicity of gaseous effluents from PIN-FRs as exhaustively as possible, the bench data should be completed by conducting a series of real scale tests involving PIN FR material and quantitative analysis of gaseous and particulates of the smoke given off.

Appendix A: Full bibliography

The list below is composed of the whole scientific papers, documents and books gathered initially on the basis of the following databases and key words screened:

1) <u>Databases</u>:

- Science Direct
- Scopus
- Web of science
- Springerlink
- Emerald
- IEEE Xplore
- NIST publications

2) <u>Key words without combination:</u>

Phosphorous, nitrogen, ATH, MDH, melamine, flame retardant, inorganic flame retardant, smoke suppressor, smoke composition, fire toxicity, gas composition, gas toxicity, soot toxicity, soot composition, FR impact on human health, soot morphology, soot diffusion in human body, external factor accelerating soot diffusion to human body.

135 documents were then identified and split into the following categories:

- 47 are dealing with general works on smoke toxicity, combustion and testing methods. That has been useful to setup the ins and outs of the toxicity topic.
- 22 (see Appendix C) emerged as the one containing the most relevant quantitative and qualitative information, as far as gas and soot toxicity of fire smoke is concerned.
- 66 have been analysed but rejected due their global irrelevance, lack of information or redundant aspect on the addressed topic.

➢ al, Wobst M., et. 'Surface Contamination with PASH, PAH and PCDD/F after Fire Accidents in Private Residences. - PubMed - NCBI'. Accessed 12 September 2016. http://www.ncbi.nlm.nih.gov.chimie.gate.inist.fr/pubmed/10070738.
➢ Alongi, Jenny, Zhidong Han, and Serge Bourbigot. 'Intumescence: Tradition versus Novelty. A Comprehensive Review'. Progress in Polymer Science 51 (December 2015): 28–73. doi:10.1016/j.progpolymsci.2015.04.010.

➢ Amon, Francine, Margaret McNamee, and Per Blomqvist. 'Fire Effluent Contaminants, Predictive Models, and Gap Analysis'. SP, n.d. http://www.brandforsk.se/MediaBinaryLoader.axd?MediaArchive_FileID=4548 23ca-1b10-4969-b0cf- 47a658b8b905&FileName=BF_700_121_Rapport.pdf&MediaArchive_ForceD ownload=true.

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