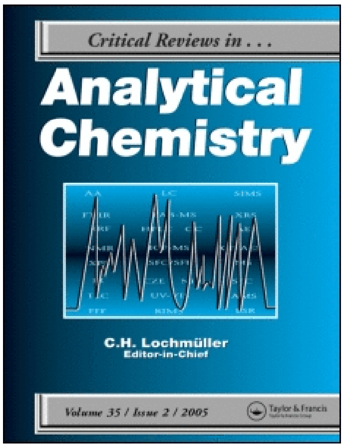

Critical Reviews in Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713400837

Combustion of Polymeric Materials

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To cite this Article Elomaa, M. , Sarvaranta, L. , Mikkola, E. , Kallonen, R. , Zitting, A. , Zevenhoven, C. A. P. and Hupa, M.(1997) 'Combustion of Polymeric Materials', Critical Reviews in Analytical Chemistry, 27: 3, 137 — 197

To link to this Article: DOI: 10.1080/10408349708052200

URL: http://dx.doi.org/10.1080/10408349708052200

Critical Reviews in Biochemistry and Molecular Biology, 27(3):137–197 (1997)

Combustion of Polymeric Materials

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1040-8347/97/$.50

I. INTRODUCTION

Polymeric materials can be natural as wood, proteins and cotton or synthetic such as most of the plastics and the elastomers. Chemically they are composed of one or more polymers and can contain other types of compounds like mineral fillers or dyes. Actually most of the organic materials in our surroundings, and even inside us, are polymeric.

The combustion of polymers has been studied for two main reasons. Firstly, the flammability of polymeric materials is a problem that has been the reason for development of test methods for a wide scale of applications. Secondly, the use of polymers as fuel and their effect in the incineration of waste have been topics of research. The first point of view aims to phenomena like ease of ignition, flammability, and flame spread. In addition the research aims to an improvement in fire safety by searching ways to reduce the ease of ignition and flame spread. On the other hand, in incineration it is beneficial that the polymer burns well and has a high caloric value.

Combustion can be defined as an exothermic reaction of a material with an oxidizing agent, accompanied by flames and/or glowing and/or smoke. [Troitzsch 1983] This definition is clarified below in section I B which deals with the modes of burning.

The knowledge of the products of burning is important in fires as well as in incineration. The physical conditions in a fire have a wide variance depending on the circumstances. Therefore, for any fire hazard assessment, it is important to notice that the circumstances change enormously during a fire. In incineration, on the contrary, one optimizes the conditions, as far as possible, for two main reasons - to maximize the power output and to minimize the emission of noxious combustion products.

The continuous growth of production and use of synthetic polymers make the knowledge of their combustion behavior of utmost importance. The production of plastics has increased much more than the production in general over the past decades. A healthier global economy and improved end-use markets will help boost world demand for thermoplastic resins by 4 percent per year to 122 million metric tons by the year 2000, according to a new market study by the Freedonia Group. [http://www.polysort.com/market_studies.htm; Cleveland, Ohio (Nov. 16, 1995)].

We provide a short introduction to the fundamental phenomena of combustion in the first chapter. Important properties of burning polymers are given in the second chapter. The second chapter also gives examples of useful methods to determine those properties. Some of these methods can be considered as fire-technological tools which are needed in the discussion of the fire safety aspects of polymeric materials in the third chapter. Noxious combustion products form common problem for all burning. Toxicity in fires and emissions of power plants are quite different topics and they are discussed in the two subsequent chapters.

A. Fundamental Phenomena of Combustion

1. Heat Balance

Fuel, air and heat can be considered as the elements of fire. [Emmons 1974] The fuel is usually in contact with air but the fire will not ignite without an elevated temperature. After the ignition, the combustion will continue if enough heat is produced in the flame to achieve a continuous evaporation of fuel and mixing of that to air.

The heat balance is essential in the combustion and it can be described schematically by a stability diagram of combustion. This diagram (Fig. 1) has been introduced among others by Frank-Kamenezky [1969].

In Fig. 1., one can see two lines that of heat generation (I) and that of heat loss (II). The generation of heat depends on the rate of combustion and increases exponentially with temperature until it will be limited by full conversion or resistance-to-mass-transport of oxygen by diffusion rate to the flame. The exponential rise of the production of heat in a small volume can be expressed in the form of equation:

$$\dot{Q}_C'' = \Delta H_C V C^n A \exp(-E_A/RT) \qquad (1)$$

where $\dot{Q}_C''$ is the heat production rate (W mol^{-1}), A is the "pre-exponential factor" whose units will depend on the order of reaction, n; C is the concentration (mol m^{-3}), DH_c is the heat of combustion (kJ mol^{-1}), E_A is the activation energy, R is the gas constant and T temperature in Kelvins. The heat loss rate is roughly proportional to the difference in temperature between the reaction volume and the environment and has therefore a linear form:

$$\dot{Q}_L'' = hS(T - T_\infty) \qquad (2)$$

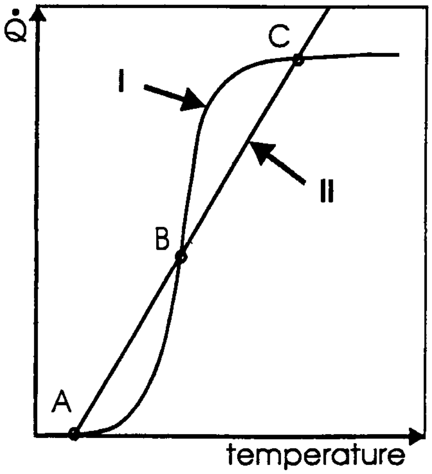
where $\dot{Q}_L''$ is the heat loss rate of the polymer, h is the heat transfer coefficient (W $m^{-2}K^{-1}$), S is the surface area of the reaction volume through which heat is lost (m^2) and T_∞ is the temperature of the environment [Drysdale 1986].

In Fig. 1 equilibrium between heat generation and heat loss is realized at the points of intersection of I and II, i.e. in points A, B and C. The situation stabilizes at points A (ambient temperature) and C (stationary combustion temperature) whereas B is unstable. To the left of B the heat loss exceeds the heat generation; to the right of B the process is just reversed. Hence the temperature corresponding to B is the ignition temperature. During a fire the material must be heated to such an extent by heat fed back from the flame that at least this ignition temperature is reached.

2. Pyrolysis

Combustible gases must be produced before the ignition of a polymeric material to flame. When an organic polymer is heated it eventually reaches a temperature at which the weakest bonds start to rupture. This breaking of only relatively few bonds is generally referred to as polymer degradation and results in only minor changes in structure and properties, e.g. discoloration. At higher temperature more extensive breakdown of the polymer structure starts to take place and this dissociation of a significant proportion of the total number of constituent chemical bonds is called polymer decomposition [Cullis and Hirschler 1981a]. Pyrolysis is defined to be: "Irreversible chemical decomposition of material due to an increased temperature without oxidation". [Troitzsch 1983] Pyrolysis plays the main role in the production of combustible gases in burning of polymers.

Polymers can be classified according to their pyrolysis products: monomer, oligomer and carbonaceous residues or those 1) which decompose by net main chain scission, 2) by stripping of the main chain; and 3) by crosslinking of the main chain followed by some production of volatiles. Highly unsaturated or aromatic chains tend to follow the latter course [Wall 1972]. The main chain scission can be divided further into depolymerization (or "unzipping") and random chain scission. The thermal degradation of organic polymers propagates mostly by radical reactions that are initiated by breaking of the thermally weakest bonds. The formation of free radicals in condensed phase as well as among the volatile degradation products has been proved by using the electron spin resonance technique. [Tkac 1976].



Sec. 1. Fig. 1. Heat balance of combustion.

A classification of the thermal decomposition mechanisms into four classes is given in Table 1. [Cullis and Hirschler 1981b].

3. Flame Reactions

Polymers burn with diffusion flames. [Hindersin 1977] Decomposition products of the polymer mix in the flame with oxygen by diffusion. The chemistry (and physics) of turbulent, fuel rich flames, which is what polymer flames tend to be in practice, is extremely complex. While some polymers undergo reactions that fall almost exclusively into one of the four classes shown, others exhibit mixed behavior. The breakdown of fuel molecules and formation of combustion products proceed in long sequences of steps; each step involves only minor rearrangements of chemical bonds. A detailed model of a flame has to take account of all such elementary reactions. The number of reactions needed is very large even for small hydrocarbons. Gardiner wrote in 1982: "Computer models for the combustion of methane (CH_4) already include more than 100 elementary reactions. Is there any hope, then, of constructing one for octane (C_8H_{18}), even assuming the availability of vast computer power? The answer is that there is no hope at all if the model is to take explicit account of all the intermediates. The number of elementary reactions required increases geometrically with the size of the fuel molecule and comes excessive long before one reaches octane..." [Gardiner 1982] Models up to at least butane have been worked out already. For instance a model of combustion of butane in a reactor is made of 344 reversible reactions. [Chakir et al. 1989] There is a trend to simplify the models by taking into account only the most important reactions. An eight-step kinetic mechanism for propane [Kiehne et al. 1987] and a global reaction scheme has been proposed for alkane hydrocarbons up to butane in mixture with air in premixed and in diffusion flames [Jones and Lindstedt 1988] The very rapid formation of carbon and polycyclic aromatic hydrocarbons (PAH) has not been solved on the level of elementary reactions. A complex route of mechanisms involving formation of PAHs and carbon in the diffusion flame of methane has been suggested. [Smyth et al. 1985] More detailed discussion of the flame reactions is out of the scope of this paper.

B. Modes of Burning

Combustion of polymers can be divided into three types: flaming combustion, smoldering, and glowing combustion. If combustion is determined more generally as a reaction between a substance with an oxidizing agent, two additive modes of oxidation, explosions and various thermo-oxidative reactions should be included. These additive modes are left outside of the discussion in this review.

Flaming combustion is the most intensive of the three types of combustion in concern. Highly exothermic oxidation reactions take place in a flame. Visible flames are due to light emitting combustion processes in the gas phase. The flame may get different forms depending of the fuel and of the flow conditions. In small scale the flame can be laminar. This is the case in candle-like burning, which is a mode of combustion often used in experimental work. In a larger scale, the flames tend to get turbulent because of the more severe flow conditions. Fig. 2. shows a schematic description of flaming combustion of a polymer. The starting compounds and the products are indicated with black boxes; chemical reactions are shown by arrow-shaped boxes; smoothed squares indicate physical changes; and heat flow is described by wavy arrows.

The importance of oxidation reactions on the surface of the burning polymer has been emphasized in several papers. [Burge and Tipper 1969] [Stuetz et al. 1975] [Stuetz et al. 1980a] [Stuetz et al. 1980b] However, a more generally accepted conclusion is that pyrolysis takes place on the surface which means thermal degradation without oxidation. [Fenimore and Martin 1972] [Seshadri and Williams 1978] [Krishnamurthy 1975] [Nelson 1979] Accordingly pyrolysis is a well distinguished and inevitable part of the flaming combustion of polymers.

There are several situations, however, in which the surface oxidation is of greater importance than in flaming conditions in general. They are

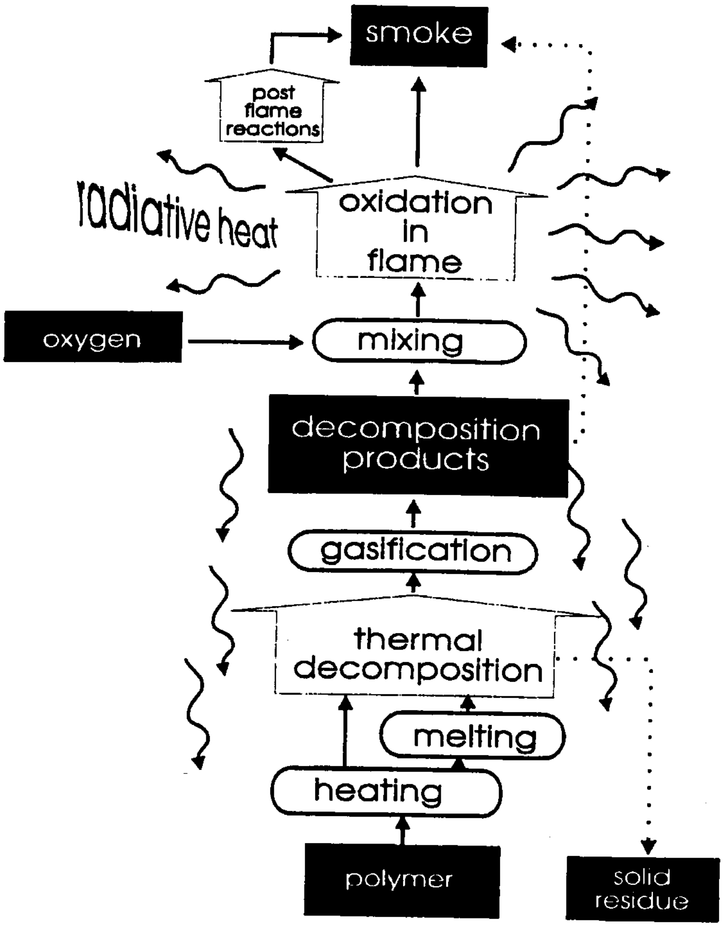
Table 1. General mechanisms of the thermal decomposition of organic polymers

Mechanism	Polymer (examples)	Products	Products in general
Random-chain scission	Polyethylene	Alkanes, alkenes,	Very little monomer
	Polypropylene	Alkanes, alkenes,	
	Polystyrene*	Styrene, dimer, trimer	Monomer and oligomers
End-chain scission	Poly(methyl methacrylate)	monomer	90 -100% monomer
	Polymethacrylonitrile		
	Poly(α-methyl styrene)		
	Polytetrafluoroethylene		
	Polyformaldehyde		
Chain stripping	Poly(vinyl chloride),	Hydrogen hloride, amatic hydroarbons, char	Small molecules and char
	Poly(vinylidene chloride)		
	Poly(vinyl alcohol)	Water, aromatic hydrocarbons and char	
Cross-linking	Polyacrylonitrile	Char	Much char, few volatiles
	Poly(oxy-m-xylene)	Char	

*Decomposes by mechanism involving both random- and end-chain scission.

near and at the point of the ignition, in very turbulent flow conditions, when evaporation of the gases from the surface decreases, and near the extinction; in general when oxygen concentration on the hot surface increases significantly. [Aseeva and Zaikov 1985].

Smoldering and glowing combustion are processes at or under the surface. Smoldering is defined to be: "slow combustion of a material without light being visible and generally characterized by smoke and a rise in temperature". [Troitzsch 1983] Smoldering can result in a very complex mixture of products, which will spread to atmosphere as solid particles, liquid droplets, and gases. Smoldering may be followed by a rapid growth of fire because the smoke produced may take fire and pre-heating increases the rate of combustion. With items of furniture and upholstery, transition from smoldering to flaming can occur after a protracted period. In experience this transition usually requires a smoldering period in excess of half an hour; with a polyurethane mattress and cotton bedclothes a transition has been observed after 2h 20 min. [Woolley 1982] Glowing combustion, instead, occurs typically in charring material



Sec. 1. Fig. 2. Schematic description of flaming combustion.

after flaming combustion. By definition glowing combustion is: "Combustion of a material in the solid phase without flame but with emission of light from the combustion zone. [Troitzsch 1983].

C. Burning Products

Smoke is basically a product of incomplete combustion. The ISO Working Draft 13943 [1993] defines smoke as a visible suspension of solid and/or liguid particles in gases resulting from combustion. Essentially the same definition has been used also by Mulholland [1988], who defines smoke as the smoke aerosol or condensed phase component of the products of combustion. Sometimes, however, the evolved gases may be included in the definition as well (e.g. ASTM). The combustion products occuring in condensed phase and in gas phase are described separatly below. The toxicity of the combustion products is discussed later in chapter IV.

1. Condensed Phase Products

Combustion processes emit large quantities of particles into the atmosphere. Particles formed in combustion fall roughly into two categories. The first category, referred to as *ash*, comprises particles derived from noncombustible constituents. The second category, referred to as *char*, *coke* and *soot*, consists of carbonaceous particles formed by pyrolysis. Particles produced by combustion sources are generally complex chemical mixtures that often are not easily characterized in terms of composition [Flagan & Seinfeld 1988].

Ash is derived from noncombustible material. Some components of ash are highly volatile; examples include sodium, potassium, and arsenic. Since the enthalpies of typical ash constituents are high, the vaporization rates are a strong function of temperature [Flagan & Seinfeld 1988].

The carbonaceous *char* residue that remains after coal is devolatilized burns slowly by surface reactions. Heavy fuel oils may produce similar carbonaceous particles, called *coke*. Coke particles are relatively large, 1 to 50 mm in diameter, with smaller numbers of much larger particles [Flagan & Seinfeld 1988].

Carbonaceous particles can also be produced in the combustion of gaseous fuels and from the volatilized components of liquid or solid fuels. The particles formed by this route, known as *soot*, differ markedly from char and coke [Flagan & Seinfeld 1988]. Most commonly, soot particles are agglomerates of small, roughly spherical particles. While the size and morphology of the clusters can vary widely, the small spheres differ little from one source to another. They vary in size from 0.005 to 0.2 mm but most commonly lie in the size range 0.01 to 0.05 mm. The structural similarity between soot particles and the inorganic particles produced from volatilized ash suggests a common origin. The genesis of soot, however, is much less well understood than that of the inorganic particles due to the extreme complexity of hydrocarbon chemistry in the flame, as well as to the fact that soot particles can burn if exposed to oxygen at high temperatures [Flagan & Seinfeld 1988].

The smallest spheres that agglomerate together to form a soot particle consist of large numbers of lamellar crystallites that typically contain five to ten sheets containing of the order of 100 carbon atoms each. The structure within each sheet is similar to that of graphite, but adjacent layers are randomly ordered in a turbostratic structure. The platelets are also randomly oriented and bound by single sheets or amorphous carbon, giving rise to the spherical particles [Flagan & Seinfeld 1988]. In a fire, the particles may further form complex soot agglomerates [Mulholland 1988].

Soot particles are not pure carbon. The composition of soot that has been aged in the high-temperature region of the flame is typically C_8H, but soot may contain considerably more hydrogen earlier in the flame. Furthermore, soot particles adsorb hydrocarbon vapours when the combustion products cool, frequently accumulating large quantities of polycyclic hydrocarbons.The presence of soot in a flame gives rise to radiative heat transfer. Because of the high emissivity of soot particles relative to that of the gases in the flame, only a small quantity of soot is sufficient to produce an intense *yellow* luminosity. Without soot, hydrocarbon flames appear either *violet* due to emissions from excited CH radicals when fuel-lean or *green* due to C_2 radical emissions when fuel-rich. The high emissivity of soot translates into a high absorptivity at ambient temperatures, leading to its *black* colour in a plume [Flagan & Seinfeld 1988].

No generally applicable model has yet been formulated to predict soot formation as a function of fuel type and combustion conditions. Soot forms in a flame as the result of a chain of events: pyrolysis and oxidative pyrolysis of the burning material into small molecules, followed by chemical reactions that build up larger molecules that eventually get big enough to become very small particles. The particles continue to grow through chemical reactions at their surface, reaching diameters in the range 0.01 to 0.5 mm at which point they begin to coagulate to form chain agglomerates [Flagan & Seinfeld 1988].

The propensity to form soot (as measured by the critical C/O ratio at which soot formation begins) is a complex function of flame type, temperature, and the nature of the burning material. There is a general agreement that the rank order of the sooting tendency of fuel components is naphtalenes > benzenes > aliphatics. However, the order of sooting tendencies of the aliphatics (alkanes, alkenes, and alkynes) varies dramatically with flame type. Much of the variability has been attributed to flame temperature. As the temperature increases, the oxidation rate increases faster than the pyrolysis rate, and soot formation decreases [Flagan & Seinfeld 1988].

The difference between the sooting tendencies of *aromatics* and *aliphatics* is thought to result from different routes of formation. The condensed aromatic systems are at present considered as the direct precursors of soot [Troitzsch 1990]. Other indications are that the conjugated polyenes, which were also considered formerly as direct precursors of soot, undergo cyclization to aromatic systems that then contribute to soot formation. Aliphatics appear to form soot primarily through formation of acetylene and polyacetylenes at a relatively slow rate [Flagan & Seinfeld 1988]. Solid particles such as minute carbon particles or inorganic fillers (in plastics) can also act as soot-forming condensation nuclei [Troitzsch 1990].

Once soot nuclei have been formed, particle growth occurs rapidly by surface reactions. Ultimately, the soot nuclei account for only a small fraction of the mass of soot formed; the remainder is material that has condensed or reacted on the initial nuclei. The yield of soot increases rapidly as the C/O ratio increases beyond the sooting threshold. Soot particle inception takes place very early in the flame, in a region where radicals are present in superequilibrium concentrations [Flagan & Seinfeld 1988].

2. Gaseous Products

Almost everything between the pyrolysis products and the products of complete combustion have been called "combustion products of burning polymers". In the following only the most important products of incomplete combustion from fires and incineration are discussed.

a. Fire

The majority of deaths and serious injuries in fires are due to victims inhaling smoke and toxic gases. [Fardell & al. 1987] The main toxic products identified in fires fall into two classes: narcotic gases and irritants. The main narcotic gases are carbon monoxide (CO) and hydrogen cyanide (HCN). Both of them have been measured in blood of both fatal and non-fatal fire casualties. Two of the known irritants are hydrogen chloride and acrolein. They cause incapacitation mainly by effects on the eyes and upper respiratory tract. Of narcotic gases, carbon monoxide is the most important and lethal concentrations of carboxyhaemoglobin are common in the All organic compounds form carbon monoxide by incomplete combustion. Hydrogen cyanide and nitrogen oxides are usually formed in fires of nitrogen-containing polymers such as polyurethanes and polyacrylonitrile, which are widely used in domestic furnishing. Hydrogen chloride is mostly formed from PVC which is commonly used in flooring, cables and pipes. Its thermal decomposition produces about 50 mass-% of hydrogen chloride at relatively low temperatures. [Simmons and Metcalfe 1987]

b. Incineration

Hydrocarbon polymers or polymers which contain only oxygen in addition to carbon and hydrogen are suitable fuels for modern incinerators. The ultimate products are carbon dioxide and water and the energy recovery is good. Most of plastic waste belong in this group. Nitrogen containing polymers produce some hydrogen cyanide and oxides of nitrogen in high temperature burning. These are acidic gases which should be washed from the flue gases. Halogen containing polymers are most problematic in incineration. Especially PVC as a common plastic material has been an object of concern. The most important reason is not that it will produce a lot of hydrogen chloride on burning. Chlorine in any form in fuel can lead to the formation of polychlorinated dibenzo-p-dioxines (PCDD) and polychlorinated dibenzofuranes (PCDF), several of which are extremely toxic. [Rappe 1986] The formation of these compounds is complex and concentrations usually very low. There are numerous examples showing that the production of these species does not correlate with the amount of chlorine in the fuel but rather with the incineration technique. In a Swedish comparison a plant having 60% chlorine in the fuel produced 0.2 ng 2,3,7,8-tetrachlorobenzodioxine equivalents (TCDD) per cubic meter of flue gas. In contrast, an incinerator produced 40 ng TCDD in a cubic meter of flue gas in spite of having a chlorine content in the fuel of only 0.7%. [Bystedt et al. 1986] However, in Denmark it has been found a correlation between hydrogen chloride and formation of dioxines in a study of ten incinerators. In the same work it was seen that incinerators of hospitals produced forty times the amount of total PCDD and PCDF compared to the average municipal incinerators, based on the amount burned. [Manscher et al. 1990] This is probably because of the higher load of PVC than in usual municipal waste.

D. The Scope

It has come evident that combustion of polymers includes a wide range of phenomena depending on the circumstances. Clearly, there is neither a single test which could describe the burning behavior of certain polymeric material nor there is a set of material properties capable to fully predict the combustion behavior.

The scope of this paper is to answer to the questions:

What should we know about materials?

a) concerning their fire safety, to assess the risks in a scientific manner and to minimize them,

b) concerning their combustion by various methods, to assess the environmental effects and to keep pollution level as low as possible?

And which kind of analytical approaches are relevant for answering the two questions above?

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II. CHARACTERISTICS OF BURNING POLYMERS

In this chapter, selected research results concerning the combustion of polymeric materials are given and related research methods and test strategies are shortly discussed.

A. Ignition

For a fire ignition a material has to be heated above its *Critical Heat Flux* value (CHF) which means the minimum heat flux at or below which a meterial cannot generate the combustile mixture. [Tewarson 1995] An other quantity very useful in description of materials fire performance is *Thermal Response Parameter* (TRP) the resistance of material to generate a combustible mixture. The higher the CHF and TRP values, the longer it takes for the material to heat up, ignite, and initiate fire and thus lower the propagation rate [Tewarson 1995].

The TRP depends on material properties: thermal conductivity (k), density (*r*) and spesific heat (C_p), the product of which krC_p is called thermal inertia, [Drysdale 1986a] and of the difference of ignition temperature (T_{ig})above ambient temperature (T_a).

$$TRP = \left(T_{ig} - T_a\right)\sqrt{k\rho C_p} \qquad (1)$$

TRP and CHF are connected to the time of ignition (t_{ig}, s) by following equation:

$$\sqrt{\frac{1}{t_{ig}}} = \frac{\sqrt{4/\pi}\left(\dot{q}_e'' - CHF\right)}{TRP} \qquad (2)$$

where $\dot{q}_e''$ is the external heat flux (kW/m^2) and CHF is in kW/m^2. The CHF value can be determined in a heat release apparatus. In a heat-release apparatus the sample is irradiated by regulated external heat flux and the time to ignition as well as the chemical heat production rate are recorded. By using different external heat flows and recording the ignition times it is possible to determine both CHF and TRP using equations 1 and 2. [Tewarson 1995] has compared three different heat release devices: the Ohio State University's (OSU) heat release rate apparatus, the Factory Mutual Research Corporation's Flammability apparatus and the Cone Calorimeter designed at the National Institute of Standards and Technology. It appears that the parameters CHF and TRP are somewhat dependent of the devices and of the procedure used.

Flash ignition temperature is measured by heating a sample to a temperature at which it ignites on applying an external ignition source. In Table 1 are CHF, TRP, and t_{ign} values measured by the Flammability apparatus and flash ignition temperatures determined by ASTM D 1927-77 (Ignition properties of plastics). The ignition temperature and time are further compared in fig 1. It appears that it is very difficult to find correlation between these two results.

B. Combustion Rate

1. Fire Propagation

The fire propagation is highly dependent on the physical form of burning material. Very thin samples, if not melting and shrinking, burn most quickly. This is because they can't cool their surface by conducting heath in the material. If the surface, in addition, is rough or fluffy (has high specific area) the situation is even worse. As the material is exposed to heat flux from internal and/or external heat sources, a combustible mixture is formed that ignites, and flame anchors itself on the surface in the ignition zone. As the vapors of the material burn in the flame, they release heat with a certain rate defined as the chemical heat release rate. As long as the Critical Heat Flux, Thermal Response Parameter, and gasification requirements of the material are sufficient to move

Table 1. **Critical heat flux, thermal response parameter and ignition times and temperatures for polymers. The t_{ign}s are calculated by Equation 2 and flash-ignition temperatures are measured by ASTM D 1929. [Troitzsch 1983]**

POLYMER	CHF	TRP	t_{ign} /s (50 kW/m^2)	t_{ign} /s (30 kW/m^2)	flash-ign. temperat °C
PE-HD	15	321	66	360	340
PVC	10	194	18	74	390
PP	15	193	24	130	360
PS	13	162	15	72	353
PMMA	11	274	38	159	300
PUR-E lower limits*	13	55	2	8.2	
PUR-E average*	26.5	138	27	1221	
PUR-E upper limits*	40	221	384	Inf	
POM	13	269	42	200	375
PA (Nylon*)	15	270	47	250	420
PC	15	331	70	380	520
FEP(Teflon)	38	682	2537	Inf	525
paper (newspaper)	10	108	6	23	230
wood (Dougls fir)	10	138	9	37	

*exact type of the polymer is not given in the reference

the pyrolysis and the flame front ahead - the fire propagation on surface continues.

2. *Flame Spread Measurements*

Ignition, spread of flame, extinguishing of flame and heat for sustained burning are measured e.g. in the IMO tests [IMO Res. A 653 and 687]. The specimen is exposed to heat radiation the intensity of which decreases towards one end of the specimen according to a defined curve.

Tunnel tests [ASTM E 84] measure the surface flame spread of a material. The specimen is exposed to an ignition source, and the rate at which the flames travel to the end of the specimen is measured. The severity of the exposure and the time a specimen is exposed to the ignition source are the main differences between the tunnel test methods.

Flame spread properties of textiles are measured in the EN ISO 6941 test. The flame spread time of vertically oriented textile fabrics is the time in seconds for a flame to travel between marker threads located at defined distances.

The Underwriters´ Laboratories test method ANSI/UL 94 for product specifications of electrical equipment and installations, subjects a plastics specimen, either in the horizontal or vertical position, to a Bunsen burner type flame. Time to flame extinguishment is measured after repeated burns. The shorter the total times the better the flame retardancy.

Common flame retardancy and flame resistancy tests on electric cables under fire conditions include cable tests on a single vertical insulated wire or cable [IEC 332-1] and on bunched wires or cables [IEC 332-3]. If an electric cable shows no functional trouble after 3 hours at 750°C [IEC 331] it is considered fire resistant.

The NT FIRE 035 test method specifies a procedure to determine the flammability and resistance to smoldering of thermal insulating materials, which may consist of loose-fill granule, beads or fibers. The specimen is inserted in a tray having a plasterboard base and wooden sides. A small wooden crib is placed on the surface and ignited. Observations are made of the occurrence and duration of flaming and smoldering of the

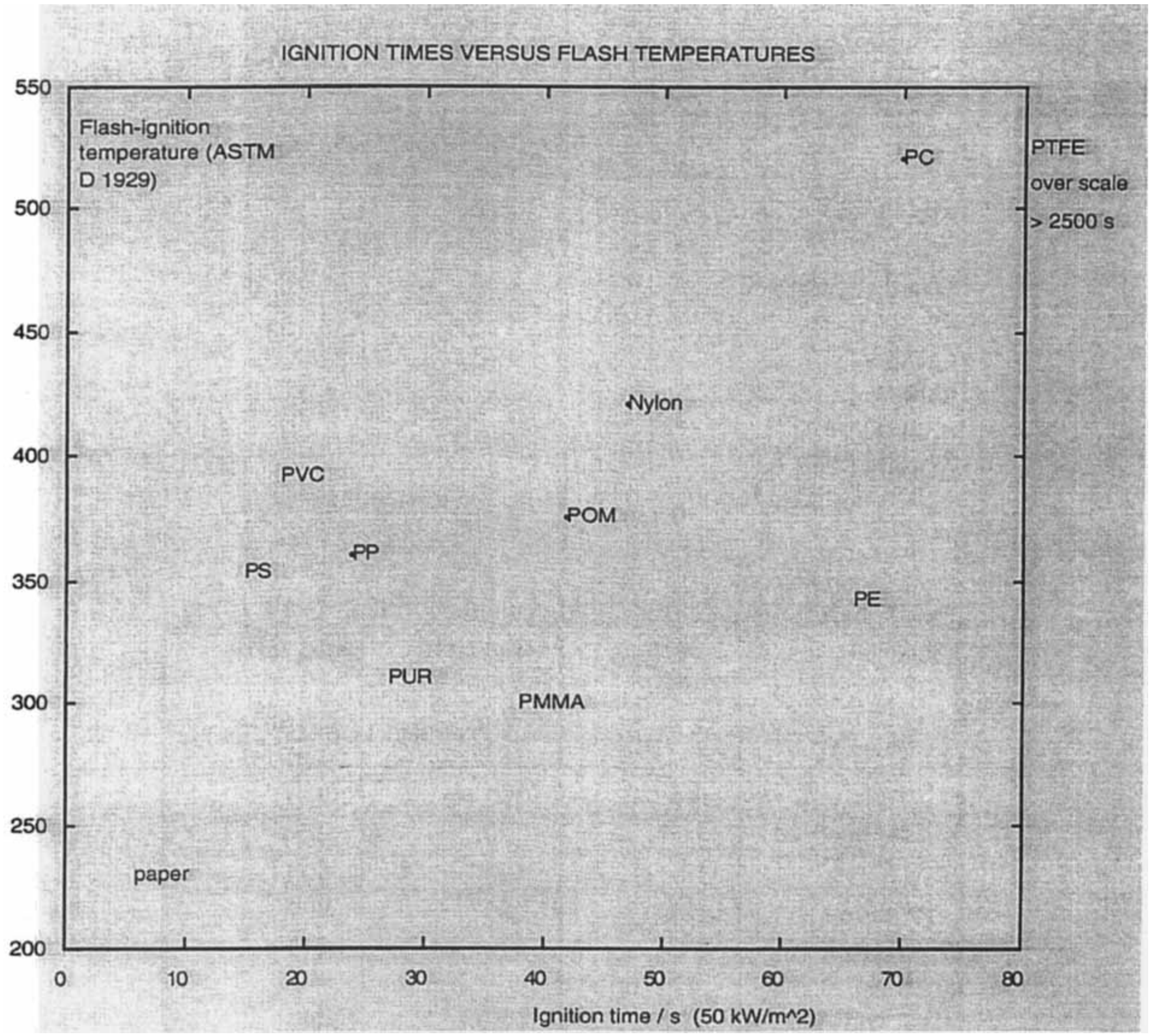

Fig. 1. Ignition temperature on ignition time.

insulation and of the extent of the combustion zone.

3. Mass Burning Rate

The rate of combustion can be presented quite generally as

$$\dot{m}'' = \frac{\dot{Q}''_F - \dot{Q}''_L}{L_V} \qquad (3)$$

where $\dot{Q}''_F$ is the heat flux supplied by the flame and $\dot{Q}''_F$ represents the losses expressed as a heat flux through the fuel surface and $\dot{m}''$ is mass loss rate per unit area. L_V is the heat required to produce the volatiles. [Drysdale1986b] Tewarson and Pion [1976] have determined 'flammability parameters' (parameters of eq (3)) using laboratory experiments. They measured the burning rate under different conditions and defined $\dot{m}''_{ideal}$ "the ideal burning rate", for several polymeric materials. A part of the results is shown in table 2. Ideal refers to a situation where just enough extra heat is added to compensate the heat loss through the surface of the fuel and the oxygen concentration is 21% (that of natural atmosphere). The circumstances of $\dot{m}''_{ideal}$ correspond to "intermediate" fire conditions, possible in real fires, usually during the growth stage [Petrella 1980].

4. Heat Release Rate

Heat release, i.e. the temperature rise, can be measured by NT FIRE 004 where the situation

Table 2. "Flammability parameters"(by Tewarson and Pion 1976)

polymer	L_V	Q''_F	Q''_L	$\dot{m}''_{ideal}$
POM	2.43	38.5	13.8	16
PE	2.32	32.6	26.3	14
PC	2.07	51.9	74.1	25
PP	2.03	28.0	18.8	14
Wood (Douglas fir)	1.82	23.8	23.8	13*
PS	1.76	61.5	50.2	35
PMMA	1.62	38.5	21.3	24
PUR				
rigid foam	1.52			45
flexible foam	1.22			32

* charring material, $\dot{m}''_{ideal}$ taken as the peak burining rate

Table 3. Some results from Mikkola and Kallonen [VTT 1994]

Material	Time to ignition s	Mean RHR (60 s) kW/m^2	Peak RHR kW/m^2
EPS	37	345	410
FR EPS	46	320	380
PS (pellets)	31	780	1005
PP (fibre)	14	440	500
PP (pellets)	29	760	900
Nylon 66 (pellets)	69	590	645
PVC (powder)	47	160	245

somewhat resembles a room lined with the investigated boards in a strongly reduced scale. An actual- size, small room is used in the ISO 9705 Room/Corner test, whereby smoke production is also measured. Rate of heat release and time to ignition (sustained flaming) and smoke production can be measured by the cone calorimeter method [ISO 5660] developed for building products.

C. Smoke and Gas Production

1. Smoke Tests

The test-based smoke production models are inherently related to the input data. Measurements in a flow through-system are dynamic [ASTM E 906, ASTM E 1354, ISO 5660, ISO 9705]. Cumulative or static methods are mainly performed in small scale and in closed systems [ASTM E 662, ISO 5659-2]. Most gas analysis methods give only total production of gases or measure single gases. The FTIR technique can be used to continuously monitor several gas compounds of polyatomic and heteronuclear diatomic molecules [e.g. NT FIRE 047]. IMO Res. MSC. 41(64) uses ISO/DIS 5659 for smoke and toxicity testing.

Measurement of the smoke density of electric cables burning under defined conditions in a 27 m3 chamber is carried out using IEC 1034. Tests on gases evolved during combustion of electric cables measure the amount of halogen acid [IEC 754-1], pH and conductivity [IEC 754-2].

The effect of flame retardants on the combustion products is of increasing concern. Smoke production can be a critical problem in flame retardant formulations. A large percentage of fire victims are overcome as a result of exposure to smoke, toxic gases, and to depleted oxygen levels. The effect of fire retardants on smoke production varies depending on the chemical.

2. Smoke Data

Despite the large number of laboratories using different fire testing methods published smoke data have been scarce. Compilations from cone calorimeter tests have been published for a few materials by Mulholland et al. [1988] and for upholstered furniture materials by Babrauskas and Mulholland [1988]. Examples of smoke data for some building products by Östman and Tsantaridis [1991] are given in Table 4, and by Mikkola and Kallonen [1994] in Table 5.

Tewarson [1988] has collected mass optical density data for various materials. Compilations of gravimetric soot data are available for a smaller range of materials, including some building products. [Östman 1992].A large number of smoke obscuration values have been tabulated by Hirschler [1992]. References to the older literature on smoke evolution has been collected by Hilado and Kosola [1977].

Data on the smoke production of different materials are available mainly from small scale testing (specific optical density, mass optical density). However, when using such data, it should be noted that there are substantial differences for the same or similar materials under similar burning and testing conditions [Östman 1992]. It should be emphasized that these smoke data represent a general level rather than "absolute" properties for different materials and products. Measurement of smoke is essentially dependent on the equipment used, and interpretation of time-dependent curves is not very simple.

3. Gaseous Combustion Products

The situation is even worse with the fire effluent gases. The problem is in selecting a fire model-*i.e.*- test conditions relevant for real fires. The problem is discussed in ISO TR 9122-1 in quite a detail and will be handled here in chapter IV especially concerning the toxicity. Table 6 provides an example of yields of gases measured by Cone calorimetery [Mikkola and Kallonen 1994].

D. Other Tests

1. Oxygen Index (O.I.) Test

One of the most popular ways to assess the flammability of polymers is by the minimum oxygen index (O.I.) test. [ASTM D 2863-77] In the test a specimen is burning with a candle like flame and the oxygen concentration of the ambient air is reduced to the limit where the flame just still exists. This oxygen concentration (measured as the volume fraction in percentage in a mixture of nitrogen and oxygen) is the OI of that particular specimen. The benefits of the method are in the simplicity, ease of execution, small demand of material, and good reproducibility [Seshadri and Williams 1978]. The method has been found to correlate with several flammability tests [Wharton 1981]. However, the test is not usually accepted for fire hazard assessments. Even in the standard is a note: ". .this test should not be used for the description or appraisal of the fire hazard of materials, products, or systems under actual fire conditions." [ASTM D 2863-77]. Instead, O.I. test has been widely used in research and development of flame-retardant fabrics and plastics.

2. Pyrolysis and Thermal Analysis

Although pyrolysis is a part of the combustion process, most studies on polymer pyrolysis have been done for purely analytical reasons without any connection to combustion. Analytical pyrolysis has been widely used in the identification of materials and the determination of the differences in their structures. Pyrolysis is usually carried out with a fast temperature rise to a constant temperature and subsequent gas chromatographic analysis of the volatile pyrolysate. A thor-

Table 4. Smoke extinction area (m^2/kg) from the cone calorimeter. Östman and Tsantaridis [1991]

BUILDING MATERIAL	IRRADIANCE LEVEL 25 kW/m^2	IRRADIANCE LEVEL 50 kW/m^2	IRRADIANCE LEVEL 75 kW/m^2
Rigid polyurethane foam	750	860	-
Textile wall-covering on rock-wool	220	210	290
Insulating fibre board	a)	70	100
Expanded polystyrene	NI	1360	-
Medium density fibre board	a)	80 b)	120
Wood panel (spruce)	a)	a)	80
Paper wall-covering on particle board	a)	a)	70
Particle board	a)	60	90
Melamine-faced particle board	NI	a)	100 b)
Plastic wall-covering on gypsum board	370	60	70
Textile wall-covering on gypsum board	70	30	40
Paper wall-covering on gypsum board	20	30	20
Gypsum board	NI	20	20

a) Test termination according to mass loss criterion of 2.5 g/(m^2s) not obtained

b) Test termination according to mass loss criterion of 2.5 g/(m^2s) not quite obtained

ough description of analytical pyrolysis is given by Irwin [1982]. Analytical pyrolysis has also been used to study the kinetics of thermal degradation. For instance many works of Lehrle and his coworkers (Lehrle et al. [1982], Dean et al. [1989], Bate et al. [1996]) give good examples of an approach of this kind.

Concerning combustion, the pyrolysis of polymers has often been studied by thermoanalytical methods. Thermogravimetry (TG) is the most commonly used of these methods. In TG it is possible to vary the conditions from vacuum to oxidizing environment and from constant temperature to high heating rate.

Table 5. Smoke extinction area from the cone calorimeter at 50 kW/m^2 irradiance level. [Mikkola and Kallonen 1994]

Material	Av. spec. smoke ext. area m^2/kg
EPS	1120
FR EPS	1220
PS (pellets)	990
PP (fibre)	590
PP (pellets)	460
Nylon 66 (pellets)	300
PVC (powder)	890

Table 6. Yields (60 s average) at 50 kW/m^2. Maximum theoretical yield values are indicated in brackets [Mikkola and Kallonen 1994].

Material	CO g/g	CO_2 g/g	HCN g/g	HCl g/g	NO_x g/g	NH_3 g/g	SO_2 g/g
EPS	0.074	1.86 [3.385]					
FR EPS	0.080	1.96 [3.385]					
PS pellets	0.082	2.54 [3.385]					
PP pellets	0.044	3.00 [3.143]					
PP fibre	0.055	2.63 [3.143]					
Nylon 66 pellets	0.028	2.21 [2.336]	0.0026		0.0069	0.0005	
PVC powder	0.043	0.53 [1.408]		0.58 [0.584]			

Note: No value means no production or production below detection limit,
NO_x: NO + NO_2,

The literature concerning the performance and mechanisms of fire retardants in polymers is full of examples of the usefulness of methods of thermal analysis. Camino and Costa [1988] have reviewed the field. The problem is often to evaluate the mechanisms in the gas phase and on the other hand in the solid phase. TG is in routine used for determination of the degradation temperatures and the formation of char. Clearly many other analytical methods together with thermal analysis are needed to study these complicated systems.

Hirschler [1983] has used TG and differential thermal analysis simultaneously with OI measurements on various flame retardant additive systems. He concludes that the thermal analysis can be a very useful guide to the flame-retardant effectiveness of the additives.

Miller, Martin and Turner [1983] have determined the minimum-heating rate required for the ignition of polymers and the initial decomposition temperature at that rate by TG. They found critical heating rates from 380°C min^{-1} (poly(vinyl alcohol)) to 3380°C min^{-1} (wool) for 14 polymers. They further derived an "ignition probability function" which combines the two parameters giving the same weight to both of them. They concluded that their method gives a reasonable ranking, based on general experience.

MacLaury and Schroll [1981] studied the kinetics of the thermal degradation of several polymers with TG and with pyrolysis GC. They could apply heating rates up to 20,000 °C s^{-1} in pyrolysis GC while the highest heating rate in TG was 100 °C min^{-1}. They found some correlation of the apparent activation energy (of degradation) determined by pyrolysis GC and the OI of the polymers. TG results did not show similar correlation. However, they suspect their own results because the pyrolysis products at the highest heating rates were not any more the same.

Brauman, Chen and Matzinger [1983] have studied the degradation of polystyrene under high flux (about 50 kW m^{-2}) of heat. The conditions simulated those of combustion. They obtained similar temperature profiles in the polymer under radiant heat as is obtained under combustion conditions. The surface temperature of the polymer was 446±3 °C in combustion, 447±2 °C in radiant pyrolysis under nitrogen and 437±1 °C in radiant pyrolysis under air. They concluded that pyrolysis under the flame was similar to that in an inert atmosphere. The temperature gradient at the surface was about 63 °C mm^{-1}. Knowing the temperature together with the mass burning rate (mideal=35 g m^{-2} s^{-1} for PS, given by Tewarson , makes it possible to estimate the heating rate. To be able to calculate the velocity of lowering the surface, the density must be known. It can be estimated to 1,100 kg m^{-3}. Dividing the ideal burning rate by density gives the rate 0.0318 mm s^{-1}. Multiplying this by the temperature gradient gives a heating rate of the surface = 2°C s^{-1}.

The important conclusion is that pyrolysis in burning of PS is similar to that in the TG experiment. It was also confirmed by comparison of the pyrolysis products. These observations are contradictory to the often expressed idea that only very high heating rates can be used in studies of combustion.

3. Gas Analysis

There is a wide range of analytical methods for analysis of gas mixtures such as flue gases and fire effluents.

In ISO/TR 9122-3 [1993] are given suitable methods for the analysis of gases and vapours in fire effluents. The technical rapport specifies methods for the individual analysis of airborne concentrations of carbon monoxide (CO), carbon dioxide (CO_2), oxygen (O_2), hydrogen cyanide (CN), hydrogen chloride (HCl), hydrogen bromide (HBr), hydrogen fluoride, (HF), oxides of nitrogen (NO_x), and acrolein (CH_2CHCHO). Most of the gases can be analyzed by gas chromatography. For continuous oxygen measurement is paramagnetic susceptibility measurement a possible method. Titrimetry and ion selective electrodes can be used to analyze hydrogen halogenates. Chemiluminescence is used to analyse oxides of nitrogen.

Fourier transform infrared (FTIR) method can be used to analyze gas mixtures of tens of compounds on ppm-level. [Ahonen, et al. 1996] The multi-component analysis method, which uses known library spectra for calculating the concentrations of the mixture components with their error limits, has been descriped by Saarinen and Kauppinen [1991]. An industrial FTIR gas analyzer can also be used for stock gas continuous emission monitoring as reported by Welch and Herman [1995]. and multicomponent emission measuring system for waste incinerators [Karfilk, and Schmaen 1996].

Several so called hyphenated methods like gas chromatography - mass spectrometry (GC-MS) and gas chromatography - FTIR (GC-FTIR) give improved possibilities of anlysing complex gas mixtures. For example Karjalainen and Kajalainen [1996] have written a book of the data analysis for hyphenated methods. The main part of the book describes the deconvolution of overlapping chromatographic peaks using a deconvolution method called OSCAR (Optimization by

Stepwise Constraints on Alternating Regression) developed by the authors.

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III. FIRE SAFETY ASPECTS

A. Assessment of the Fire Hazard

The assessment of the fire hazard in a real situation is a challenging task and can not be based to certain laboratory-scale material tests only. Assessment of the fire hazard presumes understanding of the fire dynamics and the very many variables affecting to real situation in a fire. This applies for both the risk to humans and the risk to the property. A prime cause of the fire hazard is the use of natural and synthetic flammable materials in buildings and vehicles [Troitzsch 1983]. The positions and uses of flammable materials together with the ignition source, structures and conditions of ventilation all affect to the course of a fire. Especially rates of release of heat, toxic-gases and smoke affect to the ability of humans to escape from a fire. If the fire reaches in a department so called fully developed stage a flash over will occur. It means that the flames have spread over the item first ignited and to the adjacent items, radiation heat flow at the floor level will increase 20 kW/m^2 and the ceiling temperature is approximately 600°C [Drysdale 1986]. In post flashover conditions a lot of carbon monoxide is produced and the spreading fire effluents form a big danger to people in neighboring compartments. The production of the toxic gases depend on the burning conditions, which are highly depend on ventilation, amount of combustibles and their chemical structure.

To be able to predict the course of a potential fire three types of data sources are useful.

1) Careful examinations of real fires.
2) Large-scale fire tests
3) Quantitative laboratory-scale fire performance tests of materials and items.

Combining these data with the engineering knowledge of fire dynamics is the basis of building fire simulations, so called fire scenarios, which make better assessment of the fire hazards possible. Fire scenarios are discussed in more detail in III.D.

B. Laboratory-Scale Tests

The problem of unreliability of the laboratory-scale flammability tests of materials was very clearly demonstrated by [Emmons 1968 and 1974] about three decades ago. In the early 1960's six nations undertook (in cooperation with the International Organization for Standardization, ISO) to a comparison of their national standard tests used to evaluate the flammability of building materials. It was shown that the six national rankings of 24 wall-covering materials, in order of their flammability, indicated very poor correlation between the national tests. Some materials were ranked to opposite ends in different countries.

Flisi [1989] reported later that the situation had improved and even that the national, standard fire tests gave reasonably good estimates of the behavior of materials in real fires, if the room fire test is valid in this sense. Another reason to believe that the fire tests had improved was the fact that the number of fires and civilian victims had decreased [Flisi 1989]. The number of victims by the U.S. statistics has continuously decreased a little from 1980's to 1990's until 1996 when the annual fire fatalities, rose by nearly 11% (from 4700 to 5990 deaths). On the other hand, the annual dollar losses have been increasing all the time from $4709 million in 1977 to $9400 million in 1996 [NFPA 1997].

From the viewpoint of fire safety the testing should give quantitative data about materials, in forms as near to their real use as possible, concerning their potency to participate a fire. The tests measuring the ease of ignition, combustion rate and production of smoke and toxic gases were discussed in previous chapter (II). It should be kept in mind that some "flammability tests" which are widely used as screening tests have little to do with the fire safety, as such, but can be useful in research and development of new products. Clear benefits of the small (or bench) -scale laboratory tests are their lower costs and usually better repeatability compared to the large-scale tests.

C. Large-Scale Tests

Large-scale tests are necessary for testing of materials in 1:1 scale. For instance flame spread and time to flash over can be predicted only in certain conditions basing to laboratory-scale tests that cannot include real flow conditions and interactions of the phenomena in a room space. If for instance the fire scenario is chanced predictions basing to laboratory-scale tests only may fail. At least a compartment or a large part, if not all of a building, is involved to a large-scale test. Large scale tests give basis to estimations of:

- risk of death and injuries to man
- risk to the property

Large-scale tests are increasingly used for building theoretical models. Models that are more realistic can be made because of the rapid increases in computing power and understanding of the fire dynamics. Fire scenarios are to be tested by large-scale tests. As an example a collection of data of small compartment fires with different simple furnishing elements is given by Building and Fire Research Laboratory via Internet [NIST 1997].

D. Fire Scenarios

The basics of fire scenarios were well described already in Fire Safety Aspects of Polymeric Materials [1978]. A more recently-published 'SFEP Handbook of fire protection engineering' [1995] does not use the term "fire scenario" but rather proposes as one of the objectives of the book to "promote wide spread assimilation of computer-based hazard modeling to practical use" [SFPE Handbook 1995].It has, indeed, come possible to make theoretical models of fire which have relevance to real situations. These models consist of relations describing the course of a fire from ignition and growth to possible flash over and fully developed fire, declining fire, and finally the extinction. Constructing of models which simulate real fires demand a lot of knowledge. The basic physical and chemical phenomena are mastered by the use of the knowledge of fire-engineering and fire-dynamics. One of the benefits of the modeling is saving in material costs which are remarkable especially when the amount of the full-scale tests can be limited. However, data collected from full-scale tests and real fires is used to build the models. It is even possible to simulate by the models things which are impossible to test otherwise, like human behavior, and to vary many important variables like the fire performance of the structures and ventilation of the spaces during the simulation. Such models may be called fire scenarios.

It is obvious that the fire scenarios depend of data collected from real situations, large-scale tests and laboratory-scale tests. Computational models are especially useful in the assessment of hazards but they can also be used of optimization of the extinguishing or alarm equipment.

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IV. TOXICITY OF FIRE — EVALUATION OF TOXIC POTENCY OF SMOKE INHALATION

A. Causes of Fire Death

Bowes [1974] reported a four-fold increase in deaths caused by toxic gases and smoke over the period 1955 to 1971. The conclusion was drawn from the UK fire statistics. Later, the increase has been much smaller, but those early statistics had a significant impact on the need to evaluate the toxicity of smoke from different materials. The typical explanation was that the increased use of new, synthetic materials. Other explanations might be that fire loads have increased in typical residences, and/or the reporting of fires had changed, and that actual fires may not have changed as much as appears [ISO/TR 9122-1:1989]. Although large fires that claim many lives receive the most media attention, the majority of fire deaths actually occur in two's and three's in residences[Levin 1992]. According to a 5-year study of 500 residential deaths in the state of Maryland, 80 % of the deaths were due to smoke and toxic gases inhalation and not to direct burns. [Birky et al. 1979]

B. Main Toxicants in Smoke

1. Asphyxiants

Asphyxiants are acute toxicants, which can cause narcosis. They decrease the oxygen availability in the cells (hypoxia). Nervous system is very sensitive to hypoxia and if it is extensive, it leads to the central nervous system depression with loss of consciousness and ultimately death.

a. Carbon Monoxide

CO is undoubtedly the most important toxicant and major threat in fires. Although CO is less toxic than some other gases, it is always very abundant. It combines tightly with hemoglobin in the erythrocytes forming carboxyhemoglobin (COHb). The affinity of CO for hemoglobin is about 240 times more than that of oxygen. If even a quite small part of hemoglobin has been converted to COHb, this has a high impact on the oxygen carrying capacity of blood and the supply of this vital molecule in the peripheral tissues. This hypoxia is called anemic hypoxia.

b. Hydrogen Cyanide

The lethal dose of HCN is approximately 20 times lower than that of CO. The toxicity of cyanide comes from its inhibition of cytochrome oxidase activity by forming a complex with trivalent iron of this enzyme. Cytochrome oxidase has a central role in oxidative phosphorylation (the production of ATP), the decreased energy production rapidly leads to the loss of cellular activities. The brain and heart are very susceptible to this kind of hypoxia that is called histotoxic hypoxia. The respiratory arrest from disturbed central nervous system functionality is usually the cause of cyanide induced death.

c. Decreased Oxygen Concentrations

The fire consumes oxygen and its decreased availability contributes to anemic hypoxia. Low oxygen concentration (10%-13%) causes incapacitation and under 5% death in five minutes. [ISO/TR 9122-1:1989]

d. Carbon Dioxide

Elevated concentration of CO_2 increase respiratory rate and depth - it is mixed to medicinal oxygen to augment the inhalation of oxygen - in fires it increases the intake of toxicants.

2. Irritants

The eyes and respiratory organs are the target organs of irritants in fire. Irritation can interfere with vision because of pain and lachrymation in the eyes. The respiratory tract reacts with a reflex of respiratory rate decrease and a burning sensation in nose, mouth and throat. High concentrations can cause inflammation, swelling in the upper respiratory tract, spasms and bronchoconstriction. Pulmonary hemorrhage and damage in the eyes may occur. The reduced escape capacity is probably the principal hazard caused by irritants in fires. Well-known irritative combustion products are eg. short chain aldehydes (formaldehyde, acetaldehyde, acrolein, etc) and hydrogen chloride.

3. Compounds whose Toxicity is Unknown and Unidentified Compounds

The most common asphyxiants and irritants mentioned above are normally responsible of majority or practically all of the toxic potency of the fire effluents. If, however, unusual chemical structures are abundant in the environment the possible hazard of especially toxic gases may be present. The assessment of such hazards needs usually biological tests. An example of such a case was the production of extremely toxic compounds in pyrolysis of a trimethylolpropane-based rigid-urethane foam treated with a reactive phosphate fire-retardant.[Petajan et al. 1975]

C. Toxicity Evaluation of Fire Effluents

The systematic assessment of the toxicity of smoke began with medical–physiological investigations of Zapp, who reported his results in 1951 [Zapp 1951]. The serious attention to combustion toxicology was raised in 1970s with review articles of Kimmerle [1974] and Birky [1976].

The assessment of the toxicity of smoke has used basically two methodologies –

- bioassay (animal testing) methods supplemented with chemical analysis of certain smoke components
- predictive models, which use only the analytical data on the composition of smoke (supported by the toxicological data of components from earlier animal experiments).

The toxicity of smoke is evaluated in the bioassays by recording the response of test animals (usually rats or mice) which are exposed for a specified period. The most common monitored responses are death and incapacitation (inability to escape fire). The indices, which are calculated after exposures to different concentrations of smoke, are LC_{50} and IC_{50}. The concentrations can be varied either by burning different amounts of material or by using diluting airflow. The lethality index LC_{50} is from the concentration–respose curve statistically calculated concentration, which kills 50 percent of the exposed animals and IC_{50} a corresponding index for incapacitation. The response of the animals depends also on the exposure time. The relationship between the exposure concentration (C) and exposure time (t) is expressed as:

$$Ct = k$$

where k is a constant particular to the exposing agent(s) under study. This relationship, *Haber's rule,* is a generalization, which is valid only under limited conditions. It is widely used, however, in combustion toxicology as well as in other areas of inhalation toxicology of acutely toxic gases. The mathematical models for the evaluation of the toxicity of smoke rely on *Haber's rule.* Toxicity indexes can also be given more generally as ECT_{50} values. ECT_{50} is the mathematical product of time of exposure and efective concentration statistically calculated to cause an effect (e.g. incapacitation or death) in 50% of the animals. This value is useful for comparing results obtained in experimental regimes employing different exposure times. [ISO/TR 9122-2:1990(E)].

The bioassay of sensory irritation is based on the reflex decrease of respiratory rate, which are monitored in mice in body plethysmographs. Mice are used because they are more sensitive than rats, and the sensitivity is closer to that in man. The concentration–response relationship is determined, and RD_{50} value calculated. RD_{50} is the concentration (or the amount of material) that produces 50 percent decrease in respiratory rate Barrow *et al.* 1976.

Even if quite comprehensive evaluation methodologies have been developed, the lethality of the test animals is the choice of toxic response in the practical evaluation of combustion toxicity of materials. The regulations and evaluation standards are based on LC_{50} values.

D. Criticism

There is abundanct criticism on the use of test animals. The debate between the opponents and advocates of the tests is comparable to that in the bio-sciences (for a recent example of this, see Barnard and Kaufman [1997] and Botting and Morrison [1997]. Hartzell [1989] presents the criticisms on the bioassay methods, particularly when they are used for regulatory purposes:

1. The relevance of laboratory combustion methodology to the conditions present in any real fire has not been adequately shown.
2. The applicability of laboratory animal responses to anticipate the conditions of humans being severely compromised in a fire exposure has not been demonstrated sufficiently.
3. The use of live animals for test purposes is opposed (and even prohibited) in many areas of the world.
4. Most materials do not exhibit significant differences in smoke toxicity from the norm
5. The toxic hazard in a real fire depends more on fire growth than on the smoke toxicities of the individual materials being combusted

The limitations of laboratory smoke toxicity tests are summarized in ISO technical Report [ISO/TR 9122–1:1989]:

> "In general, laboratory fire effluent toxicity tests are unable to demonstrate practical quantitative differences between most materials – differences which can be used with confidence for choosing one material over another in the interest of improving fire safety. Experience has shown that most common materials, both natural and synthetic, do not differ widely in the toxicity of fire effluents produced from combustion. Some of the differences observed, though even of statistical significance, are of questionable practical significance from the viewpoint of impact on hazard to life safety in a fire. There are, however, a very few cases of toxic potency found to be greater than the normal spectrum exhibited by most materials. Identification of such a situation appropriately causes the producers of these materials to seek additional performance information for purposes of responsible development and application of their products."

An example of the "very few cases of toxic potency found to be greater than the normal spectrum exhibited by most materials" are Teflon 100® (fluorinated ethylene/fluorinated propylene and Tefzel 200® (ethylene–tetrafluoroethylene). Insufficient quantities of CO, HF and COF_2 were reported from these materials to account for the observed toxicity [Kaplan et al. 1984]. Later it has been suggested that the gas phase in the fluoropolymer fumes does not alone cause the high pulmonary toxicity and mortality, and that the particles generated during the decomposition are also involved in the injury. The particles are ultrafine with a median diameter of ~26 nm. Fresh particles are more toxic than aged particles [Warheit et al. 1990, Lee and Seidel 1991, Oberdörster et al. 1995].

There exists also a small probability that unexpected, hypertoxic decomposition products are formed from certain materials. The well-known, classical example was reported by Petajan et al. [1975] as mentioned above (see IV B.3).

In real fires, the numerous possible combinations of different materials exist, and the formation of unexpected, perhaps very toxic compounds is also possible. The prediction of these hazards is practically impossible either with animal tests or chemical analysis.

The criticism against the use of animal tests has led ISO to propose an international standard which aims to minimize the use of test animals. The procedure is shortly as follows: First the smoke from the material is analyzed for the relevant toxicants (CO, CO_2, HCN, HCl, etc.) and "predicted" LC_{50} is calculated. The calculation is based on the LC_{50} values of the pure gases. After this an "approximate" LC_{50} is confirmed experimentally with a number of animal exposures, usually less than that is to obtain a statistically valid LC_{50}.

Many researchers feel even this proposal unsatisfactory and the use of the animals at all unnecessary because of many uncertainty factors. Some oppose the use of the animals for ethical reasons – and perhaps many for economical reasons. The animal facilities, animal care and the animals are expensive, tests also take a longer time because in addition to conduct the animal exposures, there must be a two-week follow-up period after the exposures to monitor the delayed lethality.

E. Laboratory Smoke Toxicity Testing

1. Fire Models

As defined in [ISO/IEC TR 9122-1 : 1989] *Fire model*: means for the decomposition and/or combustion of test specimens under defined conditions to represent (a) known stage(s) of fire in order to generate fire effluents for toxicity assessments. (This term is also used by the fire science community in the mathematical simulation of fire characteristics.)

Several fire models (furnaces and combustion apparatus used in small-scale testing) are described in [ISO/TR 9122-4: 1993]. Gad [1990] has also published a review on the models. The models are divided to "Box" furnace models, tube furnace models and radiant heat models. It is very difficult, however, by a small-scale test to simulate all conditions of real fire. Actually none of the models satisfy all the criteria. For example it is difficult to maintain conditions for different types of developed flaming fires having relevant atmospheres (Air/fuel and CO_2/CO ratios), temperature and heat fluxes. Despite of these limitations, small-scale tests, being relatively cheap to run, are useful for toxic hazard estimations if their limitations are recognized. The best assessment of toxic hazard consists of a combination of small- and large-scale testing together with appropriate engineering calculations [ISO/TR 9122-4:1993].

Purser [1992] summarizes the results given by the British Standards Institution [1989] as shown in Table 1.

2. Mathematical Models/A Way to Reduce Animal Testing

There is a technical report by ISO [ISO/TR 9122-5:1993(E)] which collects the knowledge of prediction of toxic effects of fire effluents. At first the given effects (incapacitation or death) of single fire gases (or gas mixtures produced by single materials) need to be determined in appropriate conditions to gain the basic toxicological data. After collecting the basic data it is possible to estimate the effects of fire effluents in different

Table 1. Toxicity data for common materials in fire obtained using a number of small and large-scale test protocols.

fire conditions	range / g min m-3	aproximate average / g min m-3	characteristics (note the variation of about two orders)
non-flaming	60-2120	720	CO, irritants, medium toxicity
early, well ventilated	72-3750	1100	low CO/CO2, lowest toxicity
vitiated, post-flashover	21-3000	611	high CO and CN, highest toxicity

situations where many materials are involved and many gases are affecting simultaneously.

The overall principle for the fractional effective dose (FED) for n separate toxicants can be written as:

$$FED = \sum_{i=1}^{n} \int_0^t \frac{C_i}{(Ct)_i} dt \qquad (1)$$

Where $(C\,t)_i$ is is a constant dose required for a given toxic effect, C_i is the concentration of the gas component i (possibly a mixture of gases produced by one material). In the mass loss models calculations are based to the knowledge of the volume in which the gases are diluted and the mass burning rate of the materials as a function of time. The time at which FED comes unity is the time of exposure which would be expected to result in 50% effect.

The more sophisticated models use analyzed concentrations of the major toxic compounds. This approach makes predictions of toxic effects based upon chemical analysis of the primary combustion products in the fire effluent along with knowledge of toxic effects and toxic interactions of these products. An example of such a model is the N-Gas Model [Levin et al. 1994]. It takes account the effects of seven gases (CO, CO_2, O_2, HCN, HCL, Hbr and NO_2). The predictions based on bench-scale laboratory tests have been verified with full-scale room burns of a limited number of materials of widely differing characteristics chosen to challenge the system. The predicted toxic potency is checked with a small number of animal tests. Benefits of such method are:

1) The number of test animals is minimized,
2) smoke may be produced under conditions that simulate the fire scenarion of concern,
3) fever tests are needed which means savings in costs
4) information is obtained on both the toxic potency of the smoke and the responsible gases [Levin et al. 1994].

Purser [1992] summarizes the three parameters determining the development of hazard to life from toxic products in a full-scale fire:

1. The fire growth curve in terms of the mass-loss rate of the fuel (kg/s) and the volume into which it is dispersed (kg/m3)
2. The yield of toxic products in the fire (for example, kg CO per kg of material burned)
3. The toxic potency of the products (the exposure dose (kg min m^{-3}) needed to cause toxic effects).

Toxicant dose methods require that the concentrations of individual gases must be measured accurately enough. There are many possibilities to do so some of which are listed in ISO/TR 9122-3:1993(E). The rapid development of instrumentation make it possible to utilize so called hyphenated techniques like GC-MS and multi-component analysis to resolve mixture data. FTIR devices with appropriate data handling systems are capable of analyzing tens of compounds from mixture spectra on a ppm level [Ahonen & al. 1996].

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V. FIRE AND FLAME RETARDANTS {FRS}

PREFACE

In this literature survey, fire retardancy is discussed mainly in terms of chemical treatments, based on research results published in the literature. This chapter is an abridgement of Sarvaranta's report "Fire retardant wood, polymer and textile materials, VTT Research Notes 1730, 1996 [Sarvaranta 1996] with minor additions.

A. INTRODUCTION

1. FR materials and Products

Improvement of fire properties of polymeric materials would enhance their use in new applications, especially in buildings, and increase the fire safety of living. E.g., because of safety requirements, flame-retardant plastics are essential for electric and electronic equipment. Flame retardant textiles find use in many applications ranging from furnishing fabrics to firemen's protective clothing. In addition, the intumescent coatings are used to protect wood, plastics and even steel from the heat of fires.

Flame retardant or fire retardant (FR) materials and products are supposed to produce "slower" fires. In principle, FR products may be obtained through chemical or structural means. There are, however, no theoretical or systematic approaches to the "slow fire performance". A number of adjectives have been used to describe a product having a low contribution to a fire [Gann 1994]. Non-quantitative terms such as fireproof, flameproof, self-extinguishing, non-burning, and noncombustible have been used. Systematic knowledge of the requirements for effective flame retardants or fire retardants, mainly considered for wood, plastics and textiles, is still lacking.

There is some confusion in terminology. The terms "flame retardant" or "fire retardant" are used in a rather arbitrary way in literature to describe various mechanisms. A common solution is to use the abbreviation "FR". According to a definition by Nussbaum [1993], "flame retardants" affect fire parameters related to the material surface such as: time to ignition, surface spread of flame and smoke production. They are thus protective in the initial stage of a fire. "Fire retardants" refer to protection in the fully-developed fire when structures start to char. The most important parameters are charring rate and char yield, i.e. the amount of char produced. This applies to charring materials. Although the heat of combustion of a material does not change, flame or fire retardants reduce the rate of heat release and extend the time at which the heat release becomes measurable [LeVan 1984].

FR agents may be halogen-containing (Br, Cl) with or without antimony trioxide (Sb2O3), organophosphorous, or nitrogen-containing. Inorganic compounds are also used (e.g. Al(OH)3, Mg(OH)2, H3BO3, ZnSn(OH)6, ammonium polyphosphate, red phosphorus). In principle, the same chemical compounds known to be effective as flame-retardants have also been used as fire retardants, although different properties may be of interest [Nussbaum 1993].

2. Scope

The scope of this section is to discuss different aspects of fire retardancy of materials and products, mainly in terms of chemical treatments of solid wood, polymers and textiles.

B. Fire Retardants

1. Different Fire Retardants - Different Modes of Action

According to a patent analysis, from 1980 to 1990, 536 patents related to fire-retardant chemicals and compositions were identified [Anon. 1991]. Depending on their nature, fire retardants can act chemically and/or physically in the solid, liquid or gas phase [Troitzsch 1990]. They interfere with the combustion during a particular stage of this process, e.g. during heating, decomposition, ignition or flame spread. It is universally accepted that fire retardants which inhibit the combustion process by chemical action are more effective than those which act by physical means. In many cases, however, the boundary between chemical and physical effects is so indistinct that it is difficult to evaluate their respective contributions. There is a trend towards synergistic combinations of retardants which are effective in smaller concentrations [Edshammer 1995].

2. Chemical Action

a. Reactions in the Solid Phase

Here two types of reaction can take place. First, breakdown of the polymer can be accelerated by the flame retardant, causing pronounced flow on the polymer and, hence, its' withdrawal from the sphere of influence of the flame which breaks away. Second, the flame retardant can cause a layer of carbon to form on the polymer surface. This can occur, for example, because of the dehydrating action of the flame-retardants' generation of double-bonds in the polymer. These form the carbonaceous layer by cyclizing and cross-linking. In addition, fire retardant chemicals lower the heat content of the combustible volatiles when the amount of char is increased and the amount of volatiles is reduced.

b. Reactions in the Gas Phase

Fire retardant chemicals release free radical inhibitors at pyrolytic temperatures, and the radical mechanism of the combustion process - which takes place in the gas phase- is interrupted by the flame retardant. The exothermic processes are thus retarded, the system cools and the supply of flammable gases is reduced.

3. Physical Action

a. By Cooling

Endothermic processes triggered by additives cool the substrate to a temperature below that required for sustaining the combustion process.

b. By Formation of a Protective Layer (Coating)

The condensed combustible layer can be shielded from the gaseous phase with a solid or gaseous layer. The condensed phase is thus cooled, smaller quantities of pyrolysis gases are evolved, the oxygen necessary for the combustion process is excluded and heat transfer is impeded.

c. By Dilution

The incorporation of inert substances (e.g. fillers) and additives, which evolve inert gases on decomposition, dilutes the fuel in the solid and gaseous phases.

4. Intumescent Coatings

Intumescent, fire- protection coatings are systems which puff up to produce foams. They are used to protect wood and plastics which are combustible and steel materials which lose strength when exposed to high temperatures [Troitzsch 1990]. Intumescent components may also be incorporated in the polymer matrix. The intumescent effect is achieved by using the following components:

a) Acid source: Salts of phosphoric acid, like ammonium phosphate or ammonium polyphosphate, liberate acid on which they are based at temperatures above 150°C, and dehydration and charring of the carbonific compound start.

b) Carbonific compounds: Polyhydroxy compounds (pentaerythritol, starch and phenolic or urea resins) dehydrate and char due to acid attack.

c) Spumific compounds: Under the effect of temperature, blowing agents such as chloroparaffins, melamine, and guanidine liberate large quantities of noncombustible gases (HCl, NH_3, CO_2) and ensure the formation of the carbonaceous foam layer over the substrate.

d) Resin binders: These cover the foam with a skin which prevents the gases from escaping- *e.g.*- chlorinated rubbers soften and melt at low temperatures, act as blowing agents and contribute to charring.

Ideally, the foam is 50 to 100 times as thick as the original intumescent layer, resulting in good thermal insulation and thus protecting the substrate from the effects of heat and decomposition.

C. Fire Retardant Wood

1. General Requirements

Most fire retardants used for wood increase the dehydration reactions that occur during thermal degradation so that more char and fewer combustible volatiles are produced. Special interest has been laid on dual-purpose fire retardants, e.g. combinations of preservative and fire retardant effects.

Fire retardant treatments for wood can be classified into two general classes: (1) those impregnated into the wood or incorporated into wood composite products, and (2) those applied as paint or surface coatings [LeVan 1984]. The surface coatings for wooden products may be non-intumescent or intumescent [Hirano et al. 1989]. Still, relatively little is known about the effects of treatment techniques and outdoor use and about the toxicity of smoke gases from flame retarded wood products. Fire retardants often tend to increase smoke production but this may be compensated by the decreased spread of flame.

Coatings are applied easily and they are economical. Their use has been limited primarily to materials in existing construction [LeVan 1984]. A coating is subject to abrasion or wear that can destroy the effectiveness of the fire retardant. Onsite application of surface coatings requires strict control of the amount applied to ensure correct loading levels.

Chemical impregnation usually involves full-cell pressure treatment and can be costly [LeVan 1984]. Impregnation may be used especially for new materials, prior to installation. Chemical impregnations deposit the fire retardant within the wood, so that if the surface is abraded chemicals are still present.

2. Fire Retardant Chemicals

Both coating and impregnation systems are based on the same chemical compounds, although the formulations for each vary [LeVan 1984]. Most formulations are based on empirical investigations for best overall performance and they include e.g. phosphates, nitrogen compounds, borates, aluminum hydroxide, silicates, and amino-resins. These compounds reduce the flame spread of wood but may have adverse effects on strength, hygroscopicity, durability, machinability, toxicity, gluability, and paintability. They are mostly applied by impregnation of the wood at large retentions, 10 - 20% by weight [Nussbaum 1993]. Some typical fire retardants for cellulosic materials are given in Table V.1. Phosphorus-containing fire retardants mainly influence the reactions taking place in the condensed phase. The fire retardant is converted to phosphoric acid which in the condensed phase extracts water from the pyrolysing substrate, causing it to char [Troitzsch 1990]. Phosphorus and nitrogen are frequently used together because they behave synergistically. A shortcoming of many inorganic salt-based formulations is that they are not resistant to leaching by water. Some of them can draw moisture into the timber and this not only leads to the decay of the wood itself, but also to the deterioration of metal fittings and building components [Morley 1991]. Some of the proposed leach-resistant systems include chemical combinations that form insoluble complexes, amino-resin systems, and monomers that polymerise in the wood [LeVan 1984].

Common barriers include sodium silicates and coatings that intumesce (puff and form a cellular structure that remains attached to the substrate).

The exact role free radicals play in the combustion of wood is not known. Halogens such as bromine and chlorine are good free radical inhibitors, but generally large amounts of halogen are required (15 - 30% by weight) to attain a practical degree of fire retardancy [LeVan 1984].

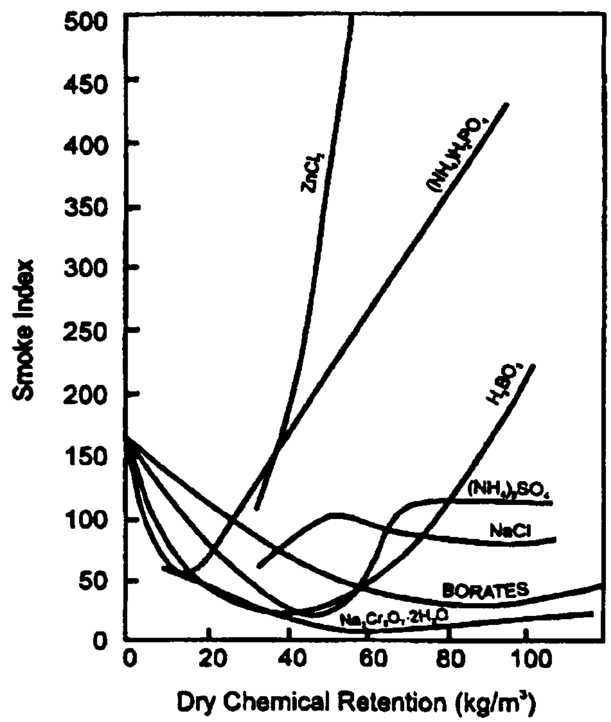
TABLE 1. Typical fire retardant chemicals for cellulosic materials [Hirano et al. 1989, Gann 1994].

Types	Chemicals
Halogenated compounds	Tetra bromobisphenol A (TBA) Deca bromodiphenyl oxide Octabromophenyl ether Tetra bromodiphenyl ether Polychloroparaffin
Organophosphorous compounds	Phosphate esters Polyphosphate
Halogenated organophosphorous compounds	Tetrakis-(hydroxymethyl)-phosphonium chloride (THPC) Trisdichloropropyl phosphate (TDCP)
Inorganic compounds	Borates (boric acid, borax) Antimony trioxide Aluminium hydroxide Magnesium hydroxide Guanidine derivative Red phosphorous derivative

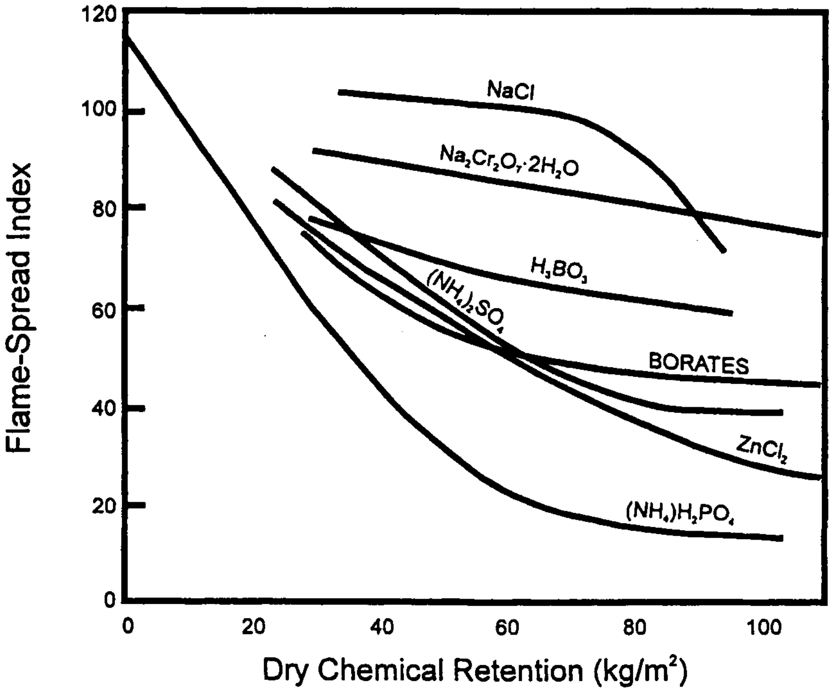
Fire retardants may alter fuel production by increasing the amount of char and reducing the amount of volatile, combustible vapours. They may also lower the temperature at which active pyrolysis occurs and enhance condensation of the char to form cross-linked and thermally stable polycyclic aromatic structures. It seems that fire-retardant chemicals inhibit the formation of levoglucosan (1,6-anhydroglucopyranose), a major volatile fraction obtained from the thermal degradation of cellulose [LeVan 1984].

3. Examples

Some examples of earlier studies are briefly discussed in the following. The effect of a fire retardant on smoke production varies depending on the type and amount of the chemical. This is demonstrated in Figure V.1. where the smoke index values were obtained from a tunnel test (ASTM E 84). However, the smoke values measured in different types of tests may not agree or correlate.



Sec. 5. Fig. 1. Effect of inorganic additives on smoke index of wood, measured in 8-ft tunnel according to Eickner & Schaffer [LeVan 1984].

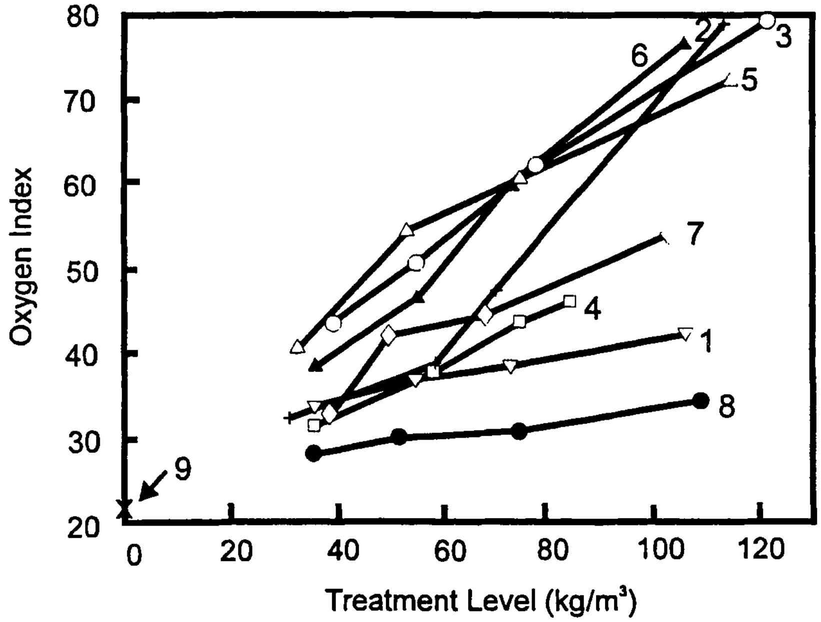


Sec. 5. Fig. 2. Effect of inorganic additives on flame-spread index of wood, measured in 8-ft tunnel according to Eickner & Schaffer [LeVan 1984].

The surface flame spread may be affected by varying types and amounts of inorganic additives, as shown in Figure V.2, where the values were obtained from a tunnel test (ASTM E 84). Figure V.3. shows the effect of chemical retention levels on the oxygen index value (ISO 4589) for different chemical treatments on Douglas fir. However, the relation between higher oxygen index and less flammable samples has not been verified for real fires.

Recently, heat release in the cone calorimeter was compared for fire retardant treated and untreated wood products [Östman & Tsantaridis 1994]. The test results show significant differences between these two groups. The wood based products were also tested in different small-scale Nordic national standard fire tests and in the full-scale room fire test. Fire retardant treated wood products achieved an improved classification both in present national systems and in possible new systems based on the cone calorimeter [ISO 5660] and the room fire test [ISO 9705].

Various chemical additives and their combinations have been applied to decrease the fire hazard of cellulosic insulation materials [Day & Wiles 1978, Day & Wiles 1979 a., Day & Wiles 1979 b.]. Many of the flame retardant chemicals are used as glow retardants for cellulosic textiles. However, Day and Wiles found that boric acid (H_3BO_3) and ammonium sulphate ($(NH_4)_2SO_4$) worked as smoulder retardants at 24% treatment levels but borax ($Na_2B_4O_7 \cdot 10H_2O$), which is known to be an effective flame retardant, did not have any effect on smouldering. Sodium phosphate and sodium chloride enhanced the smouldering tendency. To imporove the overall fire performance both flame retardants and smoulder retardants must be used. Therefor, borax is often added to cellulosic insulation materials. The minimum concentration of boric acid in a smoulder retardant cellulosic insulation was found to be 11.6% + 0.185% x concentration of borax in %.



Sec. 5. Fig. 3. Effect of fire retardant chemicals on oxygen index of wood according to White [LeVan 1984]. Key: 1 ammonium sulphate; 2 sodium tetraborate decahydrate; 3 disodium octaborate tetrahydrate; 4 boric acid; 5 monoammonium phosphate; 6 ammonium polyphosphate; 7 zinc chloride; 8 sodium dichromate; 9 untreated.

D. Fire Retardant Plastics

1. General Requirements

Stringent fire performance requirements have to be met by plastics. In many cases this can only be achieved by incorporating flame retardants [Troitzsch 1990]. The same sort of basically "trial and error" approach which has been used to render wood and other cellulosic materials less flammable has been adopted in the case of synthetic polymers [Cullis & Hirschler 1981]. In contrast to other additives, flame retardants can impair the properties of plastics appreciably. The problem is to find a compromise between the decrease in performance of the plastics caused by the flame retardant and the desired improvement in fire safety [Troitzsch 1990].

A distinction is made between reactive and additive flame retardants [Troitzsch 1990]. Combinations of flame retardants may produce a synergistic effect of great importance for practical use.

Reactive flame-retardants, mainly in thermosets (especially polyesters, epoxy resins and polyurethanes), are built chemically into the polymer molecule, together with the other starting components. This prevents them from bleeding out of the polymer and volatilising and their flame retardance is thus retained.

Additive flame retardants, especially in thermoplastics, are incorporated either prior to, during, or following polymerisation. They may act as plasticizers or fillers. Unless they are oligomeric or polymeric, they are sometimes volatile or tend to bleed so their flame retardance may be gradually lost.

2. Flame Retardant Chemicals

a. Halogen Containing Compounds

Halogen-containing flame-retardants mainly act in the gas phase. However, several authors point out that halogen-containing flame-retardants are effective also in the condensed phase [Troitzsch 1990]. Bromine is more effective than chlorine since its weaker bonding to carbon enables it to interfere at a more favorable point in the combustion process. It is assumed that HBr is liberated over a narrow temperature range so that it is available at a higher concentration in the flame zone. HCl, which is formed over a wider temperature range and is present at lower concentrations, is thus less effective. Since bromine compounds can be used in smaller concentrations than chlorine compounds, they affect the properties of the polymer material less. However, they exhibit poor stability to light.

Halogen atoms can be bound aliphatically or aromatically in flame-retardants. Their suitability depends on the plastic and method of incorporation. The more effective aliphatic halogen compounds are easier to break down and hence are less temperature resistant than aromatic retardants.

Sb_2O_3 shows no perceptible flame-retardant action on its own but together with halogen-containing compounds it produces a marked synergistic effect.

b. Phosphorous Compounds

Phosphorus-containing flame-retardants are particularly effective in materials with high oxygen content (cellulose, polyurethanes, polyester resins). They are mainly active in the condensed phase but there is evidence that they can also be effective in the gas phase [Troitzsch 1990].

c. Inorganic Compounds

Few inorganic compounds are suitable for use as flame-retardants in plastics, since such compounds must be effective in the range of decomposition temperatures of plastics. This range lies between 150°C and 400°C [Troitzsch 1990].

The most widely used inorganic flame-retardants are aluminum hydroxide, magnesium hydroxide and boron-containing compounds. $Al(OH)_3$ and $Mg(OH)_2$ also act as smoke suppressants for polyolefins. Chalk acts mainly as filler but it also acts by diluting the effect of highly filled plastics materials, reducing the amount of combustible material available per unit volume and thus reducing combustibility.

Aluminium hydroxide is low cost and easy to incorporate into plastics. It starts to break down in the temperature range 180°C to 200°C. The decomposition process is endothermic with water release. $Al(OH)_3$ is used in ethylene vinyl acetate and polyethylene compounds in applications where compounding and processing conditions are below 200°C [Molesky 1991].

Magnesium hydroxide has been used as an alternative in polyolefins. The flame retardant mechanism is based partly on its endothermic decomposition with water release at about 330°C. The net effect of various factors is a marked reduction in the rates of heat transmission from the flame to the matrix [Hornsby & Watson 1989]. Significant reductions have been observed in the rate and level of smoke evolved from ABS, modified polyphenylene oxide and polybutylene terephtalate compositions containing $Mg(OH)_2$, together with substantial increases of oxygen index.

At appropriate levels, $Mg(OH)_2$ has been shown suitable for polypropylene and elastomers [Molesky 1991, Wiklund 1992].

Wiklund [1992] tested FR compounds based on halogen flame retardants, intumescent FR systems and magnesium hydroxide. Fire properties were evaluated by using ANSI/UL 94, oxygen index and cone calorimeter measurements. The highly filled PP-$Mg(OH)_2$ compound gave interesting properties of high stiffness with excellent impact properties. Its smoke density and CO concentration were the lowest of the compounds tested.

3. Smoke Emissions

If the flame retardants act in the gas phase by interrupting the radical chain mechanism, they almost always contribute to an increase in smoke levels since they suppress the oxidation reactions occurring during combustion and promote soot formation [Troitzsch 1990]. Flame-retardants that are effective in the gas phase are used mainly in thermoplastics and cause dense smoke development even in polymers which of themselves inherently emit relatively little smoke.

Systems which act in the condensed phase by e.g. crosslinking or protecting the substrate by coating, limit the formation of gaseous decomposition products and act simultaneously as flame retardants and smoke suppressants. They are of particular interest for thermoplastics which normally do not char (e.g. polystyrene).

It is difficult to provide flexible polyurethane foams with a really effective fire retardant treatment since factors such as open cell structure, low degree of cross-linking and chemical structure impair the flame retardant effect [Troitzsch 1990]. The use of flame-retardants introduces a whole series of effects detrimental to the properties of the foam, including reduced resistance to heat and hydrolysis and increased smoke evolution.

Smoke data regarding FR treated materials or products are scarce. The overall impression with flexible polyurethane foams treated with bromine-based and phosphorus/chlorine-based FR agents has been that the resistance to small ignition sources is improved, while actual fire performance, once ignited, is not much changed [Babrauskas 1992]. With polystyrene foams the rate of heat release was found to be unchanged and ignitability was actually made worse. A systematic study by Jarvis et al. [Babrauskas 1992] showed that with PP and PMMA treated with organobromine/antimony oxide the modest benefits were outweighed by the roughly doubled emissions of toxic gases, smoke and soot. However, significant reductions have been observed in the rate and level of smoke evolved from ABS, modified polyphenylene oxide and polybutylene terephtalate compositions containing $Mg(OH)_2$.

Bench-scale, Cone calorimeter data [Babrauskas 1992] clearly showed substantial improvements in heat release performance at irradiance level 30 - 100 kW/m^2 with some selected plastics products treated with different FR agents. The yields of smoke and toxic gases, however, were in many cases higher. In real-scale tests it was demonstrated that if sufficiently effective FR agents are used, any effects of increased yields of smoke are more than compensated by decreased burning rates of polymeric materials. At the moment, however, there is no single universal predictive technique for knowing whether an FR agent being used *is* a sufficiently effective FR agent.

E. Fire Retardant Textiles

1. General Requirements

Special performance qualities for flame-retardants in textiles are required [Wyss 1990]. These include flame-retardants which are resistant to removal by repeated laundering or dry cleaning, which do not adversely affect hands or drapes and do not present potential health hazards.

2. Flame Retardant Chemicals

Man-made fibres may be chemically engineered in a flame-retardant form. This can be achieved through a number of approaches [Holme 1993, Horrocks 1993]:

a. By inherently flame retardant fibres, where either the chemical structure is flame retardant (e.g. chlorofibres and fluorofibres) or such that it does not break down to form combustible molecular fragments. Examples: aramide, polyamide-imide, polyimide, phenolic resins, polyacrylonitrile, semi-carbon, polyphenylene-sulphide, fluorocarbon and chlorofibres.
b. By incorporation of phosphorous and/or halogen based comonomers in the polymer (e.g. modacrylic and polyester) prior to fibre extrusion.
c. By incorporating organophosphorous and nitrogen- or sulphur-containing species, polysilisic acid and complexes, or brominated organic compounds in the spinning dope and/or spinning bath during fibre spinning (e.g. viscose, polypropylene).
d. By application of organophosphorous and nitrogen-containing monomeric or reactive species, antimony-organo-halogen systems, or zirconium hexafluoride complexes during textile finishing operations (e.g. cotton and wool).

In each case the nature and amounts of smoke, toxic gases and irritants will vary, according to the conditions under which burning takes place [Holme 1993].

3. Upholstered Furniture

The flammability of upholstered furniture has been an issue of constant concern to consumer safety and fire protection groups [Gandhi & Spivak 1993]. This concern has not diminished since the number of fires related to upholstered furniture remains high. The flammability character of upholstered furniture depends on many factors, of which the types of material and the construction of the furniture are of paramount importance. The range of materials used for upholstery has also increased over the past 10 to 20 years with greater use of synthetic fibres, blends, polyurethane foam paddings and barrier materials. Moreover, usage of fibres in cover fabrics tends to change according to consumer taste and preference. A vast European research programme on the fire behaviour of upholstered furniture was conducted recently [Sundström 1995]. The research was dedicated to the post-ignition behaviour of furniture.

F. Fire Retardant Chemicals Markets

Worldwide, the consumption of flame retardants in plastics and other combustible materials is closely linked to regulations covering fire precautions [Troitzsch 1990]. The principal regulations relate to the building, transportation, electrical engineering, furnishing and mining sectors. Fire retardant treatments on wood, in particular, are often done by small enterprisers [Anon. 1990 b.]. To avoid trouble chemical manufacturers should keep a close eye on the commercial uses of the products.

The total US market for flame retardant chemicals was estimated at $ 513 million in 1993 [Anon. 1993]. In 1991 the US consumption was estimated at 300,000 t [Gann 1994]. Plastics used about 77% of all flame retardants [Caney 1992]. Engineering plastics, primarily used in the electronics industry where most flame retardant polymers are required, include polycarbonate, polypropylene, polyamide and polyethylene terephtalate (PET) [Wyss 1990]. In 1991 roughly 9% of sales were to the wood and paper industries, 8% to the coatings industry, and 6% to the textile industry, which over ten years ago accounted for 32% of the market [Caney 1992]. The market for flame retardants in textiles is relatively small and also highly fragmented among a variety of end uses.

The principal groups of flame retardant chemicals and their relative markets in the USA are listed in Table 2. The data are collected from various sources and are partly incomplete.

In Western Europe, accurate figures for consumption of flame retardants are not available [Troitzsch 1990]. The following estimates for some flame retardants date back to 1985 - 1986:

aluminium hydroxide 1986:	40,000 - 50,000 t
antimony trioxide 1985:	10,000 - 12,000 t
boron compounds 1985:	2,000 - 3,000 t

Data from Japan is also sparse [Troitzsch 1990]. Annual consumption of aluminum hydroxide has been estimated to 20,000 - 30,000 t.

It has been estimated that the total annual production of fire-retardant, textile fibers in the USA, Japan and EU amounts to 400,000 t [Nousiainen 1992]. Thus, 40,000 - 50,000 t of flame retardant chemicals are annually consumed for textile purposes.

G. Health and Environment

1. Issues under Debate

There is an ongoing debate over the possible risks of halogenated, especially brominated, fire retardants [Caney 1992, Gann 1994, Troitzsch 1994]. Certain chloroparaffins and antimony trioxide have also been mentioned but the main impact lies on the PBBs (polybrominated biphenyls) and PBDEs (polybrominated diphenyl ethers, often referred to as PBBEs). They are persistent, may accumulate in the fatty tissue and, under specific conditions, lead to formation of PBDDs (polybrominated dibenzodioxins) and PBDFs (polybrominated dibenzofurans).

The issues under debate are the following:

a. Toxic smoke is produced when halogenated combustibles burn. However, it has been emphasized that if the fire retardant significantly decreases the burning rate of the products, the reductions in smoke and heat yields are more important to survivability than a modest increase in the toxic potency of

Table 2. Principal groups of flame retardant chemicals and their market shares in the USA [Anon. 1993, Anon. 1994 a., Gann 1994]. About 77% is consumed by plastics [Caney 1992).

Group	1991 1000 t	1991 million $	1993 million $	1998 million $ *
Bromine-based			181	253
Aluminium hydroxide	25	85	100 *	122
Chlorine-based			85	99
Phosphorus-based			72	96
Magnesium hydroxide	3	6	8	
Antimony trioxide	25	85		
Borates	8	10		
Total	301	510	513	658

* estimated

smoke. (The level of "modesty" has not been defined.)

b. Corrosive smoke is produced when halogenated combustibles burn, resulting in additional damage to electronic components, etc.

c. Incineration of halogenated combustibles may produce dioxin- and furan-like species. Likewise, if dioxin- and furan-like species evolve in a building fire, cleaning the building afterwards will be costly.

Another factor potentially affecting the market for halogenated flame retardants is the waste disposal of fire retardant materials and products [Gann 1994]. As landfill availability declines or becomes less popular, the remaining two alternatives are incineration and recycling. The nature of the combustion products from halogenated products requires careful construction and maintenace of incinerators to avoid damage to the incinerator itself and a public health hazard from the exhaust. The ease or difficulties of recycling also have a potential effect on the use of fire retardants.

Life cycle analyses are needed to ensure the market potential of new fire retardant products. The goal of using environmentally friendly flame retardant systems is a worthy objective [Holme 1993]. Perceivement of this by the consumer should in turn lead to a greater market share for companies that demonstrate their initiative and expertise in the environmental field.

2. Steps Taken by Authorities

In Germany, for certain areas of building, electrical engineering and transportation, products containing PBBs or PBDEs are no longer accepted by authorities or industry [Troitzsch 1994]. In the UK these flame retardants are seen in a rather positive light, because for furniture PBDEs cannot yet be substituted and furniture must meet stringent UK fire regulations. In the Netherlands steps have been taken to reduce the use of PBBs and PBDEs [Anon. 1994 c.]. In Switzerland the production, import and use of PBB is forbidden. Nordic Environmental Labelling in Finland, Iceland, Norway and Sweden have restricted the use of PBBs and PBDEs in housing and the chassis of computers [Anon. 1994 c., Anon. 1995 b.]. Use of PBBs is not allowed in textiles which come into contact with skin [Anon. 1994 c].

H. Summary

Fire performance of a material is not a material property since it may be influenced by various factors. This is also true of the secondary effects of fire such as the production of smoke and toxic gases. Nevertheless, material properties, and in particular chemical characteristics, play an important role in fire performance and smoke levels.

A multiplicity of test methods for measuring the reaction to fire performance of construction and other materials are currently in use in the member states of the European Union and other countries [EGOLF 1994]. While there may be a continuing short-term need to rationalise current test methods, there is a general recognition that the future is likely to lie with measurement techniques which provide more fundamental information on the fire performance of a material than that required for classification alone. The move towards a single European market has focused attention on the differences in regulatory requirements, design practices and performance standards that exist throughout Europe.

Increased efforts to expand the use of wood products in public buildings may require wood to be treated with fire retardants [LeVan 1984]. Therefore, considerable research on fire retardant treatments for wood has been carried out. Most fire retardants used for wood increase the dehydration reactions that occur during thermal degradation so that more char and fewer combustible volatiles are produced. However, they may have adverse effects on strength, hygroscopicity, durability, machinability, toxicity, gluability, and paintablity.

Stringent fire performance requirements have to be met by plastics. In many cases this can only be achieved by incorporating flame retardants. In contrast to other additives, flame retardants can impair the properties of plastics appreciably. The problem is to find a compromise between the decrease in performance of the plastics caused by the flame retardant and the desired improvement in fire safety [Troitzsch 1990].

Flame retardant textiles find use in many applications ranging from furnishing fabrics to firemen´s protective clothing. Special performance qualities for flame retardants in textiles include flame retardants which are resistant to removal by repeated laundering or dry cleaning, which do not adversely affect hands or drapes and do not present potential health hazards [Wyss 1990].

There is a trend towards synergistic combinations of retardants which are effective in smaller concentrations [Edshammer 1995]. Special interest has been laid on dual purpose flame retardants. The total US market for flame retardant chemicals was estimated at $ 513 million in 1993 [Anon. 1993]. In 1991 the US consumption was estimated at 300,000 t [Gann 1994]. Plastics used about 77% of all flame retardants [Caney 1992]. Roughly 9% of sales were to the wood and paper industries, 8% to the coatings industry, and 6% to the textile industry [Caney 1992]. In Western Europe, total annual consumption of aluminium hydroxide, antimony trioxide and boron flame retardants has been estimated at 60,000 - 70,000 t [Troitzsch 1990]. In Japan, annual consumption of aluminium hydroxide has been estimated at around 20,000 - 30,000 t. Total annual consumption of fire retardant chemicals for textile fibres in the USA, Japan and the EU amounts to 40,000 - 50,000 t [Nousiainen 1992].

There is an ongoing debate over the possible risks of halogenated, especially brominated, fire retardants [Caney 1992, Gann 1994, Troitzsch 1994]. Certain chloroparaffins and antimony trioxide have also been mentioned but the main impact lies on the PBBs and PBDEs.

For the future, further work is necessary on the fundamental mechanisms of individual flame retardants. These mechanisms are a function of the particular chemicals involved and the environmental conditions of the fire exposure. In particular, improved leach resistance will be necessary to expand wood products into public buildings. Life cycle analyses are needed to ensure the market potential of new fire retardant products. The goal of using environmentally friendly flame retardant systems is a worthy objective [Holme 1993]. Perceivement of this by the consumer should in turn lead to a greater market share for companies that demonstrate their initiative and expertise in the environmental field.

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VI. ENERGY RECOVERY FROM POLYMERIC MATERIALS

A. Introduction

Increasing production and use of synthetic materials has led to increased levels of these materials in human-derived waste streams. The increased level of polymeric materials in waste, especially plastics and rubber fractions, has led to the situation where the high calorific value and the composition of the fuel gives problems in conventional waste incineration [Bryers, 1991; Mosbacher, 1990)]. At the same time, the energy recovery from waste through more efficient and optimised firing is increasingly replacing conventional waste incineration methods, where volume reduction was the major objective. Moreover, since bio-degradable wastes produce greenhouse gases during landfill, the combustion of these wastes is also considered carbon dioxide neutral.

It must be noted that the classification 'waste' merely gives a description of the value of a material or product with respect to specific human needs. Many types of waste can therefore in some way or another be recycled either as the same product (e.g. bottles) or in the form of the material from which the product was originally produced. For the waste fraction that does not allow for further economically sensible material recovery (recycling), energy recovery by combustion is probably the only alternative to landfill. This especially holds when dealing with high calorific waste fractions which show little bio-degradability such as plastics.

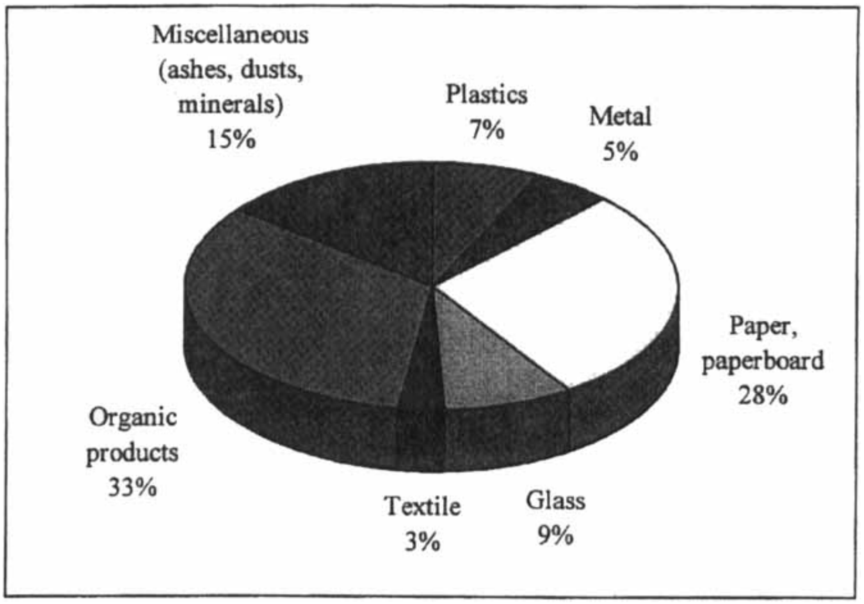
When fired in better suitable systems electrical efficiencies near 40% can be reached, as opposed to a mere 22% from conventional waste incineration. Also the co-combustion or co-gasification of wastes such as sewage sludges and refuse-derived fuel (RDF) with coal is receiving increased attention. A concise, world-wide overview on efforts towards mono-combustion of plastics waste, the co-combustion of plastics waste with coal, wood, sewage sludge and municipal solid waste (MSW) and the pyrolysis and gasification of plastics waste is given by Brossa [1995] and Harding et al. [1996]. Co-firing of coal and waste was recently reviewed by IEA Coal Research [Morrison, 1996]. Most pyrolysis and gasification processes for plastics waste in general aim at chemical recovery, energy recovery being a secondary benefit [e.g Redepenning, 1994, Schiffer and Adlhoch, 1995, Hodek et al., 1995].

The composition of MSW in Western Europe (in 1992) is given in Figure VI.1. This shows that considerable amounts of polymeric materials are present : the total of plastics, paper and paperboard, and textiles adds up to 38%. Depending on separation methods a compostable organic fraction, a non-combustible fraction and a refuse-derived fuel (RDF) can be obtained. A separately collected mixture of paper and plastics packaging material is referred to as packaging derived fuel (PDF). To illustrate the potential of the various waste streams for thermal power generation, the proximate analysis and calorific value are given in Table VI.1.

Base-plastics consumption in Western Europe is illustrated by Figure VI.2, which shows thatthermoplasts represent almost 90% of the plastics used. The properties of the main components are included in Table VI.1, distinguishing between polyvinyl chloride and some other thermoplasts.

Considering the combustion (or gasification) characteristics of a combustible solid, the fuel can produce a combustible condensed residue (charring fuel) or not (non-charring fuel), besides the generation of an inert ash residue. In general, the man-made thermoplasts, thermosets and rubbers produce no ash and are more volatile than natural polymers such as biomass and solid fossil fuels. Some building materials, like floor coverings, however, may contain considerable amounts of inorganic fillers.

In the following text the emphasis lies with the energy recovery from plastics and rubber, or MSW, RDF and PDF in general, and less with biomass and solid fossil fuels. Besides combustion, gasification and pyrolysis will only be discussed marginally.



Sec. 6. Fig. 1. The composition of municipal waste in Western Europe, 1992. (source: APME, 1994. picture from Karlsson, 1995).

B. Energy Recovery: An Alternative to Materials Recycling

1. Conventional Waste Incineration

Since the 1960s grate firing of municipal waste is standard practice, supported by a long experience of coal combustion for thermal power and electricity production. Currently in a typical western society, most of the waste, however, is still disposed of through landfill. (An exeption is Japan, where already in 1985 more than 70% of the waste was incinerated [Kotani and Mikawa, 1988]. Approximately 30% of the household waste and hazardous waste and most of the sludges are being disposed of by thermal treatment. In more than 90% of the cases means grate-firing and combustion in multiple-hearth furnaces, the rest (including the sludges) being processed in rotary kiln. Due to increasingly strict legislation a current thermal waste treatment plant combines the main thermal process with an increasingly important flue gas treatment section which is more heavily burdened than the gas cleaning section of a fossil fuel fired power plant of the same thermal capacity. Currently, the improvements in waste incineration processes lie with [Scholz et al., 1995; Cheremisinoff and Ferrante, 1989]:

- exhaust gas volume reduction and down-scaling of gas cleaning facilities
- improved energy efficiency (which is 22% for conventional grate firing of MSW)
- improved material recycling from the feedstock

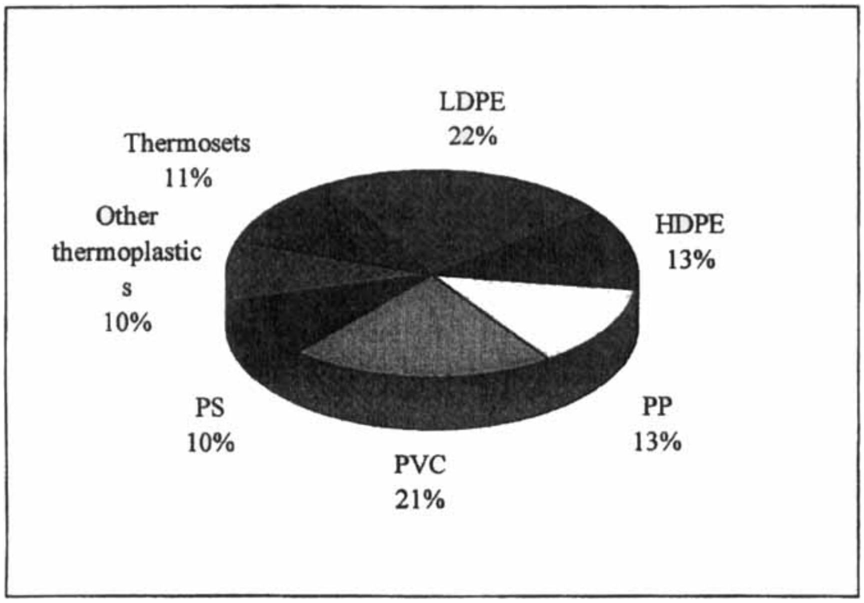
This led to various processes in which pyrolysis (air excess ratio = 0), gasification (<1) and combustion (>1) steps are combined, in attempt to reduce noxious emissions, obtain better temperature control and better burnout. In fact, many of these incinerator + post-combustion processes can be performed in a single, fluidized bed reactor [Anthony, 1995; Saxena and Jothsi, 1994]. Here, the freeboard above the fluidized bed provides the necessary reactor volume for post- combustion. Other reactor types that are under investigation for thermal waste treatment are e.g. blast furnaces [Janz, 1996]. As an illustration, three reactor types for waste-derived fuel combustion, being a rotary kiln, a bubbling fluidized bed (BFB) and a circulating fluidized bed (CFB) are shown in Figure VI.3.

Table VI.1 Typical proximate analysis* and calorific values** for the polymeric materials and wastes discussed in this section, as compared to a coal

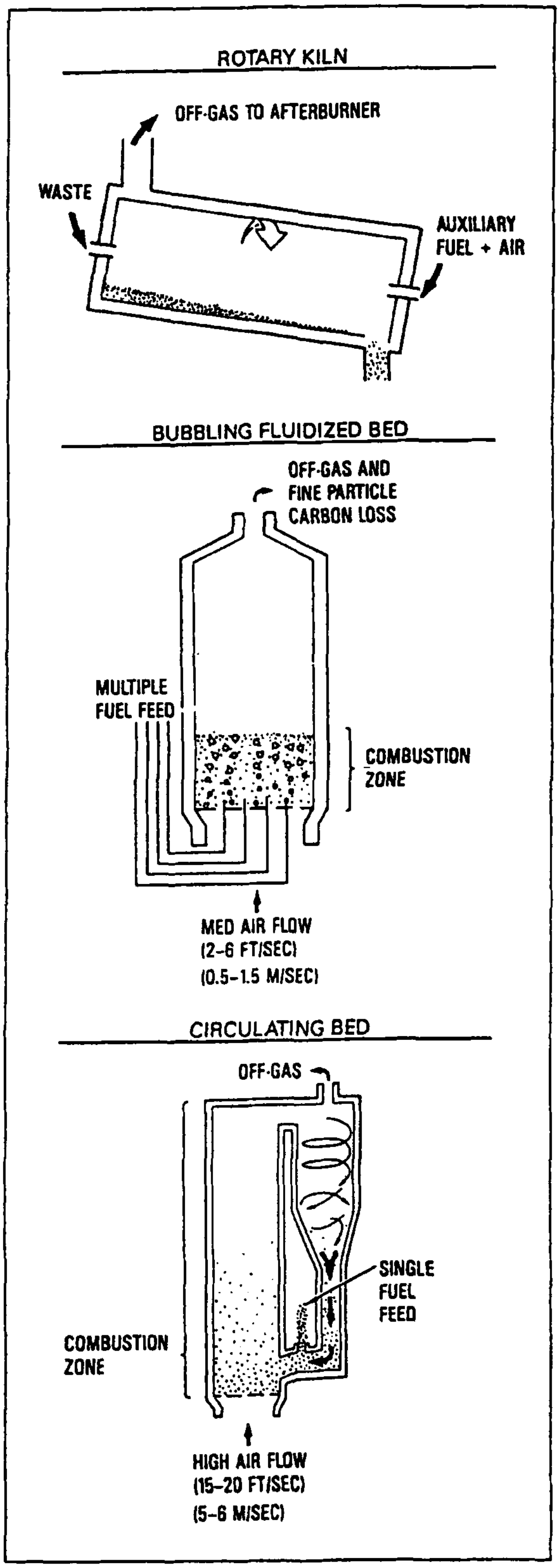
	Volatiles %wt	Moisture %wt	Fixed carbon %wt	Ash %wt	HHV MJ/kg
High volatile bituminous coal	30	5	45	20	26
Wood	85	5	15	1	19
Rubber (Car Tire Scrap)	65	2	30	3	37
PE, PP, PS (not printed)	100	0	0	0	45
PE, PP, PS (colored, printed)	98	0	0	2	41
PVC (53.8 %wt chlorine)	93	0	7	0	21
Paper	75	4	11	10	13
Municipal Solid Waste MSW	33	40	7	20	10
Refuse-Derived Fuel RDF	60	20	8	12	15
Packaging Derived Fuel PDF	73	1	3	13	21

*Proximate analysis is a relatively low-cost procedure which gives a description of a combustible solid or liquid material as moisture (water release upon heating to 105°C), volatiles (release of material upon heating in a non-oxidising atmosphere to, e.g., 900°C), ash (residue after combustion of the material in air at, e.g., 815°C, and fixed carbon,found from determining the carbon content in the residue after drying and volatiles release. In general fixed carbon is given 'by difference', i.e. 100%-moisture % - ash % - volatiles %. [see e.g. DIN 1978a,b,c].

** The calorific value is found from measuring the heat release upon combustion in a bomb calorimeter. The difference between LHV and HHV (lower and higher heating value, respectively) is merely that HHV includes condensation of water vapor released.



Sec. 6. Fig. 2. The distribution of plastics consumption in Western Europe, 1992. (source: APME, 1994. picture from Karlsson, 1995).



Sec. 6. Fig. 3. Most widely used reactors for waste-derived fuel combustion (picture from Rickman et al., 1985).

2. Fuel Preparation from Waste

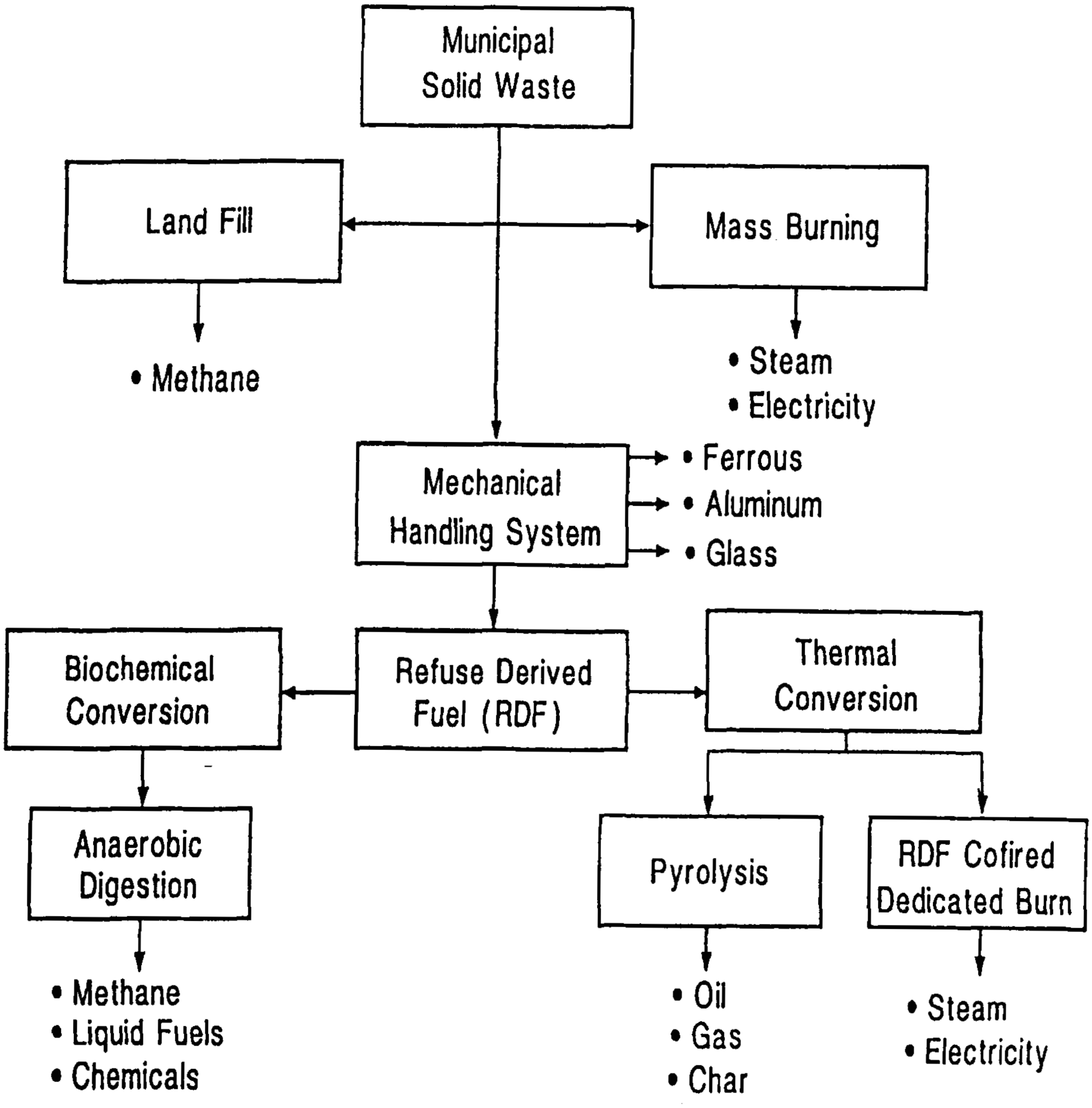
In most cases, a waste stream that contains a combustible fraction is not considered a fuel but is thermally treated ('incinerated') mainly to achieve a huge volume reduction. Waste streams that do not allow for any form of energy recovery, such as old cars and building rubble will not be considered here.The remaining waste stream can be divided into three sections : household wastes, hazardous wastes (mainly from industry and hospitals) and sludges, which in Western countries are generated roughly at a ratio 100:60:200, although it is noted that sludges in general contain only 5%wt solid mass in water [Scholz et al., 1995].

From the viewpoint of energy recovery, municipal waste can be separated into fractions with increased plastics and other polymers content : MSW → RDF → PDF → segregated plastics. Whilst the volume reduction leads to volume ratios 100 → 40 → 10 → 1, the energy content of the fractions decreases only according to 100 → 80 → 35 → 4 [Frankenhaeuser in: Bemtgen et al., 1994]. The segregated plastics fraction is, however, more suitable for material recycling than for energy recovery.

When energy recovery from wastes becomes a major objective for thermal waste treatment, a higher fraction of combustibles in the waste is required as compared to conventional waste incineration methods, in general. In fact, the waste has to be upgraded to a refuse-derived fuel (RDF). Figure VI.4 gives an optional energy and material recovery scheme for MSW [Walter et al., 1988].

A fluidized bed reactor requires a higher level of fuel homogenation (pelletising) than e.g. a rotary kiln furnace. Waste pre-treatment is largely a series of physical processes. Metals are removed from waste using magnetic separation and eddy current separation, other fractions in general must be separated manually. The average calorific value of household waste lies around 10 MJ/kg, which increases to 15 MJ/kg when compostables and non-combustibles are removed (giving RDF), see Table VI.1.

Upgrading a fuel by removing (inert) fractions results in more fluctuating fuel properties, which is more problematic in mono- combustion



Sec. 6. Fig. 4. An energy and material recovery scheme for MSW. (picture from Walter et al., 1988).

or gasification than when the waste-fuel is mixed with another fuel, such as coal, wood or peat. Fuel moisture content has a large influence on adiabatic flame temperature and thus on thermal power efficiency of a combustor. In addition, reducing particle size allows for a reduction in the excess air ratio that is needed in order to reach the combustion temperature which at the same time reduces the amount of flue gas.

The concept of waste as a fuel is discussed by McGowin [1985], who notes that mainly non-technical barriers hinder its spread. Moreover, without additional legislative impulses (such as CO_2 tax on non-renewable fuels), energy recovery from waste is only economically sensible in densily populated areas, where transport and collection do not bring in excessive waste processing costs. In Japan, for example these costs exceeded 65% [Kotani and Mikawa, 1985].

Currently, the waste-to-fuel upgrading appears to pose more problems than the thermal treatment of waste in a reactor that is more suitable for energy recovery. At the moment the furnace capacity largely exceeds the capacity of equipment for pelletising RDF or PDF for fluidized bed (co-) combustion [see e.g. Lankert, 1988], the same holds for the production of car tire scrap from waste tires.

3. Mono-Combustion vs. Co-combustion

Conventional waste incineration is still most important mono-combustion method for waste combustion. As mentioned above this, however, leads to low thermal efficiency and high peak temperatures in the furnace when too high mass fractions of high-calorific value materials are present in the fuel input. These increase the amount of volatile combustibles that may result in operational problems when heat exchange surface is not located at the right position in the furnace [Zevenhoven et al., 1997].

Since the contents of waste-derived fuels are very variable as compared to more conventional fuels, the easiest way to avoid difficulties is co-firing of these two types of fuels [Harding et al., 1996]. Even in a fuel-flexible furnace as a fluidized bed reactor, co-firing is applied in most cases [Patel et al., 1994; McCarthy and Colville, 1991]. Depending on the amount of thermal power produced in the form of steam, a bubbling or circulating fluidized bed (BFB or CFB) furnace can be used. Although a CFB is more suitable for co-combustion than a BFB, selecting a CFB requires a steam output of 50000 kilo per hour, i.e. aprox. 20 MWth. CFB incineration of (hazardous) wastes is also discussed by Rickman et al. [1985], reporting that especially the turbulence level makes the combustion in this type of boiler superior to others.

In the US, the first fluidized bed boiler (two BFB units which combust up to 300 tonnes per day producing 12 Mwth from approx. 550 tonnes of RDF per day) became operational in 1995 [Murphy, 1995, 1994]. In Sweden a similar scale CFB is fired with pure RDF nly during the summer, otherwise as co-firing with peat or wood waste [Patel et al., 1994, Hallström and Karlsson, 1990].

An important aspect in fluidized bed co-combustion of PDF or RDF is related to ash sintering. The combination of inorganic residue (ash) from the base fuel (coal, peat, wood) and the plastics-derived fuel, together with the bed material, can lead to the formation of low melting chemicals which increase the sintering tendency of the fluidized bed [Skrifvars et al., 1996]. When the problem is related to the use of sand or quartz as the bed material, the use of alumina will reduce the interaction between bed material and ashes from the fuels.

Kraft [1995] describes a Fast Internal Circulating Bed (FICB) for chipped (50 mm) car tire scrap. Due to the form in which fuel nitrogen is present in the fuel, NO control technologies that work well for fossil fuel fired systems, appear not to work. The FICB process was also described by Steinrück [1989]. An example of an integrated process of waste densification, pyrolysis and (oxygen) gasification is the so-called Thermoselect process [Gäng et al., 1996].

C. Fuel Properties of Polymeric Materials

1. Plastics

The goal of the major part of the work reported in literature on the thermal decomposition of plastics so far was to retrieve monomers or other valuable products through thermal processes in various types of reactors. In that work the temperature levels and heating rates were generally lower than in technical combustion systems [Kaminsky, 1992; Darivakis et al., 1990; Scott et al., 1993; Redepenning, 1994; Wey et al., 1997]. The production of liquid products by thermal decomposition of polymers in a fluidized bed at temperatures up to 850°C was extensively studied in the US [Sharp et al., 1994].

Mechanisms for thermal decomposition of plastics and pyrolysis product compositions have been given by Cullis and Hirschler [1981]. The pyrolysis of PE was found to give alkanes and alkenes, whilst PP gave a very small amount of its monomer during pyrolysis. PS yields more than 50% styrene during pyrolysis, together with its dimers and trimers. The pyrolysis of PVC gives HCl, aromatic hydrocarbons (e.g. benzene) plus a considerable amount of char. Elomaa [1991] also reported the soot formation tendency of PVC and PS. Kaminsky [1992] found up to 56% HCl and 9% solid char residue resulting from pyrolysis of PVC in a fluidized bed at 740°C. Under the same conditions PS gave 65% styrene and 0.6% solid residue, for PE and PP the solid residues found were 1.8% and 1.6% of the initial mass, respectively. Darivakis et al. [1990] pyrolysed PE and PS samples at a heating rate of 1000 K/s and report a complete pyrolysis without solid residue for final temperatures above 700°C.

A fundamental study on polymer pyrolysis, addressing PMMA, PE and PS was conducted by Khalturinskii [1987], who gave activation energies of 160, 147, and 190 kJ/mol for degradation of these materials, respectively. Branderup and Immergut [1975] report higher values, i.e. 200-300 kJ/mol for most plastics and a much lower 85-140 kJ/mol for PVC. The latter could explain the relatively short pyrolys and faster ignition of PVC when compared with other plastics as reported by Zevenhoven et al. [1997].

Kinetic parameters for PVC pyrolysis and PVC co-pyrolysis with PE, PS and poly (amide 6) are reported by Knümann and Bockhorn [1994], including a 2-step mechanism for PVC. Kinetic paremeters for PE / PS mixture pyrolysis are given by Koo and Kim [1993], using five different reaction schemes for modelling.

Panagiotou and Levendis [1994] investigated the combustion properties of PS, PVC, PE and PP. Spherical particles with a size from 53 to 300 µm were burnt at 930-1230°C in 21%, 50% and 100% oxygen in an atmospheric drop-tube furnace. Time required for combustion was found comparable to that of an equally sized droplet of light oil. PVC and PS burned with a luminous yellow flame, giving a lot of soot. PVC was reported to give the shortest time for combustion, whilst PE and PP appeared to burn slower and with a less clear flame. Wheatley et al. [1993] investigated the combustion of powdered PS, PE, PP, PMMA and PVC and monitored the emission of principal organic hazardous compounds (POHCs), especially polynuclear aromatic hydrocarbons (PAHs), in order to correlate emissions and combustion parameters. This showed high soot levels with PS and PVC, the latter forming a char residue.

The destruction of unburned hydrocarbons increased with temperature and residence time.

Thermal degradation of PVC has been studied intensivelyfor decades. For instance O'Mara [1977] proved the intramolecular nature of the dehydrochlorination. Evaluation of aromatic compounds in themal decomposition of vinyl polymers was studied systematically by Ballistreri et al. [1980]. Benzene formation mechanism was descriped by Bellenger et al.[1982]. PVC releases HCl at relatively low temperatures beween 200 and 300°C. Clorine is stripped out almost quatitatively as HCl in the intramolecular degradation process which also produces some benzene. The polymer backbone converts to conjagated polyenen structure which decomposes further to benzene and polyaromatic compunds at around 350°C. As an other result of aromatization of the diene structure is tendence of forming char.

McGhee et al. [1995] gave a very simple model for the pyrolysis of municipal waste based on co-pyrolysis tests with PVC and cellulose-based material. It was concluded that co-pyrolysis gives an increased amount of solid char residue with a lower reactivity as compared to the char residue of the separate materials. Pyrolysis of RDF at temperatures between 500 and 900°C was recently reported on by Cozzani et al. [1996, 1995]. It was found that interactions between RDF components (plastics, paper and cardboard, wood-like materials) can be neglected with respect to solid- phase reactions. It was also stated that methane and light hydrocarbons are formed in gas-phase reactions at sufficiently high temperatures. The effect of PVC in co-firing of high-sulfur coals with refuse-derived fuel was studied by Lu et al. [1996] by TGA/FTIR/MS.

Wey and Chang [1995] analysed the incineration kinetics of PP, PE, HDPE and ABS (acrylonitrile-butadiene-styrene) particles (8-20 mm) at temperatures ranging from 571 to 775°C. At this temperature level it was found that the time to ignition was the rate controlling mechanism. Due to the relatively low temperatures, accumulating combustible gases tended to give explosive behaviour. The combustion of the plastics considered here could be modelled using a vaporising fuel droplet combustion model, following an approach by Spalding [see e.g. Kuo, 1986; Williams, 1985].

Zevenhoven et al. [1997] analysed the combustion and gasification characteristics of several thermoplasts at 750-950°C, at 1 bar and 25 bar.

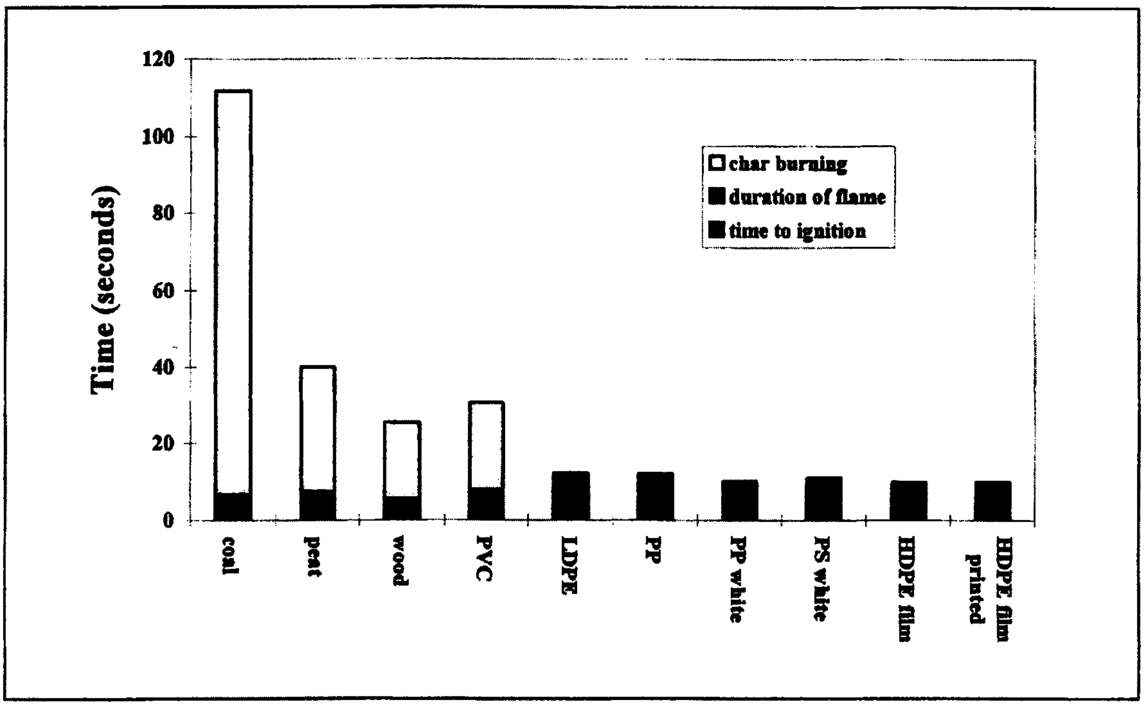
These characteristics were compared with coal, peat and wood, a result of this is given in Figure VI.5. It was found that only PVC produced a carbonaceous residue after pyrolysis, which consisted for more than 99% of carbon. The reactivity of this 'char' is comparable to that of char from coal. The other plastics studied burned completely during devolatilisation and volatiles burnout, i.e. like oil droplets.

Recent work by Conesa et al. [1997, 1994] focuses on the products of pyrolysis of various types of PE in a fluidized bed reactor. Correlations between methane and other products are given. Gaseous products yields increase in the range 500-800°C.

The specific problems related to poly urethane pyrolysis, a thermoset, are discussed by Takamoto and Petrich [1994]. The extremely viscous liquid product from primary pyrolysis makes secondary pyrolysis, using activated carbon, necessary.

Frankenhaeuser [1995; Frankenhaeuser et al., 1995, 1994, 1993] investigated the co-combustion of PDF and RDF with coal, peat and wood in a full-scale circulating fluidized bed combustor (65 MWth). Tests showed no significant harmful side-effects with respect to pollution as compared to firing with conventional fuel. Emissions (less than 500 mg $SO_2/m3_{STP}$ and less than 200 mg $NO_2/m3_{STP}$) were of the same level as obtained from conventional fuels although HCl emissions increased with increasing chloride content in the fuel mixture. It was also found that the emissions of poly-chlorinated di-benso-p-dioxines and di-benso-furanes (PCDD/F) did not correlate with the chlorine content of the fuel mixture, but were more related to the combustion process conditions. Fuel sulphur appeared to have a clear reducing effect on PCDD/F emissions. This was also found with limestone added to the bed for the capture of SO_2 and HCl [Kojo, 1992], giving increased PCDD/F concentrations in the ash. No increased levels in corrosion were found [Frankenhaeuser et al., 1995].

More recently, Huotari and Vesterinen [1996], while studying RDF co-combustion in six fluidized bed combustors (15 kW - 117 MW), reported a relation between fuel chlorine and PCDD/F emissions, which were below acceptable levels at a fuel chlorine content below 0.3% (dry weight).



Sec. 6. Fig. 5. Comparison of the duration of stages in combustion for 50-mg fuel samples in oxygen/nitrogen 7%/93%, at 850°C. (picture from Zevenhoven et al., 1997).

Air staging for NO reduction causes a shift in PCDD/F concentration from the gas phase to the ash. Increased combustion temperature and residence time both decreased PCDD/F concentrations. Manninen [1996] reports a correlation between PCDD/F and the contents of Cr, Cu, Sn and especially Pb in the fuel, studying RDF and PDF co-combustion in a 7 MW bubbling fluidized bed combustor and a 65 MW circulating fluidized bed combustor, respectively. Increased fuel chlorine content gave increased HCl emissions, which did not, however, correlate with PCDD/F levels.

The thermal decomposition of poly (vinylidene chloride) in air at temperatures up to 500°C was investigated by Yasuhara and Morita [1988]. Even at temperatures as low as 200°C, significant amounts of chlorinated organic compounds, especially furanes, were found. It is suggested that poly (vinylidene chloride) is an intermediate in the formation of polychlorinated bi-phenyls (PCBs) and naphtalenes (PCNs).

The co-gasification of municipal waste and wood in an atmospheric fluidized bed was investigated by Czernik et al. [1994] Wood waste and wood waste containing 10% PE and RDF were gasified at 50 kg/h. The facility operated satisfactorily at 700-850°C, producing 1.7-2.4 $m3_{STP}$ dry gas / kg dry solids, at a calorific value of 5.2-8.2 $MJ/m3_{STP}$.

The presence of PAHs in soot from PS, PP and wood combustion was studied by Elomaa and Saharinen [1991], showing identical orders of magnitudes for these three fuels. The amount of soot, however, was much higher for PS than wood. Interesting was that the quite different chemical structures of wood and thermoplasts led to PAH profiles resembling each other.

2. Rubber

In waste, rubber occurs mainly in the form of car tires. Car tires are discarded at a rate of almost a billion pieces per year worldwide. Tires are discarded mainly into landfill sites, the markets for reuse after re-treading are very small. The enormous fuel potential of this waste stream is being hindered by the wires in the tires which produce iron clinkers after melting or 'birdnests' at lower temperatures. A practical problem is the costly process of cutting the car tires to smaller pieces, which is often done cryogenically.

A fundamental comparison study for pulverised coal and pulverised waste tire combustion at 1170 K was recently reported by Atal and Levendis [1995]. This high temperature level was chosen since at lower temperatures incomplete burnout and significant PAH production occurs. It was found that the tire particles burn partly during a volatile combustion process which is similar to a coal particle, followed by a char burnout stage which is considerably faster than for a coal char particle of similar size.

An analysis on car tire scrap pyrolysis by Williams and Besler [1995] shows that char yields around 31% wt are obtained from devolatilisation in nitrogen, mainly being carbon black. It was found that natural rubber, styrene-butadiene rubber and polybutadiene rubber, the major rubber components in car tires, decompose at different temperature levels between 350 and 550°C.

Karlsson et al [1996] reports a characterization of car tire scrap as compared to bituminous coal in laboratory furnaces in the temperature range 800 - 1000°C. The aim was to verify the suitability of car tire scrap as a substitute fuel in a cement kiln. It was found that under pyrolysis in nitrogen most of the fuel-nitrogen leaves the fuel (as NO, HCN and NH3) whilst the fuel-sulphur remained in the char, at a char solid yield of 31%. NO production levels were in the order of 90 mg per 100 grammes of car tire scrap, which corresponds to approx. 28% of the fuel-nitrogen.

Avenell et al. [1996] described a pyrolysis process for car tire scrap which, at 50% fuel excess with air, yielded significant amounts of acetylene. The char however is, due to its high ash content, unsuitable as a feedstock for activated carbon, but could serve in heavy metal removal from waste water. The optimum pyrolysis temperature range reported is 600-730°C, minimising tar release and energy consumption.

Recently, Conesa et al. [1996] reported gaseous products amounts and compositions from scrap tire pyrolysis in a fluidized bed. Quantitative modelling work on vacuum pyrolysis of car tire scrap in the temperature range 450-800°C is reported by Yang et al. [1995a,b].

3. Wood and Solid Fossil Fuels

Wood can be regareded as bio-polymer which is composed of cellulose, lignin and hemicellulose, roughly distributed as a ratio 2:1:1, on a dry basis. Due to the high fraction of cellulose, fundamental research on the thermal decomposition of wood is largely directed towards this compund [e.g. Antal and Varhegy, 1995; Milosavljevic and Suuberg, 1995]. A recent review of the state-of-the-art in understanding the combustion of cellulosic materials was given by di Blasi [1993]. Besides this theoretical work wood, and biomass in general, is currently receiving much attention as a renewable fuel, see e.g. Bemtgen et al [1994], Bridgwater [1995, 1993].

Coal and peat are organic macromolecular materials formed from vegetable matter under suitable conditions in swampy environments. They can contain significant amounts of inorganics, mostly as a separate phase. After a wet (humification) stage during which peat is formed from vegetable matter, hard coal is formed via lignite during the coalification stage, after being covered by sediments. The coal consists of a three-dimensional polymer network of mono-, di-, tri- and tetracyclic aromatic monomers which are connected by methylene linkages into linear polymers, with cross-linking via oxgen-carbon and oxygen-sulphur bonds.

Being one of the major fossil energy sources, thermal power generation from coal receives a tremendous amount of research and development attention, where the aims are to minimise environmental impact and optimise energy efficiciency. Some key handbooks on coal and coal technology are by van Krevelen [1993], Kural [1994] and Wen and Lee [1979].

4. Paper and Textile

MSW generally contains 30-50 %wt waste paper. Waste paper combustion, however, occurs only up to a surprisingly limited extent when its economic value is considered. A reason for this is that local legislations have artificially made the market for waste paper (from newsprint and other text-related use) highly beneficial for paper production. However, degradation of the paper fibres limits the recycling of paper to five or six cycles [Smosarski,1995]. Preparing the re-collected paper for re-use, de-inking sludge is produced (among other wastes) which generally is incinerated. Nevertheless, paper used in packaging is often mixed with plastics, producing packaging-derived fuel (PDF) which the packaging industry regards as a high-grade fuel. Even more than is the case with paper holds for textile: extensive recycling leads to complete wear-out of the material after approximately 50 years [Smosarski, 1995].

Paper is mainly composed of cellulose and lignin, at a ratio of about 4:1, therefore the thermal decompostion behaviour of paper is very much like wood, the main differences resulting from the shape in which the paper occurs. A thin sheet of paper or newsprint will burn very violently due to the absence of mass transfer limitations.

Contemporary textiles are in fact either biomasses (cotton, wool, henp etc.), plastics (e.g. acrylic polymers) or mixtures of these. Thus, the behaviour of textile in thermal decomposition is according to their basic components, as described above.

A large fraction of wet paper or textile in a waste-derived fuel can influence a combustion process by reducing the temperature.

One process for thermal paper conversion is mild hydrotreatment, where paper is converted with pressurised steam at 250-350°C into gases, liquids and a slurry that can be fed to a gasifier [e.g. Reynolds et al., 1997].

D. Emissions and Emissions Control

1. Pollutant Formation

Solid wastes that are disposed of by thermal treatment include a high load of potential pollutant forming compounds, which can be largely reduced by pre-treatment before firing. The range of pollutants and their levels per unit thermal power generated exceeds that of fossil fuels. Besides CO_2 and H_2O, NOx and SO_2 significant amounts of HF, HCl, polyaromatic hydrocarbons (PAH), poly chlorinated bi-phenyls (PCB) polypolychlorinated dibenso-p-dioxines and -furanes (PCDD/F), heavy metals, particulates and liquid waste streams can be produced.

NO release can partly result from a temperature level high enough (i.e. well above 1000°C) for air-oxygen and air-nitrogen to form NO. At lower temperature levels such as those in fluidized bed incineration, NO is more directly linked to fuel-nitrogen, nitrogen chemistry being determined by gas-solid reactions. In many cases a waste derived fuel has a high fuel nitrogen content when compared to a fossil fuel. NO concentration increases when lime or other calcium-based sorbents for sulphur and/or chlorine capture are added [e.g. Hallström and Karlsson, 1990]. A specific problem related to fluidized bed combustion of coal is the relatively high emission of nitrous oxide (N_2O). This is produced by a heterogeneous reaction of NO with fuel-nitrogen, which acts as a greenhouse gas and ozone depleting agent in the stratosphere [e.g. Hupa and Matinlinna, 1994]. There is no evidence that this also holds for fuel nitrogen from waste-derived fuels.

Depending on the chlorine content of the fuel, metals are converted to oxides or chlorides, or (for Se and Hg) as volatile elements, thus distributing between bottom ash, fly ash and the combustion gases [Saxena and Jotshi, 1996]. Increased levels of fuel chlorine lead to increased levels of HCl production, which can lead to hot corrosion especially in reducing zones in the boiler. The relation between fuel chlorine and PCDD/F formation (see section C.1) has received tremendous attention lately. The current state of knowledge implies that PCDD/F formation (especially on the surface of particulates) is mainly affected by the speed at which gases are cooled and the residence time at a temperature of ~300°C. Other factors are fly ash concentration, the presence of trace metals such as copper, fly ash chlorine and carbon content and the presence of oxygen [Rigo et al., 1995]. Carugati et al. [1995] compare the gasification (air/steam) and combustion of RDF in a bench scale fluidized bed reactor and report no PCB or PCDD/F present in gas, ash or tar during gasification, however, these compounds were found during combustion. As shown by Anthony et al. [1994], increased levels of halogens (excluding fluorine) in the gas phase lead to increased levels of CO emissions from fluidized bed boilers.

Depending on carbon/oxygen ratio during thermal decomposition, considerable amounts of soot (carbonaceous particulates) can form, with typical unit compositions such as C25H20O5. Generally soot clusters are formed from thousands of primary particles which have a size of the order of 20 nm. The combustion of soot, which forms a potential threat to human health, can be a serious problem. Soot formation is discussed extensively by Haynes and Wagner [1981].

Methods to reduce stack emissions range from dust filtering and activated coal filtering to wet scrubbing (giving aqueous waste streams) and catalytic or non-catalytic selective reduction (SCR/SNCR) of NO [see e.g. Brna, 1988]. In addition, vast amounts of ashes and other solid residues are produced which may require post-treatment before disposal or further use.

2. Emission Standards and Regulations

The current, international emission-standards for waste incineration plants, for several countries in Europe, Japan and USA are given in Table VI.2. It is noted that for waste combustion an excess air of 11% oxygen is required, as opposed to 6% when referring to fossil fuel combustion for thermal power generation. Higher excess oxygen leads to a reduced energy efficiency of the system due to the larger gas flow. Some regulations require e.g. a residence time of at least 2 seconds at a temperature of at least 900°C.

3. Analytical Methods

The composition of wastes that are incinerated or subjected to another form of thermal treatment for energy or material recovery, makes extensive monitoring of solid, gaseous and liquid effluents and by-products detrimental. When compared to fossil fuel based thermal power generation, a much wider range of elements and chemical compounds has to be monitored, in some cases (such as for dioxines and furanes) at extremely low concentrations [Cleverly et al., 1988].

Table VI.2 International MSW incineration emission limit ranges
Compiled from [Patel et al. 1994]. Corrected to 11% oxygen.

Particulates		5 ... 50	mg/m3STP
Acid gases	HCl	10 ... 100	
	HF	1 ... 5	
	SO2	50 ... 500	
	NOx as NO2	70 ... 500	
	CO	50 ... 500	
	Dioxines (PCDD/F)	0.0001	
Heavy metals			
Class I	Cd,Hg	0.02 ... 0.2	mg/m3STP
Class II	As,Co, Ni, Se, Te	0.05 ... 0.1	
Class III	Sb,Pb,Cr,Cu,Mn,Pt,Pd,Rh,V,Sn	0.05 ... 5	

A typical monitoring set-up involves stack gas analysis for the most common compounds (CO, CO_2, SOx, NOx, O_2) plus HCl, HF, metals such as As, Ba, Be, Cr, Cd, Ni, Pb, Se and Zn, polynuclear aromatic hydrocarbons (PAH), polychlorinated bi-phenyles (PCBs) and polychlorinated dibenso-p-dioxines and -furanes (PCDD/F). In addition, ashes and polluted water (e.g. from flue gas scrubbing) have to be analysed. CO_2 and CO, NO and SO_2 can be relatively easily measured using non-dispersive infrared, chemiluminiscent and UV-VIS methods, respectively. For oxygen, measurement procedures are based on zirconia elements, for particulate emissions opacity measurements can be applied.

In (hazardous) waste combustion systems, requirements such as 99.99% destruction and removal efficiency (DRE) of principal organic hazardous compounds (PHOC), 99% removal of HCl and a particulate emissions norm are to be met [e.g. Oppelt, 1986]. Especially the 99.99% DRE for PHOC standard can be hard to meet at low concentrations (<500 ppm). In general, however, the particulate emissions pose the greatest problems. Monitoring CO, oxygen and total halogenated carbon, or products of incomplete combustion (PICs) does not guarantee 99.99% DRE. One method for monitoring an incineration process is to add a 'spike' of a component that is difficult to combust (SF6, or a freon).

Methods of sampling and analysis of PHOCs were discussed by Johnsson [1985], who describes the 'source assesment sampling system' (SASS), the 'modified method five train' (MM5) and the 'volatile organic sampling train' (VOST). In general, XAD-type sorbents and glass fiber filters are used in order to collect PHOC and PICs such as PAH [Wheatley et al., 1993; Johnson, 1985].

E. Conclusions

Energy recovery from waste provides an enormous source for renewable energy. Due to the increasing amount of polymeric fractions in non-recyclable waste, incineration in conventional systems will meet the objective of reducing the volume of the waste, failing seriously, however, from the viewpoint of thermal power efficiency. When a waste stream is upgraded to a refuse derived fuel (RDF), waste firing at higher thermal efficiencies can be achieved in fluidized bed furnaces. Depending on the waste fuel, co-firing with a primary fuel (coal or wood) is most beneficial. Another option is waste co-firing in rotary kilns such as in the cement production process.

The recovery of energy from waste is, however, still a relatively young technology and needs much more fundamental knowledge in order to obtain maximum thermal power efficiency at a minimum of environmental impact. Therefore, more research on lab-scale, pilot-scale and large-scale combustion, gasification and pyrolysis of polymer-based fractions in waste, such as reviewed in this chapter, is a first need. So are the measurement techniques to support such an effort.

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VII CONCLUSIONS

Combustion is a complicated phenomenon and the course of reactions highly dependent on the conditions. That is why it is almost impossible to get very relevant data about the real combustion processes of polymeric materials by use of simple laboratory tests only. On the other hand basic chemical and physical properties provide useful quantitative data which is necessary for understanding the fire phenomena.

The combustion of polymeric materials include two distinct reactions. The first of them is thermal decomposition of the polymer that leads to gaseous and/or condensed products of a nature depending mostly of the chemical structure of the material. The second reaction, exothermic oxidation of the decomposition outputs, leads to the final combustion products. Both of the reactions consist actually of very complicated sets of elementary steps. The conditions, especially the availability of oxygen at the oxidation stage, determine highly the composition of the combustion products. In the cases of very effective combustion, the flue gases can be estimated by the empirical (gross) formula of the polymer. In real fires and in real ovens the situation is much more complicated.

To understand the combustion processes, and to be able to make predictions about them, computational models, which include the most important factors under consideration, are very useful.

In such models quantitative material properties, such as the chemical structure and physical measures, which can be gained by laboratory experiments are essential parts of the input data. On the other hand, full scale experiments and studies of real conditions are necessary for understanding of both the fires and the performance of firing equipment. What are needed are quantitative models for prediction of the macroscopic properties if combustion and fire which are material based. Those means that physical and chemical parameters must be fed to either truly physical or, more likely, abstract factorial models with the result that prediction is achieved. This could require a far better time and spatial dependence data base for combustibles and fire products -gas and condensed phase. That suggests that new, measurement approaches may be needed and techniques perfected for pristine laboratory pure chemical work by comparison to fire, may need to be understood in terms of information content in this, more complex case.

A scientific approach to these problems requires combination of:

a) Classical methods of determining material properties like the heat of combustion, melting temperature (if any), thermal inertia etc.
b) Quantitative (to certain conditions related) test results like the ease of ignition, the composition and the toxicity of the flue gases and
c) Methods of modeling including fire scenarios, combustion models, and the utilization of the ideas of chemometrics.

Many of the problems concerning the combustion of polymeric materials are multivariate in nature. The process towards making a better material for the consumers factors like the ease of ignition, the heat release rate, the formation of toxic gases and smoke, the suitability for recycling or suitability for a waste fuel and finally the costs of production are all of importance. It is, however, the final application of the material that determines the importance of each factor. The analyst working in research and development should be able to optimize the material's many properties according to their use during their whole life cycle. It appears that understanding the combustion behavior of a polymeric material has importance from both the fire safety and the environmental point of view.