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# Mechanisms of pollutant formation in fires

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## ABSTRACT

While emissions of pollutants from conventional sources, such as industrial and thermal processes, have been in decline over the last two decades, fires have become major sources for the emission of several contaminants. This review summarises chemical mechanisms pertinent to the formation of prominent pollutants, such as NO<sub>x</sub>, HCN, HCl, soot, and trace species, such as PCDD/Fs (dioxins). We commence by discussing the most important groups of fire pollutants and the types of fires responsible for their formation. This is followed by short descriptions of main reaction pathways operating in the formation of pollutants; i.e., pyrolysis and oxidation. We then tackle contaminant formation in fires of biomass, before proceeding to discuss the formation of soot, PCDD/F and PBDD/F (brominated dioxins). This leads us to reviewing of pollutants produced in fires involving polymers (with focus on PVC and nylon) and polyfluorocarbons.

**KEYWORDS:** Fires, Pollutants, Reaction mechanisms, Biomass, PCDD/Fs

## INTRODUCTION

Emissions from open and enclosed fires carry far greater amount of pollution (on a basis of emission factors) than those from well-controlled combustion sources, including energy generation and municipal waste incineration. Fires involve discharging products of combustion directly into the surroundings without hindering of control devices such as scrubbers, adsorbers, afterburners, fans, ducts or chimneys. Common examples include post-harvest fires of agricultural residues, forest fires, backyard trash burning, and fires in dwellings and warehouses. While emissions from global-scale sources such as industrial and thermal processes have been in decline over the course of the last two decades, open burning has become a major source of the emission of many pollutants [1]. In conventional combustion, many factors interact to minimise emission of pollutants, such as high temperature, induced mixing of air and fuel, adequate gas-phase residence time and rapid cooling of exhaust gases. Furthermore, pollution control devices remove the majority of hazardous pollutants before they are emitted to the environment. On the other hand, poor mixing, low temperature, uncontrolled temperature regime and smouldering conditions highlight fires as a “worst-case” scenario for the formation of pollutants [2]. For instance, poor gas-phase mixing, low combustion temperature, and the presence of particulate matter (PM) with elevated content of soot and transition metals as well as incidence of hydrogen chloride [HCl]/chlorine [Cl<sub>2</sub>] in the gas phase liaise to enhance the formation of the notorious polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs).

In-situ and simulated experiments on open burning have demonstrated that fires produce a wide spectrum of pollutants, such as volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), soot, ash, particulate matter (PM), heavy metals, polyaromatic hydrocarbons (PAHs) and nitrogen oxides (NO<sub>x</sub>), HCN and CO [3]. Emissions from fires display great sensitivity to local burning conditions, as opposed to conventional combustion where the emissions are dominated by a fuel type. However, emissions from fires also vary significantly from source to source. A consensus of opinions in the literature indicates that, fires

of anthropogenic materials (such as vehicles or household wastes) produce higher amounts of VOCs and PAHs than those involving biomass burning. As fire is a transient combustion phenomenon with a large number of reacting species, often with heterogeneous speciation, it is a colossal task to identify the precise source and the governing mechanism of emissions. Despite complexities pertinent to the fire environment, great deal of bench-scale experiments, large-scale fire tests, sophisticated chemical analyses and accurate quantum chemical calculations have started to provide comprehensive insights into the chemical mechanisms of pollutant emissions in fires. In this contribution, we will present a critical and stimulating review of such mechanisms for the most important pollutant types.

## MAJOR POLLUTANTS AND THEIR SOURCES

The composition of fire effluents depends mainly on the elemental composition of the burned materials, their organic contents and the prevailing conditions of fires in terms of temperature, and availability of oxygen, as defined by imposed or fire-induced air ventilation. Analytical sampling of fire gases is often a difficult task. This is primarily due to the fact that, concentrations of pollutants change significantly in the smoke plume during the course of fires. Furthermore, high content of CO<sub>2</sub> and water obscures chemical analysis by spectroscopic instruments, such as infrared analysers, and complexities of ash and soot matrices induce analytical complications of quantitating trace pollutants by gas chromatography-mass spectrometry. Despite these difficulties, comprehensive emission inventories from various types of fires have been established. Andrea and Merlet [4], Lemieux et al. [1] and Estrellan and Iino [5] published detailed reviews on emission of pollutants from various types of fires. Surveyed data afforded tabulation of emission factors, and pollutant concentrations in the plume and in the ambient air. Table 1 summarises main categories of pollutants formed in fires.

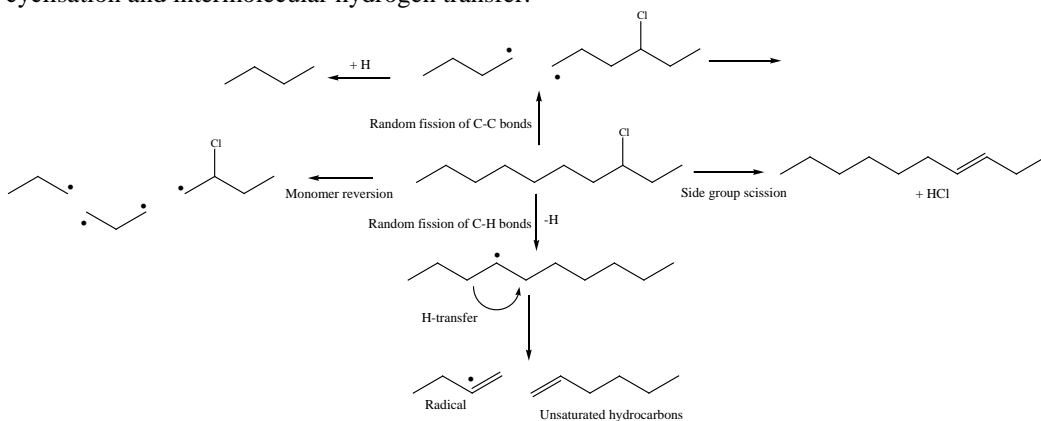
**Table 1.** Categories of fire pollutants and their sources.

<i>Category</i>	<i>Examples</i>	<i>Types of fire</i>
VOC	Phenol, benzene, styrene, formaldehyde	Polymers, wood, household wastes, shredded tyres, vehicles
SVOC	PCDD/F, PBDD/F, PXDD/F, PCB, PBDE, PAH	Electronic wastes, cables, liquid fuels, agricultural residues, biomass, plastics, household materials including flame-retarded electronic devices and fabric
Inorganic gases	- CO <sub>2</sub> , CO - NO <sub>x</sub> - HCN - HBr, HCl - SO <sub>x</sub>	- All fires - Biomass, explosives, fireworks - Plastics, nylons - Any fuels containing Br or Cl; i.e., PVC - Coal, wools
Solid particulates	Soot	All fires

## BASIC CHEMICAL REACTIONS

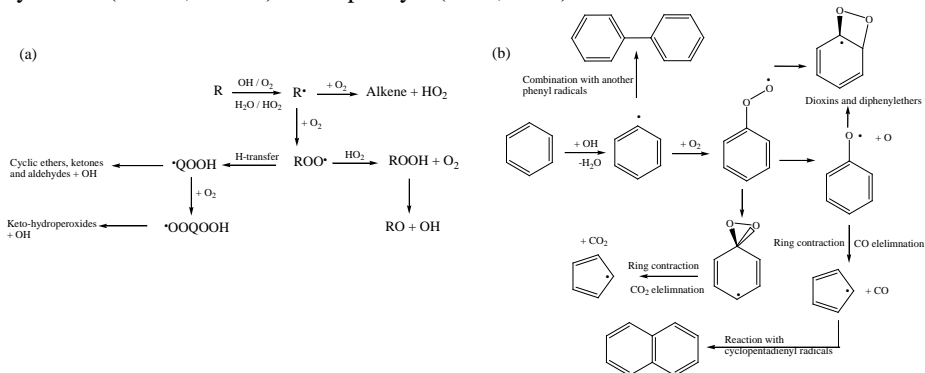
Under well-controlled laboratory conditions, complete combustion leads to formation of water and carbon dioxide. However, in fires, combustibles materials and oxygen are not present in their stoichiometric proportions, resulting in the generation of a wide range of chemical species. Emission of pollutants takes place during the two stages of fires, flaming and smouldering. Unoxidised pyrolysates represent additional pollutants. The flaming phase is characterised by four homogenous gas-phase reactions; chain initiation, chain propagation, chain branching and

chain termination. Flaming combustion requires the presence of at least 10 % oxygen in the air. Volatile organic compounds are initially ejected from the surface of the fuel under the influence of heat. The smouldering stage involves the oxidation of char, commencing once volatiles cease to be given off by the pyrolysing material. In this stage, oxygen diffuses into the char to participate in a direct solid-gas chemical reaction. As fires are often associated with oxygen deficient conditions, pyrolysis is an important chemical process in fire development. Thermal decomposition of chemicals in pyrolysis commonly follows three main reaction mechanisms, namely, random scission, side-group scission and monomer reversion (i.e., depolymerisation) [6], as illustrated in Fig. 1. These reactions prevail during the decomposition of synthetic and natural polymers alike, such as biomass and plastics. The other two important reaction mechanisms are cyclisation and intermolecular hydrogen transfer.



**Figure 1.** Main reactions operating in pyrolysis.

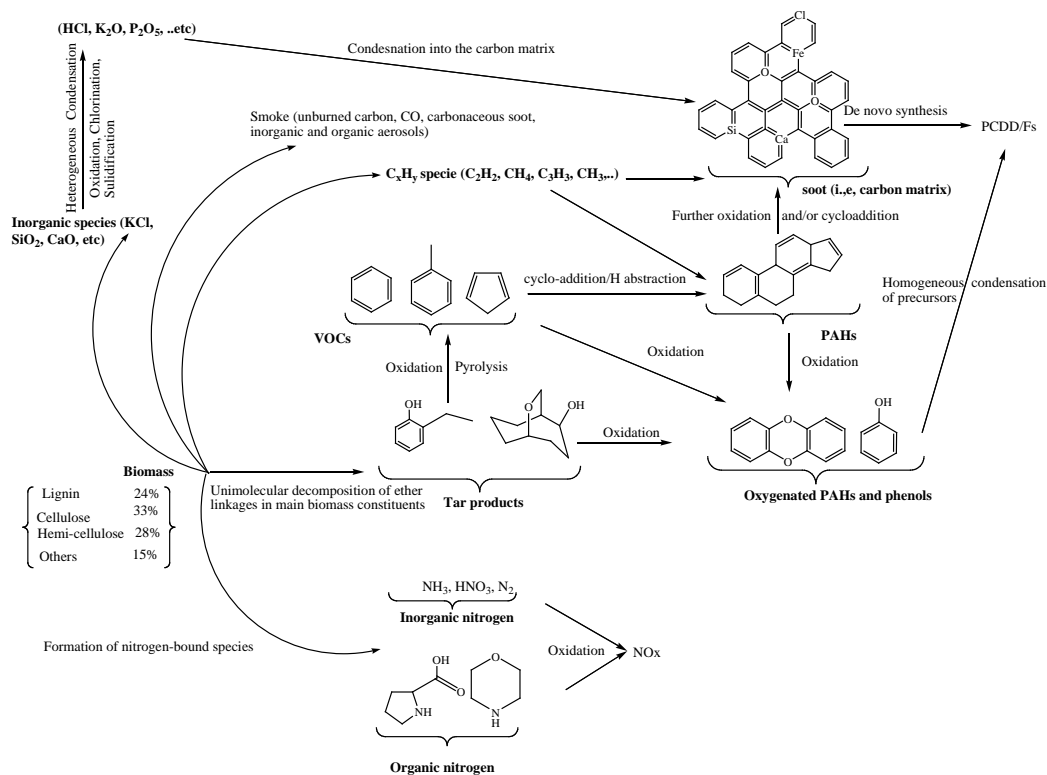
Emission of pollutants from fires of various hydrocarbon fuels takes place through the well-documented low-temperature oxidation mechanisms consisting of large numbers of concurrent and competitive reactions. Main chemical features of these pathways involve H abstraction from carbon atoms, followed by addition of oxygen molecules and the formation of peroxy adducts (ROO) [7]. Subsequent steps comprise unimolecular isomerisation of the ROO adducts and the formation of cyclic ethers. Figure 2a presents a simplified reaction scheme for the oxidation of alkanes. Oxidation of cyclic compounds follows a different pathway as shown in Fig. 2b for benzene. The main characteristic corresponds to the formation of phenyl/phenoxy-type radicals at higher temperatures of around 700 °C that serve as precursors for chlorinated and brominated dibenzo-*p*-dioxins (PCDD, PBDD), dibenzofurans (PCDF, PBDF), naphthalenes (PCN, PBN), diphenylethers (PCDE, PBDE) and biphenyls (PCB, PBB).



**Figure 2.** Oxidation of alkanes (a) and benzene (b).

## POLLUTANTS FROM FIRES OF BIOMASS

Early models of combustion and pyrolysis of biomass utilised generic reaction schemes to account for the emission of pollutants from biomass fires. These schemes incorporate heating-up, drying, formation of volatiles and char and further decomposition of pyrolysates into smaller entities such as CO, CO<sub>2</sub> and unburned hydrocarbons [8]. Global reaction schemes were derived for key reaction steps. Thermal pyrolysis or devolatilisation plays an important role in emission of pollutants in fires as large portion of the biomass is transformed into volatile components. Thermal pyrolysis of biomass typically starts at temperatures between 160 and 250 °C [9]. Combustion of volatiles, tars and char results in formation of soot and PAH. Trace minerals in biomass, especially potassium, act as catalysts [10]. Figure 3 outlines general mechanisms for the formation of various pollutants in fires of biomass.

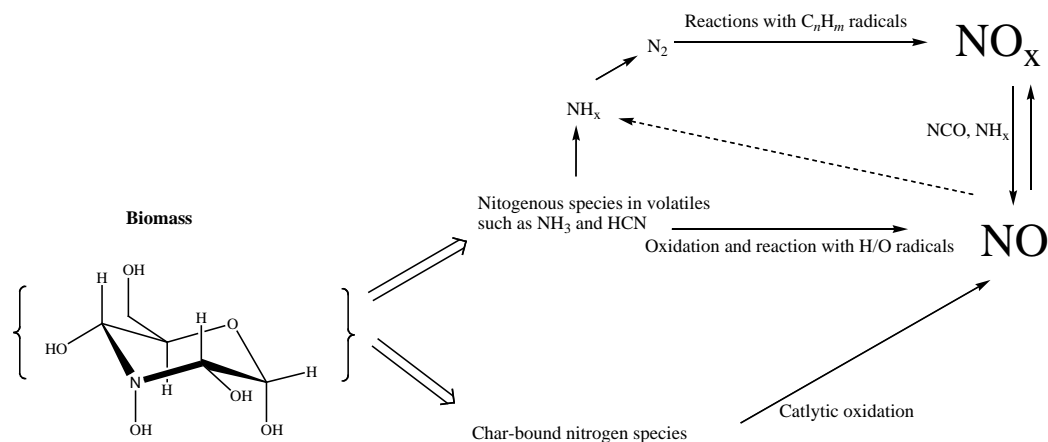


**Figure 3.** General pathways for the formation of various pollutants from fires of biomass, i.e., forest fires.

Modelling the formation of pollutants from biomass has developed from deploying general expressions for key global steps to inclusion of detailed biomass-specific chemistry that takes into account structural entities of biomass, such as those of lignin and cellulose [11]. It is generally accepted that, decomposition of cellulose and hemicelluloses, i.e., the two main components of biomass, proceeds in three temperature-dependent pathways. At lower temperatures (i.e.,  $T \leq 280$  °C), degradation of cellulose involves random C-H and C-C bond fission, dehydration, formation of reactive radical pool, formation of oxygenated hydrocarbons and the evolution of carbonaceous residues. At intermediate temperatures (i.e., between 280 and 500 °C), the decomposition behaviour is dominated by the cleavage of glycosidic and ether

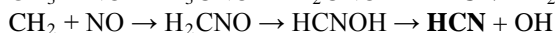
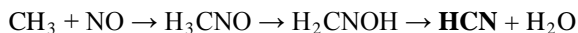
linkages as well depolymerisation reactions. The latter reactions result in the formation of smaller fragments, such as anhydrosugars and levoglucosan. At elevated temperatures, cellulose decomposes directly into low-weight species via bond fissions reactions, dehydration and disproportionation. Overall, efforts to reveal how pollutants form in biomass fires are hindered by the complexity of the chemical composition of biomass that comprises numerous structural entities, further complicated by added preservatives and flame retardants. Accordingly, considerable efforts have focused on gaining improved understanding of the decomposition behaviour of individual functional groups in biomass such as ethers, esters and alcoholic entities based on representative model compounds.

Owing to the nitrogen-bound components in biomass, fires of biomass result in the emission of  $\text{NO}_x$ , hydrogen cyanide (HCN), isocyanuric acid (HNCO) and ammonia ( $\text{NH}_3$ ) [9]. Researchers have investigated the oxidation and pyrolysis of several model compounds in order to elucidate pathways for the emission of nitrogen-compounds from combustion of biomass. Recently, Lucassen et al. [12] studied pyrolysis of morpholine as a surrogate model compound to mimic nitrogen transformation during the thermal decomposition of biomass. The experimental results, supported by quantum chemical calculations [13], revealed that, reactions leading to smaller nitrogenated-species could compete with oxidation reactions that commonly prevail in oxidation of hydrocarbons.  $\text{NO}_x$  gases arise from the decomposition of all nitrogen-bounded components, especially inorganic nitrates and ammonium ions, as well as heterocyclic structural moieties such as pyroles and pyridines. Another pathway for  $\text{NO}_x$  emissions, known as prompt as it occurs at early stage of combustion, involves reactions of  $\text{N}_2$  with hydrocarbons radicals [9]. Finally, the so-called “nitrous oxide” mechanism, that reversibly converts  $\text{N}_2\text{O}$  and  $\text{NO}_x$ , also contributes to the burden of  $\text{NO}_x$  emission from biomass. Figure 4 depicts the chemical cycle of nitrogen-species emission from biomass.



**Figure 4.** Nitrogen conversion during decomposition of biomass.

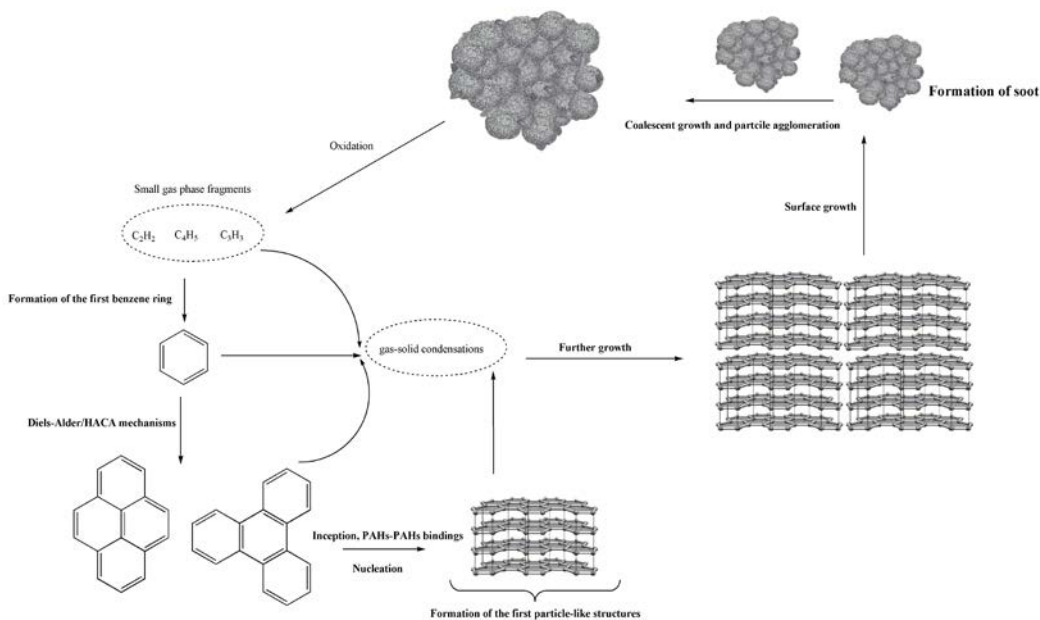
On another note, the coupling between mechanisms of production of  $\text{NO}_x$  and HCN is well-documented in the literature. For example, HCN could be formed via  $\text{NO}$ -induced reactions with  $\text{CH}_x$  radicals [14]:



## FORMATION OF SOOT

Formation of soot in fires and combustion systems has emerged as a fundamental research topic, both from experimental and theoretical perspectives. Generation of soot spans four major phenomena: condensation of gas phase precursors, coagulations of particles, growth and surface oxidation and particle agglomeration [15]. Formation of soot is a very complex process in which a soup of small gas phase molecules endures numerous homogenous and heterogeneous reactions to end up with sophisticated graphite-like structures in a time scale of milliseconds. Proposed potent precursors for the formation of soot include PAHs, ionic  $C_xH_y$  moieties, and polyacetylenes  $C_{2n}H_2$ . Experimental evidence points out to soot particles being produced from PAH species [16]. The most widely accepted mechanism for the formation is the hydrogen-abstraction-carbon-addition (HACA) mechanism ( $n-C_4H_5 + C_2H_2 \rightarrow C_6H_6 + H$ ). Formation of the first benzene ring have been also postulated to proceed through a combination of propargyl radicals ( $C_3H_3 + C_3H_3 \rightarrow C_6H_6$ ).

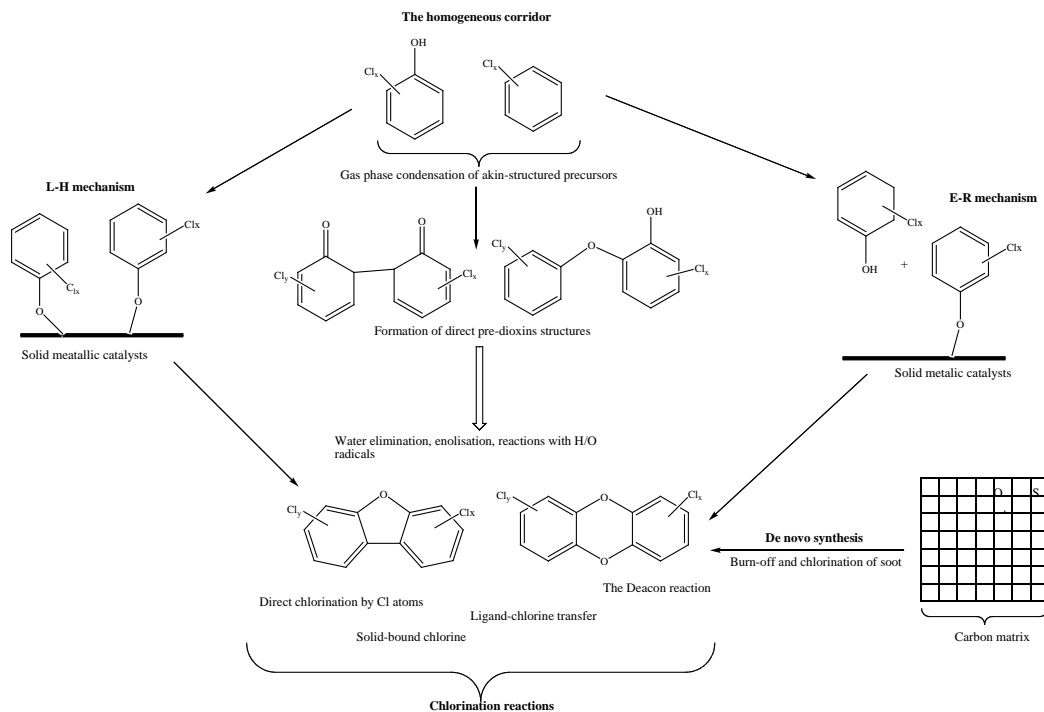
Simple PAH molecules such as naphthalene, phenanthrene and pyrene form via the Diels-Alder mechanism which incorporates H abstraction,  $C_2H_2$  cycloaddition and ring closure. Growth of higher PAHs includes radical-radical and radical-molecule combination reactions involving mainly benzene,  $C_6H_x$ ,  $C_4H_x$  and  $C_{2n}H_2$  species. Successive PAH-PAH binding represent the bottleneck for the nucleation and the formation of the first particle-like structures. Eventually, these primary structures further grow to form soot through gas-solid addition of  $C_xH_y$  and PAH species, surface growth, coagulations and agglomerations. Oxidation of soot reproduces gas phase molecules. A schematic diagram for the mechanism of soot formation is sketched in Fig. 6. Recently proposed steps include PAH inception via the formation of aliphatic-aromatic bridged structures [17]. Overall, formation of soot is a kinetically governed process, in which the formation of the first benzene ring from small aliphatic species is the rate determining step.



**Figure 6.** Formation of soot.

## FORMATION OF PCDD/Fs AND PBDD/Fs

Emissions of PCDD/Fs from fires of native [18] and treated wood [19], pesticides and other chemicals [20], agricultural residues, houses, tyres and PVC-containing materials have been under investigation for many years. Apparently, the open burning of households wastes in barrels constitutes a significant contribution to emissions of PCDD/Fs in the US [1]. The contribution of open burning to emission of PCDD/Fs might be substantial even in developed countries owing to contaminant generation in fireplaces and household heating stoves. PCDD/Fs are produced generally via homogeneous and heterogeneous corridors [21], with Fig. 7 outlining the major reactions leading to the formation of PCDD/Fs.



**Figure 7.** Pathways for the formation of PCDD/Fs.

The homogeneous pathway constitutes gas phase reactions of structurally-related precursors in the temperature window of 400 to 800 °C [21]. The most potent precursors are chlorinated phenols and their derived chlorinated phenoxy radicals. The underlying reactions in the gas-phase conversion of chlorophenols/chlorophenoxy into of PCDD/Fs involve oxidative coupling of these species into pre-PCDD/Fs intermediates, cyclisation of these intermediates into PCDD/Fs, and their destruction in chlorination/dechlorination and oxidation reactions. Formation of PCDDs and PCDFs require different patterns of chlorination. The presence of at least one *ortho* chlorine in chlorophenoxy radicals represents a pre-requisite for the formation of PCDDs, while the formation of PCDFs necessitates the availability of two chlorophenoxy radicals, each with one *ortho* hydrogen atom. Enolisation and water molecule elimination mark the rate-determining steps in the homogenous formation of PCDD/Fs. Bimolecular reactions involving H/O radical pool greatly reduce the overall reaction barriers. Recent studies highlighted the roles of other persistent free radicals such as those derived from 1,2- and 1,4-dihydroxybenzenes as precursors for the formation of PCDD/Fs [22].



Heterogeneous generation of PCDD/Fs involves catalytic-assisted coupling of precursors and the so-called de novo synthesis [23]. It is well-documented that, certain metallic compounds such as copper oxides greatly facilitate the formation of PCDD/Fs through the Ullmann type reactions [24]. Catalytically-assisted condensation of chlorophenols into PCDD/Fs follows the Langmuir-Hinshelwood (L-H) and Eley-Rideal (E-R) mechanisms. The L-H mechanism denotes reactions between two adsorbed species while the E-R mechanism refers to reaction between gaseous and adsorbed species. De novo synthesis is regarded as the main route for the formation of PCDD/Fs in the smouldering stage through the oxidative destruction of the carbon matrix, primarily in the temperature range of 200 to 400 °C. PCDD/Fs emission from fires of treated wood involves mainly catalytic condensation of chlorinated organic preservative such as tebuconazole [19]. It has been shown that metal-based preservatives, for example chromate copper arsenate, promote the formation of dioxins during flaming and smouldering of char. Chlorination of PCDD/Fs occurs through several mechanisms including the Deacon reaction, gas phase chlorination mainly by Cl atoms and addition of gaseous chlorine into the carbon matrix. Experimental evidence suggests that, formation of PCDD/Fs might be thermodynamically controlled, especially for higher chlorinated homologue groups.

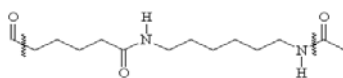
Open burning of materials laden with brominated flame retardants (BFRs), such as electronic parts, paints, solvents and textiles, constitutes a major source for the emission of brominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs) [25]. Strong correlations between concentrations of PBDD/Fs and PCDD/Fs suggest that, both groups of pollutants are formed via analogous mechanisms, viz., homogeneous condensations of bromophenols and surface-mediated reactions. Other suggested mechanisms highlight oxidative transformation of polybrominated diphenylethers directly into PBDDs via a complex series of reactions [26]. The formation of the sulfur analogues of dioxins, i.e., polychlorinated dibenzothiophenes (PCDTs) and polychlorinated thianthrenes (PCTAs), has been found to proceed with significantly reduced activation barriers in reference to the well-documented mechanisms of gaseous formation of PCDD/Fs [27].

## **POLLUTANTS FROM FIRES OF POLYMERS**

Decomposition of polymeric materials is governed by complex physical and chemical processes. When subjected to heat, polymers start to melt and degrade into smaller liquid and gaseous fragments. Liquid fragments continue to decompose until they form volatile compounds. However, some polymers can decompose before melting. Carbonaceous char formed on the surface of such polymers tend to slow down further their decomposition. Chemical make-up of polymers plays an important role in their decomposition behaviour. As an illustrative example of chemical reactions occurring during the decomposition of polymers, herein, we briefly describe behaviour of polyvinyl chlorides (PVC) and nylons in fires.

Emission of pollutants from fires of PVC-containing materials takes place during two stages of degradation [28]. The first stage is characterised by dehydrochlorination involving the emission of HCl gases and the formation of unsaturated hydrocarbons of long conjugated double bonds. In the second stage, breakdown of the -CH=CH- backbones produces smaller hydrocarbons fragments. Unimolecular elimination of HCl also acts to catalyse formation of small volatile aromatic compounds, especially toluene and benzene. The presence of defects in the structure of PVC greatly accelerates the thermal decomposition of PVC in fires. Polychloropropene decomposes in a similar fashion to PVC.

As an aliphatic polyamide, a typical nylon is formed from blocks of  $-\text{CH}_2-\text{CONH}-\text{CH}_2-$  with the chemical formula:



Fires of nylons produce appreciable concentrations of  $\text{NH}_3$ ,  $\text{CO}_2$ , small alkanes and alkenes, as well as PAH, in addition to HCN. Thermal decomposition of nylon commences with random fissions of HN-CO bonds and leads to the formation of smaller hydrocarbons and nitrogen-containing fragments such as nitriles, acetamide and pyridine [29]. Formation of HCN is a result of a series of H-abstraction reactions from major intermediaries such as ethylamine ( $\text{CH}_3\text{CH}_2\text{NH}_2$ ) [14]:



The yield of HCN increases with temperature both under pyrolytic and oxidative conditions. HCN survives destruction through or past the flame during atmospheric burning of nylons.

Table 2 summarises chemical features that signify the decomposition of commonly deployed synthetic polymers. The majority of these polymers start to decompose at around 300 °C [6].

**Table 2:** Decomposition behaviour of main synthetic polymers in fires.

<i>Polymer</i>	<i>Main mechanistic features</i>	<i>Main pollutants</i>
Polystyrene	End-chain initiation, depolymerisation, intermolecular hydrogen transfer and bimolecular terminations	Styrene, benzene, toluene and char
Polyethylene (PET)	Random scission of alkyl-oxygen bonds, formation of cyclic chain oligomers	Acetaldehyde, anhydride compounds
Polycarbonates (PC)	Scission of O-CO <sub>2</sub> linkages, random chain-scission and cross linking	Phenol, bisphenol and char
Phenolic resins	Scission of methylene-benzene bonds	C <sub>3</sub> compounds and phenolic voltaic compounds
Polyoxymethyl (POM)	Random chain initiation and depolymerisation	Formaldehydes and CO
Wool	Dehydration, cleavages of disulphide bonds in amino and cystine acids	HCN, benzene, toluene and CO
Rubber (Polyisoprene)	Random chain-scission and intermolecular hydrogen transfer	Isoprene and volatile compounds

## POLLUTANTS FROM FIRES INVOLVING POLYFLUOROCARBONS

As polyfluorinated compounds are being incorporated in a vast range of industrial and household applications, formation of pollutants from fires of polyfluorinated-treated objects has been gaining increasing interests. A growing body of literature has found that, decomposition of polytetrafluoroethylene (PTFE) yields a number of perfluorinated alkanes and alkenes such as tetrafluoroethylene (TFE), hexafluorpropene (HFP) and fluoroformaldehyde [30]. Oxygenated compounds with the functional groups of  $-\text{OCF}_3$  and  $-\text{OC}_2\text{F}_5$  have also been observed. Thermal decomposition of PTFE commences via the cleavage of carbon-carbon bonds in the polymer and the formation of the carbene unit of difluorocarbon biradical,  $\text{CF}_2$ . Subsequent self-addition of

CF<sub>2</sub> forms longer carbon fluorinated chain, such as C<sub>4</sub>F<sub>8</sub> and C<sub>3</sub>F<sub>6</sub>. Reaction of CF<sub>2</sub> with hydrocarbon radicals is shown to produce fluorinated alkenes [31]. Profiles of products appear independent of the oxygen content, with no oxygenated products observed under atmospheric oxidation. The pyrolysis of polyethyltetrafluoroethylene (PETEF) differs from that of PTFE, as a consequence of the formation of several isomers of polyfluorinated cyclohexane. The difference arises owing to facile fission of -CH<sub>2</sub>-CH<sub>2</sub>- bonds, in reference to -CF<sub>2</sub>-CF<sub>2</sub>-. The formation of polyfluorinated cyclohexane points to the occurrence of Diels-Alder cycloaddition involving CF<sub>2</sub> and CF<sub>3</sub> groups. HF elimination and the formation of a  $\alpha$ -lactone intermediates [32] control the initial decomposition of perfluorobutanoic acid, deployed in experiments as a model compound for longer perfluoroalkyl acids.

## ACKNOWLEDGEMENTS

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