

THERMAL DEGRADATION OF TETRABROMOBISPHENOL A: EMISSION OF POLYBROMINATED DIBENZO-P-DIOXINS AND DIBENZOFURANS AND OTHER ORGANIC COMPOUNDS

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Introduction

Brominated compounds are widely used as flame retardants in industrial operations. Due to their high efficiency, compatibility and small influence on mechanical properties, brominated flame retardants (BFRs) have a broad application area, mainly in the field of polymeric materials. Tetrabromobisphenol A (TBBPA) is the most important BFR, representing around 60 % of BFR total production. The estimated global consumption of TBBPA was around 170000 metric tons for 2004¹.

TBBPA contributes to the fire safety of electrical and electronic equipment and installations where printed wire boards are used, such as consumer electronics (TVs, vacuum cleaners, washing machines,...), office and communication equipment (copiers, computers, printers, fax machines, radios,...), automotive, aviation and entertainment equipment. According to the Bromine Science and Environmental Forum (BSEF), 58 % of TBBPA is used as a reactive flame retardant in epoxy, polycarbonate and phenolic resins in printed circuit boards, 18 % is used for the production of TBBPA derivatives and oligomers, while 24 % is used as an additive flame retardant in the manufacture of acrylonitrile-butadiene-styrene (ABS) resins or high impact polystyrene (HIPS)¹⁻².

Some studies have focused on the formation of hazardous products during thermal degradation processes of materials containing TBBPA³⁻⁴, as well as on the analysis of the TBBPA degradation process⁵⁻⁶, but there is still a lack of quantitative data on TBBPA decomposition products in the scientific literature.

A study of the thermal degradation of TBBPA has been carried out in the present work to assess the emission of pollutants under different operating conditions. The analysis, identification and quantification of gases, semivolatiles (bromophenols, polycyclic aromatic hydrocarbons and others) and polybrominated dibenzo-p-dioxins and dibenzofurans (PBDD/Fs) have been done. A special effort has been made to identify brominated compounds in the combustion gases.

Materials and methods

4,4'-isopropylidenebis(2,6-dibromophenol), commonly known as TBBPA, was supplied by Alfa Aesar GmbH & Co; all solvents for organic trace analysis were purchased from Merck (Germany); the standards for the bromophenols analysis were supplied by Wellington Laboratories (Ontario, Canada); the standards for the PAHs analysis were supplied by Dr. Ehrenstorfer-Schäfers (Augsburg, Germany); and the standards of PBDD/F were obtained from Cambridge Isotope Laboratories (Andover, USA).

Pyrolysis and combustion runs were carried out in a laboratory reactor in order to study TBBPA decomposition products under different operating conditions. The experiments were carried out in a tubular quartz reactor located inside a horizontal laboratory furnace (see Figure 1). The sample is placed in a holder and a small engine introduces it inside the reactor. During each run, after the furnace had reached the nominal temperature, approximately 50 mg of sample were introduced into the reactor at constant speed (1 mm s⁻¹). The carrier gas (nitrogen or air, for pyrolysis and combustion runs, respectively) was introduced parallel to the sample, at a constant flow of 300 mL min⁻¹. Both pyrolysis and combustion experiments were conducted at two different temperatures (650 and 850 °C), except for the analysis of PBDD/Fs where only runs at the higher temperature were carried out.

The compounds leaving the laboratory reactor were sampled for subsequent analysis. For each experimental condition, four experiments were carried out: in a first run, evolved gas was passed through two consecutive impingers containing a sodium carbonate/sodium bicarbonate solution in order to retain the released HBr. The amount of bromide ion in the solution was analyzed by ion chromatography (IC) in a Dionex DX500.

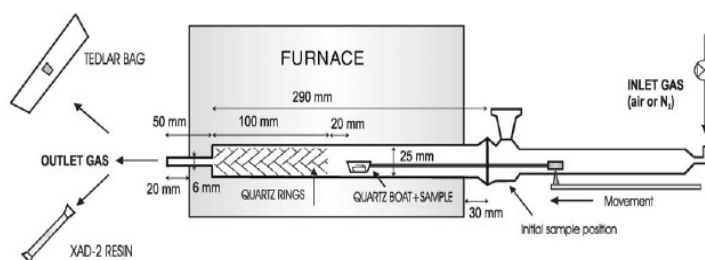


Figure 1. Scheme of the laboratory scale tubular reactor.

In a second run, the non-condensable gases were collected using Tedlar[®] bags at the outlet of the reactor for a time long enough to collect all the compounds. These samples were analyzed by gas chromatography using different detectors: flame ionization (FID), thermal conductivity (TCD) and mass spectrometer (MS) detectors. Finally, semivolatile compounds and PBDD/Fs were collected in two different experiments with sorbent (polyaromatic Amberlite[®] XAD-2, Supelco, Bellefonte, USA) placed at the outlet of the furnace during the entire experiment. Before the decomposition runs, a blank run was conducted, using the laboratory-scale reactor and reproducing the same experimental conditions.

For the analysis of PAHs, brominated phenols and other semivolatile compounds, the resin was extracted with a mixture of dichloromethane/acetone (1:1 vol.), using Accelerated Solvent Extraction in a DIONEX ASE[®] 100. The samples were analyzed by HRGC-MS in an Agilent 5973N spectrometer with a gas chromatograph Agilent 6890 N. A chromatographic column Agilent HP5-MS (30 m x 0.25 mm i.d. x 0.25 μ m) was employed.

The XAD-2 resin where PBDD/Fs were collected was extracted with dichloromethane and purified using an automated clean-up system (Power Prep, FMS Inc., Boston, MA) with two different columns: silica and alumina. The method is based on that for chlorinated analogues⁷, with some modifications pointed out in scientific literature⁸⁻⁹. The purified extract was analyzed for tetra- through hexabrominated dioxins and furans by HRGC-HRMS, on an Autospec Ultima-NT high resolution mass spectrometer (Micromass, UK) with a positive electron impact (EI+) source and interfaced with a Hewlett-Packard (Palo Alto, CA, USA) 6890 Plus gas chromatograph equipped with a split/splitless injector. An Agilent DB5-MS chromatographic column (60 m x 0.25 mm x 0.25 μ m) was used. The identification and quantification of each compound was performed by the isotope dilution method.

Along all the experimental process, restrictive measures were adopted to avoid direct sunlight exposure (covering the laboratory material with aluminum foil) in order to minimize brominated compounds degradation.

Results and discussion

Hydrogen bromide is the main decomposition product from TBBPA thermal degradation. In the pyrolysis at 600 °C, the amount of HBr evolved is 28 % of initial sample weight, whereas in combustion, this value rises to 42 %. In the experiments at 850 °C, the quantity of HBr emitted is higher (46 % in pyrolysis and 55 % in combustion).

High yields of some brominated light hydrocarbon have been observed, as well as phenolic derivatives from the cracking and decomposition of TBBPA. Most of these compound yields decrease with temperature, except for bromomethane, dibromomethane and tribromomethane, which show an increase.

Within the semivolatiles there are three groups of compounds identified: PAHs, brominated compounds and other aromatic compounds. The 16 priority PAHs were searched for in the four runs. Only in the pyrolysis at 850 °C were all 16 PAHs detected. This run also had the highest yields: naphthalene (3660 mg/kg), phenanthrene (1200 mg/kg), fluoranthene (1090 mg/kg) and chrysene (350 mg/kg) were the most abundant. In the other runs, naphthalene was the main product (20 – 1190 mg/kg), detecting minor quantities of phenanthrene, anthracene, chrysene and benzo(b)fluoranthene (yields between 10 and 110 mg/kg).

A great effort was made to identify and quantify more than one hundred species adsorbed or condensed in resin XAD-2. The main ones, with yields ranging from 70 to 23850 mg/kg, were phenol, benzoic acid, 2-bromo-4-methyl-phenol, 1-bromo-2,4,5-trimethyl-benzene, 2-bromo-4-isopropenylphenol, 2,6-dibromo-4-methyl-phenol and 2,6-dibromo-4-isopropenylphenol, as well as derivatives from TBBPA (bromobisphenol A, dibromobisphenol A, tribromobisphenol A and TBBPA), 2-bromo-4-(1-(3,5-dibromophenyl)-1-methylethyl)-phenol and 2,6-dibromo-4-(1-(3,5-dibromophenyl)-1-methylethyl)-phenol.

Both in pyrolysis and combustion runs carried out at 600 °C, many compounds from cracking of TBBPA were detected: bromobisphenol A, dibromobisphenol A, tribromobisphenol A and TBBPA itself. On the other hand, in the experiments executed at 850 °C, the formation of non-brominated phenolic species and derivatives from bisphenol A was favored.

The concentration of bromophenols is shown in Table 1. In the experiments carried out at 850 °C, bromophenols were detected to a lesser extent, in comparison with the experiments at 600 °C. The presence of oxygen does not seem to have a determinant influence in the formation of these compounds. A clear predominance of mono-, di- and tribrominated phenols was observed, particularly those with bromine in the positions 2-, 2,6- and 2,4,6-. The concentration of PBDD/Fs analyzed in the pyrolysis and combustion experiments at 850 °C is shown in Table 2. The profiles of the PBDD/F analysis are shown in Figure 2 and Figure 3. In the pyrolysis run, the main isomers are the tetrabrominated ones, whereas in combustion the hexabrominated furans predominate. The yields obtained in the combustion experiment are nearly four times higher than those from pyrolysis.

An overall examination of the degradation products emitted during thermal decomposition of TBBPA has been carried out. More than one hundred semivolatiles compounds have been identified with special interest in brominated ones. The levels of PBDD/Fs have been evaluated, detecting amounts close to the ppm range. These results should be considered in the assessment of thermal treatment of materials containing brominated flame retardants, as TBBPA, since the emissions could pose a health and environmental risk.

Table 1. Concentration of bromophenols.

EXPERIMENT	P600	C600	P850	C850
ISOMERS	mg compound/kg sample (ppm)			
2-	7860	6810	2	-
3-+4-	3190	3040	2	3
2,3-+2,4-+2,5-	10590	6210	2	19
2,6-	11210	12510	3	-
3,5-	20	70	-	-
3,4-	20	30	-	1
2,3,5-	10	50	-	-
2,4,6-	11440	8860	-	3
2,3,4-	20	30	-	2
2,4,5-	10	10	-	1
2,3,6-	1	10	-	-
3,4,5-	-	5	-	-
2,3,5,6-	1	2	-	1
2,3,4,5-+2,3,4,6-	1	6	-	2
penta-	-	-	-	1
TOTALS				
mono-	11040	9850	4	3
di-	21840	18810	5	20
tri-	11480	8970	-	6
tetra-	2	10	-	3
penta-	-	-	-	1
total bromophenols	44370	37630	9	33

where: (-): not detected (< LOD).

Table 2. Concentration of PBDD/Fs obtained.

EXPERIMENT	P850	C850
ISOMERS	ng compound / kg sample (ppt)	
2,3,7,8-TBDF	40	19190
2,4,6,8-TBDF	10870	10200
1,2,3,7,8-PeBDF	-	32350
2,3,4,7,8-PeBDF	310	8990
1,2,3,4,7,8-HxBDF	-	-
2,3,7,8-TBDD	-	1320
1,2,3,7,8-PeBDD	-	-
1,2,3,4,7,8+1,2,3,6,7,8-HxBDD	-	-
1,2,3,7,8,9-HxBDD	-	-
Total	11220	72050
HOMOLOGUES	ng compound / kg sample (ppt)	
Total-TBDF	12400	214460
Total-PeBDF	310	214310
Total-HxBDF	-	533490
Total-TBDD	12530	17900
Total-PeBDD	-	2540
Total-HxBDD	-	-
Total PBDD/Fs	25240	982700

where: (-): not detected (< LOD).

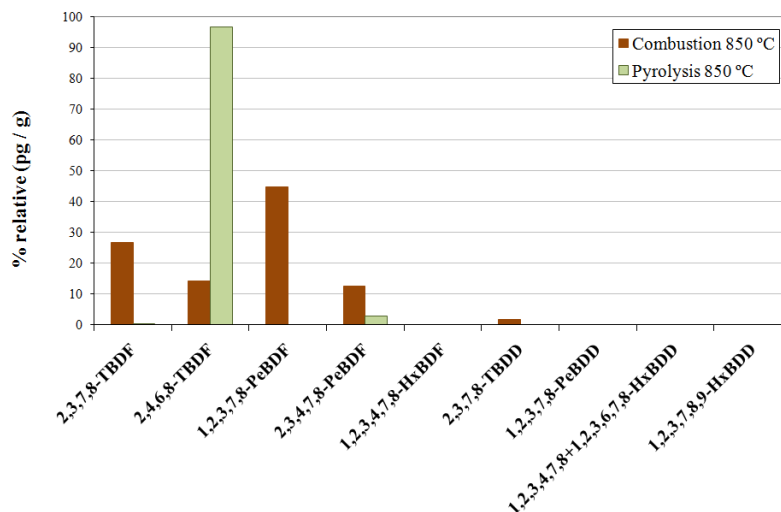


Figure 2. Congener specific 2,3,7,8-PBDD/Fs distribution.

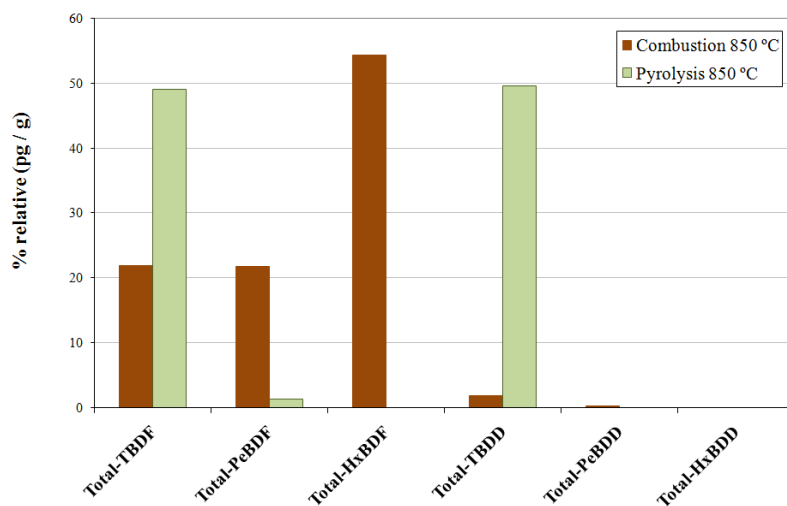


Figure 3. Homologue profile of the samples.

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