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Semivolatile and volatile compounds from the pyrolysis and combustion of poly(vinyl chloride)

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Abstract

Emissions evolved from the pyrolysis and combustion of poly(vinyl chloride) were studied at four different temperatures (500, 700, 850 and 1000 °C) in a horizontal laboratory tubular quartz reactor in order to analyse the influence of both temperature and reaction atmosphere on the final products from thermal and oxidative reactions. It was observed that the CO_2/CO ratio increased with temperature. Methane was the only light hydrocarbon whose yield increased with temperature up to 1000 °C. Benzene was rather stable at high temperatures, but in general, combustion at temperatures above 500 °C was enough to destroy light hydrocarbons. Semivolatile hydrocarbons were collected in XAD-2 resin and more than 160 compounds were detected. Trends on polyaromatic hydrocarbon (PAH) yields showed that most had a maximum at 850 °C in pyrolysis, but naphthalene at 700 °C. Formation of chlorinated aromatics was detected. A detailed analysis of all isomers of chlorobenzenes and chlorophenols was performed. Both of them reached higher total yields in combustion runs, the first ones having a maximum at 700 °C and the latter at 500 °C. Pyrolysis and combustion runs at 850 °C were conducted to study the formation of polychlorodibenzo-*p*-dioxins (PCDDs) and polychlorodibenzofurans (PCDFs). There was more than 20-fold increase in total yields from pyrolysis to combustion, and PCDF yields represented in each case about 10 times PCDD yields.

Keywords: PVC; PAHs; Dioxins; Chlorobenzenes; Chlorophenols; Hydrocarbons

1. Introduction

Thermal treatments, both pyrolysis and combustion, are important alternatives to the disposal of plastic waste in landfills. Poly(vinyl chloride) (PVC) is currently the third most consumed plastic in Western Europe, accounting for 5792 million tonnes in 2002, only surpassed by polyethylene (PE) and polypropylene (PP) [1]. Some of the numerous applications of PVC are pipes, window frames, cables, flooring, packaging and car under-floor protection.

According to a report produced for the European Commission Environment Directorate to assess the influence of PVC on the quantity and hazardousness of flue gas residues from incineration [2], about 15% of total PVC waste is incinerated, and most is landfilled; end of life PVC, when disposed by incineration, mainly involves municipal solid waste (MSW) incinerators; the influence of PVC on MSW composition is mainly related to the chlorine content of the waste sent to incineration; PVC is responsible for 38–66% of the chlorine content in MSW (total Cl in MSW containing PVC is 5.3–7 kg Cl/tonne MSW); PVC also influences the heavy metal content in the MSW (10% of cadmium in MSW is attributable to PVC); the presence of PVC in MSW has a direct effect on the quantity of chlorine in the raw gas and therefore on the corresponding effluents generated by the different gas treatment systems.

Many studies have justified concern about compounds evolved when PVC is burnt. According to some authors [3–5], PVC thermal degradation consists of two main steps: hydrogen chloride is firstly released and then, aromatic hydrocarbons are subsequently formed from cyclization reactions of the remaining polyene chain and also a residual char is generated. The presence of oxygen in the atmosphere instead of an inert gas allows the char to volatilize completely.

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Due to the high temperatures, the presence of oxygen and the chlorine content of the polymer, combustion of PVC produces different kinds of compounds, some of them with a high level of toxicity. Benzene, which is a carcinogenic compound, is one of the main products resulting from the thermal degradation of PVC [3–5]. Other substituted monoaromatic and polyaromatic hydrocarbons (PAHs) are reported to appear in pyrolysis and combustion of PVC at different temperature ranges [5–13]. Some PAHs are classified in EPA's National Toxic Inventory as hazardous air pollutants (HAP), and even, seven of them are thought to be probable human carcinogenic compounds [14].

Apart from hydrogen chloride, chlorinated aromatic compounds are evolved during pyrolysis or combustion of PVC, such as light chlorinated aliphatic hydrocarbons [5], chlorinated PAHs [15], chlorobenzenes (ClBzs) [6,16,13], chlorophenols (ClPhs) [13], chlorobiphenyls (PCBs) [13,17], polychlorodibenzo-*p*-dioxins (PCDDs) and polychlorodibenzofurans (PCDFs) [11,13,17–22].

Formation of chlorobenzenes may occur by different ways, according to Ballschmiter et al. [23]: (i) direct scission of non-totally dehydrochlorinated PVC chain, (ii) chlorination of benzene or lower chlorinated benzenes by Cl_2, (iii) cyclization of chloro-C_1/C_2 units and (iv) pyrolytic isomerization of the chlorobenzenes formed. Lattimer and Kroenke [3] reported that direct scission of PVC chains to form chlorinated-containing compounds is a very minor decomposition pathway because an inappreciable amount of chlorine remains in the polyene after dehydrochlorination. However, McNeill et al. [19] suggested the possibility of a small-scale readdition of HCl or Cl_2 to polyenes after dehydrochlorination in the vicinity of head-to-head defects already containing chlorine atoms to create zones of high Cl concentration that can eventually lead to chlorinated aromatics such as PCDD/PCDFs.

Chlorobenzenes can form PCBs in pyrolytic conditions. Biphenyls can then generate PCDFs by oxidation with the loss of one or two chlorine atoms or two H atoms from the *ortho* position [24]. Chlorophenols can be formed from chlorobenzenes in the presence of oxygen via reaction of a chlorophenyl radical with an ·OH radical. [23]. ClPhs can subsequently react to form both PCDDs and PCDFs [25,26].

PCDD/Fs are one of the most toxic chemicals known. They have been demonstrated to occur ubiquitously in the environment and they appear as by-products of chemical processes such as the manufacture of herbicides, the smelting of copper and scrap metal and incineration processes. Heterogeneous formation of PCDD/Fs on the surface of fly ash particles is generally accepted to be much more important than homogeneous formation in gas-phase. Two formation pathways relevant to incinerator conditions have been identified to generate PCDD/Fs on heterogeneous formation: (i) reactions between chlorinated aromatic precursors previously formed in gas-phase and (ii) de novo synthesis, in which the carbon present in the solid phase material of fly ashes reacts in the presence of chlorine, oxygen and hydrogen to give chlorinated aromatic compounds, both PCDD/Fs or precursors [27–29]. Reactions are catalysed by metals, such as Cu, and principally occur in the post-combustion zone of incinerators where temperatures ranging 250–450 °C favour formation [30].

There are many papers in which PCDD/F formation from combustion of PVC alone or the influence of PVC as a chlorine source in MSW incinerators have been studied, as in [31–33]. Results obtained are sometimes difficult to compare because of the variety of operating conditions and systems used. But there is not much research on concurrent emission analysis of PAHs, ClBzs, ClPhs and PCDD/Fs from the pyrolysis and combustion of PVC at different temperatures [13]. The aim of this work is to provide a comprehensive laboratory study of the pyrolysis and combustion products of pure PVC at different temperatures, mainly focusing on a detailed analysis of the great amount of PAHs generated by pyrosynthesis reactions and the chlorine aromatic compounds evolved. Some hypotheses are discussed concerning the relationship between PCDD/Fs and ClBzs and ClPhs precursors. Since the PVC used in this work, hardly, has no inorganic content and forms no ashes on combustion, the catalysed formation of PCDD/Fs by metals has been assumed not to occur.

2. Experimental

2.1. Material

Experiments were carried out with white powdery PVC resin Etinox-450 free of additives obtained by emulsion polymerization, which is commonly used in low viscosity plastisols. It has a medium molecular weight (104,000 and 40,000 for M_w and M_n, respectively) and a very small particle size, ranging between 1.4 and 24.4 μm. Table 1 shows the chemical composition of PVC analyzed by two complementary techniques: elemental analysis with a Perkin-Elmer 2400 CHN (for C, H, N and S) and X-ray fluorescence with an automatic sequential spectrometer model PW1480 (semiquantitative analysis for elements with an atomic weight higher than that of Mg).

Table 1
Chemical composition of PVC resin

Element	In wt.%
Cl	55.2
C	38.4
H	4.80
S	1.40
Na	0.12
O	0.076
Zn	0.034
K	0.018
Ca	0.017
Si	0.0095
Al	0.0057

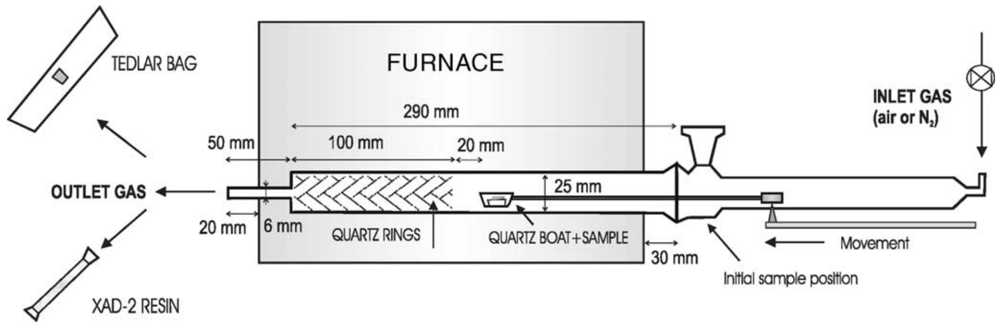

Fig. 1. Scheme of the reactor inside the furnace.

2.2. Experiments in furnace

All the experiments were performed in a horizontal quartz tube-type reactor (Fig. 1), which has already been described in previous papers [34]. This reactor is situated inside a furnace consisting of two independent heating zones and hence the reactor is uniformly heated. Fig. 2 shows temperature profiles measured in the reactor at the four nominal temperatures at which experiments were carried out. It is observed that a temperature close to the nominal one is reached in most of the reactors. Distance values *d* in Fig. 2 range from −20 to 290 mm, and cover the reactor length from the outlet point (at the left in Fig. 1) up to the initial zone inside the furnace.

On the other hand, the sample was placed in a narrow boat; this was put inside a holder, and a small electric motor moved it allowing the sample to be introduced through the reactor at controlled speed (1 mm s^{-1} in this case). Before the sample insertion, the furnace nominal temperature had to be stabilized and the gas flow adjusted. Then, the sample was moved into the reactor to the first half, where it remained for 100 s, to assure total decomposition of the sample. In the end, the holder came back out of the furnace. The second half of the reactor was filled with quartz rings. Thus, the volatile compounds evolved from the primary decomposition were here assumed to undergo further reactions because the packing of quartz rings produced a good local mixing of the gas, avoiding gas bypass.

As previously commented, both pyrolysis and combustion experiments were conducted at four different temperatures (500, 700, 850 and 1000 °C) with about 30 mg of PVC. Air or nitrogen gas was used in combustion or pyrolysis, respectively, with a flow of 300 mL/min (measured at 1 atm and 20 °C). The residence time of gases was calculated both in the total reactor volume and in the packing for each nominal temperature considering the measured temperature profiles, obtaining that the first one ranged from 9 to 17 s (1000 and 500 °C, respectively) and the latter from 3 to 6 s. Table 2 presents the eight different conditions performed in this work. The mass flow of the sample was calculated assuming that the sample was uniformly distributed along the boat (2.5 cm) and burnt in a fixed front when entering the reactor, as well as taking into account the inlet speed, so the rate of advance of the boat is related with the burning rate of the sample.

The bulk air ratio (λ) parameter was defined as the ratio between the actual air flow and the stoichiometric air flow necessary for complete combustion, assuming that the combustion of the solid occurs at the same rate as that being introduced. It can be proved that in the case that the sample contains carbon, hydrogen, sulphur, chlorine and oxygen, the expression to calculate λ is:

$$\lambda = \frac{(m_{\text{air}})_{\text{actual}}}{(m_{\text{air}})_{\text{stoichiometric}}} = \frac{m_{\text{air}}23}{\frac{w_{\text{sample}}v}{L}\left(\frac{\%\text{C}}{12} + \left(\%\text{H} - \frac{\%\text{Cl}}{35.5}\right)\frac{1}{4} + \frac{\%\text{S}}{32} - \frac{\%\text{O}}{32}\right)32} \quad (1)$$

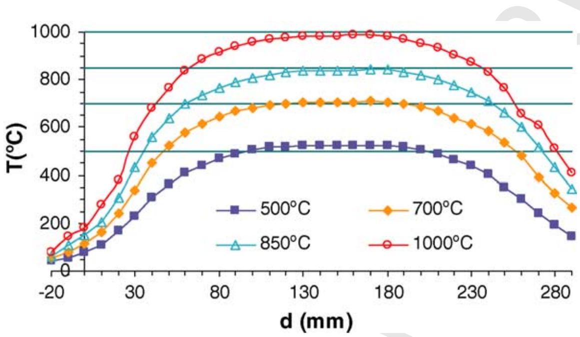

Fig. 2. Temperature profiles.

Table 2
Experimental conditions

Run	Nominal temperature (°C)	Sample mass (mg)	Gas	Bulk air ratio (λ)
P5	500	31	N_2	0
P7	700	30	N_2	0
P8	850	30	N_2	0
P10	1000	30	N_2	0
C5	500	31	Air	0.86
C7	700	30	Air	0.89
C8	850	30	Air	0.89
C10	1000	31	Air	0.86
P8D	850	89	N_2	0
C8D	850	30	Air	0.89

In the previous expression, m_{air} is the air flow introduced ($mg\ s^{-1}$), w_{sample} the total sample mass (mg), v the rate of sample inlet ($mm\ s^{-1}$), L the length of the boat (mm) and %C, %H, %Cl, %S and %O are, respectively, the weight percentages of carbon, hydrogen, chlorine, sulphur and oxygen in the sample. It is clear that $\lambda < 1$ refers to substoichiometric conditions, whereas $\lambda > 1$ corresponds to an excess of oxygen. The calculated value for combustion runs was around 0.89, which indicates a value very close to stoichiometric conditions.

Two different series of experiments had to be carried out to collect the different compounds. On the one hand, gases and volatile compounds (defined here as compounds with boiling point below 130 °C) were collected in Tedlar bags at the outlet of the reactor for a time long enough to ensure total collection of compounds. The eight runs were then repeated to collect semivolatile compounds (boiling point above 130 °C), and this was performed by placing a tube at the outlet of the reactor filled with XAD-2 resin, in which this kind of compounds were adsorbed or condensed. Compounds such as PAHs, chlorophenols or chlorobenzenes were included among these. There was no glass–fiber filter before the resin to independently collect some possible soot with condensed compounds, so the results reported included both the gaseous and condensed-phase amounts.

On the other hand, in order to analyse PCDD/PCDFs it was necessary to carry out additional experiments to collect them in the XAD-2 resin, since they needed a different treatment process before the analysis, so the resin could not be the same, although the operating mode to perform the runs was the same. Moreover, only two pyrolysis and combustion experiments were conducted in this case, at the temperature of 850 °C, 89 and 30 mg of PVC were used in pyrolysis and combustion, respectively. In the beginning, it was not the objective of the work to make a study of PCDD/F formation so full as that conducted for the other compounds, and this is the reason of having only two experiments for PCDD/Fs; the attention was mainly focused on PAHs, chlorobenzenes and chlorophenols, but it was also intended to show that PVC pyrolysis and combustion at high temperatures can be a source of dioxins.

2.3. Extraction and purification

The XAD-2 resin was pre-cleaned with dichloromethane by Soxhlet extraction for 20 h prior to use. After each pyrolysis or combustion run to collect semivolatile compounds, the resins were placed in the Soxhlet thimbles, extracted in accordance with the US EPA 3540C method with 80 mL dichloromethane for 20 h, and previously spiked with 10 μL of a solution 4000 μg/mL containing six deuterated aromatic compounds: 1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} and perylene-d_{12}. These were used as internal standards to quantify semivolatile compounds. The extracts were subsequently concentrated in a rotary evaporator and with a gentle stream of nitrogen up to 1.5 mL. Finally, 10 μL of a solution 2000 μg/mL anthracene-d_{10} was spiked to the vials as a recovery standard. The highest recoveries were obtained for the heaviest internal standards (around 80–90%), and somewhat lower for the lighter and more volatile ones (between 20 and 60%).

The resins corresponding to the two experiments aimed at analysing PCDD/PCDFs were extracted in a Soxhlet apparatus with toluene, changed to hexane, filtered and cleaned-up using an automated Power Prep™ system (FMS Inc., MA) equipped with three different columns (silica, alumina and activated carbon) and eluted with toluene. After that, the extracts were concentrated in a rotary evaporator and under a gentle stream of nitrogen up to 0.3 mL. ^{13}C labeled compounds included in the US EPA 1613 method were used to quantify (20 μL of labeled-compound spiking solution (LCS) added prior to extraction) and to calculate final recovery (10 μL of internal standard solution (ISS) added to the final volume). Recoveries were rather acceptable (70% mean value).

2.4. Analysis

The analysis of CO_2, CO, oxygen and nitrogen from Tedlar bags was carried out in a Shimadzu GC-14A gas chromatograph equipped with a concentric packed Alltech CTR I column (6 ft × 1/8 in. and 6 ft × 1/4 in. for inner and outer columns, respectively) and a thermal conductivity detector. Gases and volatile compounds collected in Tedlar bags consisting of light hydrocarbons (ranged from methane to xylenes) were detected in a Shimadzu GC-17A gas chromatograph with a Supelco capillary Alumina-KCl Plot column (30 m × 0.32 mm) in split injection and a flame ionization detector. For the identification and quantification of all these compounds, external standard calibration of each compound was carried out.

Semivolatile compounds collected in XAD-2 resin were analysed by GC–MS. The equipment and method analysis was different depending on the specific group of compounds. At first, a Fisons MD8000 mass spectrometer in selected scan mode ranging from 40 to 500 amu to detect all the possible semivolatile compounds formed coupled to a Fisons GC8000 gas chromatograph with a J&W Scientific Products DB-5 MS column (60 m × 0.25 mm) in splitless mode was used. The analysis was semiquantitative, since total areas were used to estimate the mass of each compound by interpolating calculated response factors (mass:area ratios) between each pair of deuterated standards. Identification was performed by comparing mass spectrum of each compound with those of the NIST database. However, compounds with similar retention times and mass spectral features were sometimes difficult to differentiate, so other indicators such as Lee retention indices [35–36], boiling points of compounds, correlation among chromatograms at different temperatures and other results obtained in previous works [34,37] were also very useful, although absolute certainty is often not possible. Logically, a standard for each one would have been required for an exact identification and quantification of every compound.

Selected ion monitoring (SIM) mode was used with the same equipment to specifically analyse the 16 PAHs listed as HAP in [14], which are: naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), benzo(*a*)anthracene (BaA)*, chrysene (Chr)*, benzo(*b*)-fluoranthene (BbF)*, benzo(*k*)fluoranthene (BkF)*, benzo(*a*)pyrene (BaP)*, indeno(1,2,3-*cd*)pyrene (Icd)*, dibenz(*a*,*h*)anthracene (DbA)* and benzo(*g*,*h*,*i*)perylene (BgP). Those marked with an asterisk have also been reported to be probable human carcinogenic compounds. For these 16 PAHs, both identification and quantification were performed with an authentic standard of each compound by making a calibration straight line for each one with the nearest internal deuterated standard relating mass ratio with primary ion area ratio to calculate a mean response factor (RF).

Both chlorobenzenes and chlorophenols were also specifically analysed with mixture standards of each compound on an Agilent 5973N mass spectrometer in SIM mode coupled to an Agilent 6890N gas chromatograph with an Agilent HP-5 MS column (30 m $\times$ 0.25 mm) in splitless mode, checking primary:secondary ion area ratio for each compound and using deuterated PAHs as internal standards.

Finally, PCDD/PCDFs were analyzed by HRGC/MS on a Micromass AutoSpec-Ultima NT mass spectrometer in SIM mode coupled to an Agilent 6890 gas chromatograph with a DB-5 MS column (60 m $\times$ 0.25 mm) in PTV injection. Molecular ions monitored where those of tetra-, penta-, hexa-, hepta- and octachlorodibenzo-*p*-dioxins and dibenzofurans.

Before each experiment, a blank run was conducted following the same procedure as sample runs to identify possible interferences. Mainly siloxanes, bis(2-ethylhexyl)phthalate and xylenes were observed in considerable quantities so they were subtracted from the sample data.

3. Results and discussion

3.1. Gases and volatile compounds

Table 3 shows the results corresponding to CO_2, CO and light hydrocarbon yields obtained in the experiments. Firstly, it can be observed that CO_2 presents a maximum at 850 °C in combustion, whereas CO does so at 700 °C. Much more CO_2 than CO appears. Fig. 3 gives an idea of combustion efficiency. As temperature rises, CO_2/($CO + CO_2$) ratio increases and no CO is detected at 1000 °C. On the other hand, some CO_2 has been produced in pyrolysis, what could mean that some oxygen could have remained in the furnace despite the purge with nitrogen before each experiment in pyrolysis. The small content of oxygen in the sample is not enough to react with carbon to produce the CO_2 observed.

Regarding light hydrocarbons, some comments can be made. Aliphatic hydrocarbons from C_1 to C_6 were identified, and also benzene, toluene and xylenes were present among the gases and volatile compounds. The largest yields correspond to methane, ethylene, benzene and toluene. There are some compounds which were not able to be identified (named as unknown in Table 3) because the retention times of these compounds did not match up with any of the available standard used, and the FID detector does not give information about the structure of compounds. These could be other light hydrocarbons or even light chlorinated hydrocarbons. They have been quantified by using the response factor of the closest known compound. McNeill et al. [5] reported the existence of light chlorinated hydrocarbons from PVC pyrolysis, like 2-chloro-1-butene, 3-chloro-1-butene, 2-chloro-2-butene or 2-chloro-butane, among others. It is interesting to observe that some of these unknown compounds present a considerable yield even at high temperatures. It is also remarkable that combustion at relatively high temperatures is enough to destroy or avoid formation of almost all compounds.

In Table 3, some symbols appear which have been used to characterize the behavior of compounds regarding temperature and atmosphere of the reaction:

(a) Type A, B or C behavior is for those compounds whose yields decrease, have a maximum or increase with temperature in pyrolysis, respectively.
(b) Type A′, B′ or C′ behavior refers to a decrease, a maximum or an increase in yields with temperature in combustion, respectively.
(c) Type I or II behavior indicates that yields decrease or increase, respectively, from pyrolysis to combustion. If no clear behavior has been observed, no symbol has been written.

On the whole, compounds disappear at high temperatures since they present type A or B behavior. When presenting type B, the maximum usually appears at 700 °C more than at 850 °C. Only methane and benzene seem to raise their yields with temperature in pyrolysis, but none in combustion. H-

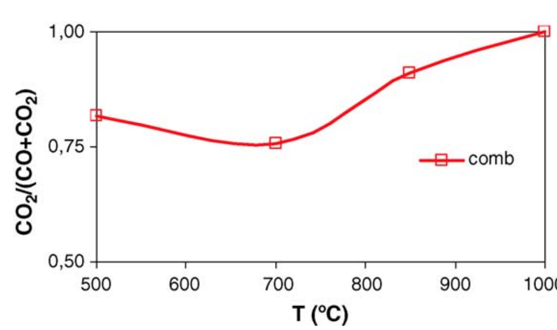

Fig. 3. CO_2/($CO + CO_2$) ratio in combustion.

Table 3
Gases and volatile compounds obtained (mg compound/kg sample)

M_W	Experiment compound	In mg compound/kg sample								Behavior
		P5	P7	P8	P10	C5	C7	C8	C10	
44	CO_2	5980	14120	10900	22870	347540	929120	1308420	1120400	A, B′, II
28	CO	nd	nd	nd	nd	78730	301040	131820	nd	B′, II
16	Methane	4294	19098	25771	27752	7698	3319	nd	nd	C, A′
30	Ethane	3784	6250	859	nd	3741	236	nd	nd	B, A′, I
28	Ethylene	2751	15007	19376	3534	3866	nd	nd	nd	B, A′
44	Propane	1772	1060	nd	nd	1436	nd	nd	nd	A, A′, I
42	Propylene	2152	7513	1197	nd	2462	nd	nd	nd	B, A′, I
	Unknown	nd	*266*	*2751*	*12177*	nd	*1013*	nd	nd	C, B′
58	*n*-Butane	768	480	285	nd	532	nd	nd	nd	A, A′, I
56	*t*-2-Butene + 1-butene	1222	907	nd	nd	907	nd	nd	nd	A, A′, I
56	Isobutene	524	874	nd	nd	360	nd	nd	nd	B, A′, I
56	*c*-2-Butene	182	nd	nd	nd	nd	nd	nd	nd	A, I
	Unknown	*213*	nd	nd	nd	nd	nd	nd	nd	A, I
72/40	*n*-Pentane + propyne	389	nd	nd	nd	243	nd	nd	nd	A, A′, I
54	1,3-Butadiene	723	5480	1632	nd	833	nd	nd	nd	B, A′, I
	Unknown	*474*	nd	nd	nd	*229*	nd	nd	nd	A, A′, I
70	1-Pentene	402	nd	nd	nd	340	nd	nd	nd	A, A′, I
54	2-Butyne	281	203	922	nd	nd	nd	nd	nd	B, I
86	*n*-Hexane	1064	3374	292	nd	513	nd	nd	nd	B, A′, I
	Unknown	*445*	nd	nd	nd	nd	nd	nd	nd	A, I
	Unknown	*408*	nd	nd	nd	nd	nd	nd	nd	A, I
	Unknown	*243*	nd	nd	nd	nd	nd	nd	nd	A, I
84	1-Hexene	371	nd	nd	nd	nd	nd	nd	nd	A, I
78	Benzene	21821	28070	31225	30558	23082	nd	nd	nd	C, A′, I
	Unknown	nd	nd	*5617*	nd	nd	nd	*4376*	nd	B, B′, I
92	Toluene	4337	9989	9289	nd	3856	nd	nd	nd	B, A′, I
106	Xylene	617	2701	829	nd	508	nd	nd	nd	B, A′, I
	Unknown	*520*	*1303*	*648*	nd	*337*	nd	nd	nd	B, A′, I
Total light hydrocarbons		49757	102576	100693	74021	50942	4568	4376	nd	

owever, they behave differently; whereas methane yields rise clearly from a relatively low yield at 500 to 1000 °C, benzene is emitted early at 500 °C in a high quantity and then it withstands higher temperatures and even slightly grows. The different behavior can be explained taking into account that methane is a final product from cracking reactions occurring at high temperatures, while benzene is known to be a primary decomposition product from thermal decomposition of PVC [3–5] and also has a great thermal stability [38]. On the other hand, types A′ and I behaviors are almost general, that indicates that the combination of oxygen and high temperatures significantly depletes formation of light hydrocarbons.

3.2. Semivolatile compounds

Table 4 presents the yields obtained for semivolatile compounds. The results include both compounds detected in scan mode and PAH quantified in SIR mode by GC/MS analysis, but neither chlorobenzenes nor chlorophenols are shown, because they have been analysed separately.

As done with light hydrocarbons, three kinds of characterizations regarding their behavior have been performed: type A, B or C (temperature effect in pyrolysis); type A′, B′ or C′ (temperature effect in combustion); and I or II (atmosphere effect). Moreover, some new indices appear related to the confidence on identifying compounds:

(a) An authentic standard was used.
(b) The coincidence between the experimental mass spectrum and the proposed compound mass spectrum of the NIST database was higher than 90%.
(c) The coincidence between spectra was 80–90%.
(d) The coincidence between spectra was 70–80%.
(e) Differences in Lee retention indices were lower than 1%.

A great effort has been made to identify and quantify (or semiquantify) the large number of species adsorbed or condensed in resin XAD-2, more than 160. Panagiotou et al. [9] described some classes of compounds found on pyrolysis and combustion of PVC at high temperatures in different laboratory furnaces and operation modes. The compounds presented here can also be classified as in that paper:

Table 4
Semivolatile compounds obtained (mg compound/kg sample)

Form	M_w	Calculated Lee	Experiment		In mg compound/kg sample								Behavior		
			Compound	Type	P5	P7	P8	P10	C5	C7	C8	C10			
C_8H_{10}	106	118.9	Ethyl–benzene	c	1368	527	nd	nd	590	nd	nd	nd	A	A′	I
C_8H_{10}	106	121.2	*p*-Xylene	c	1091	4286	2773	nd	446	nd	nd	nd	B	A′	I
C_8H_6	102	122.7	Ethynyl–benzene	b	nd	96	1374	579	nd	nd	nd	nd	B		I
C_8H_8	104	127.7	Styrene	b	1004	9311	772	nd	925	nd	nd	nd	B	A′	I
C_8H_{10}	106	128.4	*o*-Xylene	c	1463	4604	1402	nd	494	nd	nd	nd	B	A′	I
C_9H_{10}	118	143.1	Allylbenzene	d	163	nd	nd	nd	38	nd	nd	nd	A	A′	I
C_9H_{12}	120	145.1	*n*-Propylbenzene	c	259	nd	nd	nd	40	nd	nd	nd	A	A′	I
C_7H_6O	106	147.0	Benzaldehyde	c	nd	234	65	36	nd	28	nd	37	B		I
C_9H_{12}	120	147.3	1-Ethyl-3-methylbenzene	d	276	nd	nd	nd	484	nd	nd	nd	A	A′	II
C_9H_{12}	120	148.3	1-Ethyl-4-methylbenzene		nd	nd	37	nd	nd	nd	nd	nd	B		I
C_6H_6O	94	150.4	Phenol	a	47	86	16	11	197	12	9	5	B	A′	
C_9H_8	116	151.8	1-Ethynyl-4-methylbenzene	b	nd	nd	92	nd	nd	nd	nd	nd	B		I
C_9H_{12}	120	152.1	1,3,5-Trimethylbenzene	c	354	nd	nd	nd	60	nd	nd	nd	A	A′	I
C_9H_8	116	153.3	1-Propynyl–benzene	b	nd	nd	70	nd	nd	nd	nd	nd	B		I
C_9H_{10}	118	155.1	α-Methylstyrene	c	nd	514	168	nd	nd	nd	nd	nd	B		I
C_9H_{12}	120	155.4	1-Ethyl-2-methylbenzene	c	133	514	168	nd	60	nd	nd	nd	B	A′	I
C_9H_{10}	118	156.2	*m*-Methylstyrene	c	213	566	177	nd	nd	nd	nd	nd	B		I
C_8H_6O	118	156.7	Benzofuran	c	nd	nd	nd	nd	165	nd	nd	nd		A′	II
C_7H_7Cl	126.6	160.7	1-Chloro-3-methylbenzene	c	nd	nd	nd	nd	407	nd	nd	nd		A′	II
C_9H_{10}	118	163.2	*o*-Methylstyrene	c	201	nd	nd	nd	25	nd	nd	nd	A	A′	I
C_9H_{10}	118	166.5	1-Propenylbenzene	c	315	nd	nd	nd	23	nd	nd	nd	A	A′	I
C_8H_9Cl	140.6	167.2	2-Chloroethylbenzene	c	64	nd	nd	nd	nd	nd	nd	nd	A		I
C_9H_8	116	168.8	Indene	b	1121	16778	4114	55	161	nd	nd	nd	B	A′	I
$C_{10}H_{14}$	134	170.0	*n*-Butylbenzene	c	170	nd	nd	nd	19	nd	nd	nd	A	A′	I
$C_{10}H_{14}$	134	172.8	1-Methyl-4/2-propylbenzene	c	101	nd	nd	nd	nd	nd	nd	nd	A		I
C_8H_8O	120	173.0	Acetophenone	d	nd	nd	nd	nd	87	nd	nd	nd		A′	II
$C_{15}H_{14}O$	210	173.6	Dibenzylketone	d	nd	nd	nd	nd	92	nd	nd	nd		A′	II
$C_{10}H_{12}$	132	174.8	Ethylstyrene/allyltoluene/similar	c	24	nd	nd	nd	nd	nd	nd	nd	A		I
$C_8H_{16}O_2$	144	180.8	2-Ethylhexanoic acid	c	217	nd	nd	nd	nd	nd	nd	nd	A		I
$C_{10}H_{12}$	132	189.4	Ethylstyrene/allyltoluene/similar	b	100	nd	nd	nd	nd	nd	nd	nd	A		I
$C_{10}H_{10}$	130	191.4	1-Butynyl–benzene	b	438	543	nd	nd	nd	nd	nd	nd	B		I
$C_{10}H_{12}$	132	191.9	Ethylstyrene/allyltoluene/similar	c	438	nd	nd	nd	nd	nd	nd	nd	A		I
$C_{10}H_{10}$	130	192.9	1-Methyl indene	c, e	487	1020	nd	nd	nd	nd	nd	nd	B		I
$C_{10}H_8$	128	193.4	1-Methylene indene	b, e	nd	nd	nd	nd	nd	nd	nd	nd	B		I
$C_7H_6O_2$	122	193.9	Benzoic acid	b	1346	5317	2964	3819	2516	3390	6061	1049		B′	
$C_{10}H_{10}$	130	195.5	1,2/1,4-Dihydronaphthalene	c, e	1346	nd	nd	nd	nd	nd	nd	nd	A		I
$C_9H_{10}O$	134	197.0	4-Ethyl-benzaldehyde	b	nd	nd	106	nd	nd	nd	113	nd	B	B′	
$C_{10}H_8$	128	200.0	Naphthalene	a, e	2448	22248	13715	14905	2147	36	nd	nd	B	A′	I
$C_9H_{14}O$	138	199.8	Trimethyl-2-cyclohexen-1-one	c	nd	nd	nd	nd	nd	nd	78	nd		B′	II
$C_{11}H_{14}$	146	201.2	3-Methyl-2-butenyl-benzene	c	36	nd	nd	nd	nd	nd	nd	nd	A		I
$C_6H_{14}O_4$	150	206.8	Triethylene glycol	c	nd	nd	nd	nd	14132	14756	nd	nd		A′	II
$C_{11}H_{10}$	142	221.2	2-Methyl naphthalene	b, e	565	2817	3062	nd	115	nd	nd	nd	B	A′	I
$C_{11}H_{10}$	142	224.4	1-Methyl naphthalene	b, e	414	2350	2296	nd	175	nd	nd	nd	B	A′	I
$C_9H_{10}O_2$	150	226.4	Ethylbenzoic acid	d	51	44	62	54	36	63	112	21		B′	
$C_{12}H_{14}$	158	227.9	1-Hexynyl-benzene	d	43	nd	nd	nd	nd	nd	nd	nd	A		I
$C_9H_{10}O_2$	150	228.7	Dimethylbenzoic acid	d	15	21	26	23	13	20	48	10		B′	
$C_{13}H_{16}$	172	230.2	3-Heptynyl-benzene	d	29	nd	nd	nd	nd	nd	nd	nd	A		I
$C_9H_{18}Cl_2$	197	232.7	3-Chloro-decane	b	48	nd	nd	nd	nd	nd	nd	nd	A		I
$C_{12}H_{10}$	154	235.5	Biphenyl	b, e	142	461	1184	204	109	nd	nd	nd	B	A′	I
$C_{10}H_7Cl$	163	235.9	2-Chloro-naphthalene	b	3	12	40	35	15	5	nd	nd	B		I
$C_{10}H_7Cl$	163	236.9	1-Chloro-naphthalene	b	1	22	107	22	nd	9	nd	nd	B		I
$C_{13}H_{12}$	168	238.2	2-Methylbiphenyl	c, e	nd	nd	21	nd	nd	nd	nd	nd	B		I
$C_{12}H_{12}$	156	238.5	2-Ethylnaphthalene	b, e	159	19	nd	nd	31	nd	nd	nd	A	A′	I
$C_{12}H_{12}$	156	239.3	1-Ethylnaphthalene	e	37	nd	nd	nd	nd	nd	nd	nd	A		I
$C_{12}H_8$	152	240.0	Biphenylene	c	nd	nd	145	nd	nd	nd	nd	nd	B		I
$C_{12}H_{12}$	156	240.3	2,7-/2,6-Dimethylnaphthalene	c	24	79	145	20	nd	nd	nd	nd	B		I
C_9H_7ClO	166.6	240.5	3-Phenyl-2-propenoyl chloride	d	nd	nd	nd	nd	176	nd	nd	nd		A′	II
$C_{12}H_{10}$	154	241.8	1-Vinylnaphthalene	c	19	52	45	nd	13	nd	nd	nd	B	A′	I
$C_{12}H_{12}$	156	243.1	1,3-Dimethylnaphthalene	b, e	73	113	176	nd	nd	nd	nd	nd	B		I
$C_{12}H_{12}$	156	243.8	1,7-/1,6-Dimethylnaphthalene	b	54	23	125	nd	nd	nd	nd	nd	B		I
$C_{12}H_{10}$	154	244.8	2-Vinylnaphthalene	b, e	42	204	397	nd	16	nd	nd	nd	B	A′	I

Table 4 (*Continued*)

Form	M_w	Calculated Lee	Experiment		In mg compound/kg sample								Behavior		
			Compound	Type	*P5*	P7	P8	P10	C5	C7	C8	C10			
$C_{12}H_{12}$	156	246.5	2,3-/1,4-Dimethylnaphthalene	b	nd	81	79	nd	nd	nd	nd	nd	B		I
$C_{12}H_{25}Cl$	205	246.6	1-Chloro-dodecane	c	173	nd	nd	nd	nd	nd	nd	nd	A		I
$C_{12}H_{12}$	156	247.3	1,5-Dimethylnaphthalene	b, e	54	57	54	nd	nd	nd	nd	nd	A		I
$C_{12}H_{8}$	152	249.2	Acenaphthylene	a, e	12	1764	5067	1548	10	nd	nd	nd	B	A′	I
$C_{13}H_{12}$	168	252.6	Methylbiphenyl	c	34	71	170	nd	nd	nd	nd	nd	B		I
$C_{12}H_{10}$	154	254.5	Acenaphthene	a, e	22	18	21	nd	nd	nd	nd	nd	A		I
$C_{11}H_{8}O$	156	257.9	2-Naphthaldehyde	c	nd	nd	nd	nd	16	nd	nd	nd		A′	II
$C_{13}H_{12}$	168	258.6	2,4A-Dihydro-fluorene	c	nd	nd	33	nd	nd	nd	nd	nd	B		I
$C_{14}H_{14}$	182	258.9	Bibenzyl	d	71	nd	nd	nd	16	nd	nd	nd	A	A′	I
$C_{13}H_{12}$	168	262.4	Methylbiphenyl	c	nd	20	34	nd	nd	nd	nd	nd	B		I
$C_{13}H_{12}$	168	263.4	Methylbiphenyl	c	nd	16	9	nd	nd	nd	nd	nd	B		I
$C_{13}H_{14}$	170	263.4	Trimethylnaphthalene	c	nd	16	9	nd	nd	nd	nd	nd	B		I
$C_{13}H_{12}$	168	264.5	Methylbiphenyl	c	nd	nd	14	nd	nd	nd	nd	nd	B		I
$C_{13}H_{12}$	168	265.2	Methylbiphenyl	c	nd	12	10	nd	nd	nd	nd	nd	B		I
$C_{11}H_{9}Cl$	176.6	266.23	1-Chloromethyl-naphthalene	c	nd	nd	5	nd	nd	nd	nd	nd	B		I
$C_{13}H_{14}$	170	266.2	Trimethylnaphthalene	c	nd	13	5	nd	nd	nd	nd	nd	B		I
$C_{13}H_{10}$	166	267.2	Phenalene	c, e	nd	81	199	nd	nd	nd	nd	nd	B		I
$C_{13}H_{10}$	166	269.5	Similar phenalene	c	nd	87	220	nd	nd	nd	nd	nd	B		I
		269.8	Alkyl–phenol	c	92	nd	nd	nd	nd	nd	nd	nd	A		I
$C_{13}H_{10}$	166	270.3	Fluorene	a, e	132	2080	3952	14	20	nd	nd	nd	B	A′	I
$C_{13}H_{10}$	166	271.0	Similar phenalene	c	nd	nd	156	nd	nd	nd	nd	nd	B		I
$C_{14}H_{12}$	180	271.5	9-Methylfluorene	e	nd	16	24	nd	nd	nd	nd	nd	B		I
$C_{13}H_{12}$	168	273.3	Methylbiphenyl/similar	c	131	nd	nd	nd	nd	nd	nd	nd	A		I
$C_{13}H_{10}$	166	273.8	Similar fluorene	c	nd	57	117	nd	nd	nd	nd	nd	B		I
$C_{13}H_{12}$	168	274.6	Methylbiphenyl/similar	d	54	nd	nd	nd	nd	nd	nd	nd	A		I
$C_{14}H_{12}$	180	275.6	4-Vinylbiphenyl	d	nd	nd	111	nd	nd	nd	nd	nd	B		I
$C_{13}H_{10}$	166	275.8	Similar fluorene	d	nd	56	nd	nd	nd	nd	nd	nd	B		I
$C_{13}H_{10}$	166	276.8	Similar fluorene	c	nd	223	275	nd	nd	nd	nd	nd	B		I
$C_{16}H_{33}Cl$	261	277.6	1-Chloro-hexadecane	c	41	nd	nd	nd	nd	nd	nd	nd	A		I
$C_{14}H_{10}$	178	279.3	9-Methylene fluorene	c	nd	nd	40	nd	nd	nd	nd	nd	B		I
$C_{14}H_{12}$	180	286.9	3-/4-Methylfluorene	c	72	219	248	nd	nd	nd	nd	nd	B		I
$C_{14}H_{12}$	180	288.4	2-Methylfluorene	c, e	80	120	nd	nd	nd	nd	nd	nd	B		I
$C_{14}H_{12}$	180	290.2	1-Methylfluorene	c, e	15	113	102	nd	nd	nd	nd	nd	B		I
$C_{14}H_{10}$	178	291.7	Diphenylethyne	c, e	nd	nd	98	nd	nd	nd	nd	nd	B		I
$C_{14}H_{12}$	180	293.0	3-/4-Methylfluorene	c	nd	28	47	nd	nd	nd	nd	nd	B		I
$C_{13}H_{8}O$	180	293.7	9-Fluorenone	c	nd	nd	nd	nd	40	nd	nd	nd		A′	II
$C_{14}H_{14}$	182	296.0	1,2,3,4-Tetrahydrophenanthrene	c, e	37	nd	nd	nd	nd	nd	nd	nd	A		I
$C_{15}H_{12}$	192	296.0	9-Ethylidenefluorene	c	nd	nd	50	nd	nd	nd	nd	nd	B		I
$C_{14}H_{10}$	178	300.0	Phenanthrene	a, e	145	2037	5498	2420	95	nd	nd	nd	B	A′	I
$C_{14}H_{10}$	178	301.4	Anthracene	a, e	23	233	1690	61	nd	nd	nd	nd	B		I
$C_{15}H_{14}$	194	307.3	2,3-Dimethylfluorene	c	8	nd	nd	nd	nd	nd	nd	nd	A		I
$C_{16}H_{12}$	204	308.8	1-(Phenylmethylene)-1H-indene	b	16	41	187	nd	nd	nd	nd	nd	B		I
$C_{15}H_{12}$	192	309.7	9-Methyl–anthracene	c, e	nd	34	45	nd	nd	nd	nd	nd	B		I
$C_{15}H_{12}$	192	314.9	Methyl–anthracene/phenanthrene	b	35	110	295	nd	nd	nd	nd	nd	B		I
$C_{15}H_{12}$	192	315.9	Methyl–anthracene/phenanthrene	b	54	131	350	nd	nd	nd	nd	nd	B		I
$C_{15}H_{12}$	192	316.9	Methyl–anthracene/phenanthrene	b	20	71	197	nd	10	nd	nd	nd	B	A′	I
$C_{15}H_{12}$	192	318.4	Methyl–anthracene/phenanthrene	b	47	374	nd	nd	11	nd	nd	nd	B	A′	I
$C_{15}H_{10}$	190	319.1	Benzo(*d*,*e*,*f*)fluorine	c, e	nd	nd	857	9	nd	nd	nd	nd	B		I
$C_{15}H_{12}$	192	319.1	Methyl–anthracene/phenanthrene	d	41	92	312	nd	nd	nd	nd	nd	B		I
$C_{16}H_{12}$	204	324.1	Phenyl–naphthalene/similar	b	20	116	492	17	15	nd	nd	nd	B	A′	I
$C_{16}H_{10}$	202	330.3	Similar fluoranthene/pyrene	d	nd	nd	12	nd	nd	nd	nd	nd	B		I
$C_{16}H_{14}$	206	330.3	Dimethyl–phenanthrene/anthracene	d	nd	nd	12	nd	nd	nd	nd	nd	B		I
$C_{16}H_{12}$	204	332.4	Phenyl–naphthalene/similar	b	nd	14	37	nd	nd	nd	nd	nd	B		I
$C_{16}H_{14}$	206	332.9	Dimethyl–phenanthrene/anthracene	d	14	25	40	nd	nd	nd	nd	nd	B		I
$C_{16}H_{12}$	204	334.5	Phenyl–naphthalene/similar	c	nd	54	65	nd	nd	nd	nd	nd	B		I
$C_{16}H_{12}$	204	336.6	1,4-Dihydro-1,4-ethenoanthracene	c	nd	28	45	nd	nd	nd	nd	nd	B		I
$C_{16}H_{10}$	202	338.2	Fluoranthene	a	6	83	985	1071	5	nd	nd	nd	C	A′	I
$C_{17}H_{14}$	218	339.2	2-(Phenylmethyl)-naphthalene		nd	nd	22	nd	nd	nd	nd	nd	B		I
$C_{16}H_{10}$	202	341.5	Acephenanthrylene/aceanthrylene		nd	144	646	50	nd	nd	nd	nd	B		I
$C_{16}H_{10}$	202	344.2	Acephenanthrylene/aceanthrylene		nd	nd	170	nd	nd	nd	nd	nd	B		I
$C_{16}H_{10}$	202	346.3	Pyrene	a	5	47	610	291	4	nd	nd	nd	B	A′	I
$C_{18}H_{14}$	230	351.7	*m*-Terphenyl	c	nd	nd	10	nd	nd	nd	nd	nd	B		I

Table 4 (*Continued*)

Form	M_w	Calculated Lee	Experiment: Compound	Type	In mg compound/kg sample: *P5*	P7	P8	P10	C5	C7	C8	C10	Behavior
$C_{18}H_{12}$	228	353.0	Similar benzophenanthrene	d	nd	nd	17	nd	nd	nd	nd	nd	B I
$C_{17}H_{12}$	216	354.3	Benzofluorene/methylpyrene	b	nd	21	101	nd	nd	nd	nd	nd	B I
$C_{17}H_{12}$	216	358.5	Benzofluorene/methylpyrene	c	22	276	868	nd	nd	nd	nd	nd	B I
$C_{17}H_{12}$	216	360.9	Benzofluorene/methylpyrene	c	19	159	548	nd	nd	nd	nd	nd	B I
$C_{17}H_{12}$	216	365.3	Benzofluorene/methylpyrene	c	nd	nd	56	nd	nd	nd	nd	nd	B I
$C_{18}H_{12}$	228	365.3	Similar benzophenanthrene	c	nd	nd	56	nd	nd	nd	nd	nd	B I
$C_{17}H_{12}$	216	366.6	Methylpyrene	d	nd	nd	57	nd	nd	nd	nd	nd	B I
$C_{17}H_{12}$	216	367.9	Methylpyrene	b	nd	28	151	nd	nd	nd	nd	nd	B I
$C_{18}H_{14}$	230	375.7	Dimethylpyrene	d	nd	nd	21	nd	nd	nd	nd	nd	B I
$C_{18}H_{14}$	230	376.5	Dimethylpyrene	c	nd	nd	32	nd	nd	nd	nd	nd	B I
$C_{18}H_{14}$	230	378.9	5,12-Dihydronaphthacene	d, e	nd	nd	25	nd	nd	nd	nd	nd	B I
$C_{18}H_{14}$	230	379.6	Dimethylpyrene		nd	nd	37	nd	nd	nd	nd	nd	B I
$C_{18}H_{14}$	230	381.0	Dimethylpyrene	d	nd	nd	42	nd	nd	nd	nd	nd	B I
$C_{18}H_{10}$	226	388.2	Benzo(*g*,*h*,*i*)fluoranthene	d, e	nd	nd	89	nd	nd	nd	nd	nd	B I
$C_{19}H_{14}$	242	390.3	9-Phenyl-fluorene	c	nd	nd	13	nd	nd	nd	nd	nd	B I
$C_{18}H_{12}$	228	397.7	Benzo(*a*)anthracene	a, e	15	111	705	42	nd	nd	nd	nd	B I
$C_{18}H_{12}$	228	400.0	Chrysene	a, e	24	121	772	77	13	nd	nd	nd	B A′ I
$C_{20}H_{14}$	254	401.9	4,5-Dihydrobenzo(*a*)pyrene	b	nd	nd	23	nd	nd	nd	nd	nd	B I
$C_{17}H_{10}O$	230	404.4	Benzanthrenone	b	nd	nd	34	nd	nd	nd	nd	nd	B I
$C_{19}H_{14}$	242	413.7	Methyl–benz(*a*)anthracene/chrysene	c	nd	nd	195	nd	nd	nd	nd	nd	B I
$C_{20}H_{14}$	254	416.9	Phenyl–phenanthrene/similar	c	nd	nd	117	nd	nd	nd	nd	nd	B I
$C_{19}H_{12}$	240	417.7	Cyclopentachrysene/similar	c	nd	nd	129	nd	nd	nd	nd	nd	B I
$C_{19}H_{14}$	242	419.0	Methyl–benz(*a*)anthracene/chrysene	c	nd	nd	64	nd	nd	nd	nd	nd	B I
$C_{20}H_{14}$	254	419.0	Phenyl–phenanthrene/similar	c	nd	nd	64	nd	nd	nd	nd	nd	B I
$C_{19}H_{12}$	240	419.6	Cyclopentachrysene/similar	c	nd	nd	141	nd	nd	nd	nd	nd	B I
$C_{20}H_{14}$	254	421.3	2,2′-Binaphthalene	c, e	nd	nd	59	nd	nd	nd	nd	nd	B I
$C_{20}H_{12}$	252	435.4	Benzo(*b*)fluoranthene	a, e	nd	108	403	206	nd	nd	nd	nd	B I
$C_{20}H_{12}$	252	436.0	Benzo(*k*)fluoranthene	a, e	nd	132	505	126	nd	nd	nd	nd	B I
$C_{20}H_{12}$	252	438.9	Benzo(*a*)acephenanthrylene/similar	b	nd	39	340	nd	nd	nd	nd	nd	B I
$C_{20}H_{12}$	252	444.4	Benzo(*e*)pyrene	c	nd	nd	204	86	nd	nd	nd	nd	B I
$C_{20}H_{12}$	252	446.2	Benzo(*a*)pyrene	a, e	nd	110	402	142	nd	nd	nd	nd	B I
$C_{21}H_{14}$	266	453.6	2,3,6,7-Dibenzofluorene/similar		nd	nd	130	nd	nd	nd	nd	nd	B I
$C_{21}H_{14}$	266	455.0	2,3,6,7-Dibenzofluorene/similar		nd	nd	158	nd	nd	nd	nd	nd	B I
$C_{22}H_{14}$	278	477.7	Benzo(*a*)naphthacene/similar	c	nd	nd	66	nd	nd	nd	nd	nd	B I
$C_{22}H_{14}$	278	480.1	Benzo(*a*)naphthacene/similar		nd	nd	66	nd	nd	nd	nd	nd	B I
$C_{22}H_{14}$	278	483.8	Pentacene/similar		nd	nd	39	nd	nd	nd	nd	nd	B I
$C_{22}H_{12}$	276	484.7	Cyclopenta(*cd*)perylene/similar		nd	nd	55	nd	nd	nd	nd	nd	B I
$C_{22}H_{12}$	276	488.6	Indeno(1,2,3-cd)pyrene	a, e	nd	nd	209	60	nd	nd	nd	nd	B I
$C_{22}H_{14}$	278	489.0	Dibenz(*a*,*h*)anthracene	a, e	nd	nd	104	nd	nd	nd	nd	nd	B I
$C_{22}H_{14}$	278	493.5	Benzo(*b*)chrysene/similar	d	nd	nd	93	nd	nd	nd	nd	nd	B I
$C_{22}H_{14}$	278	495.3	Picene/similar	c	nd	nd	132	nd	nd	nd	nd	nd	B I
$C_{22}H_{12}$	276	500.0	Benzo(*g*,*h*,*i*)perylene	a, e	nd	nd	152	nd	nd	nd	nd	nd	B I
$C_{22}H_{12}$	276	506.4	Anthanthrene/similar	c	nd	nd	30	nd	nd	nd	nd	nd	B I
$C_{24}H_{14}$	302	559.4	Dibenzopyrene/similar	c	nd	nd	44	nd	nd	nd	nd	nd	B I
			Total		18480	83032	67492	25984	24063	18319	6420	1123	

(I) Substituted monoaromatic compounds, including ethylbenzene, xylenes, dimetilbenzenes, styrene or ethylmethylbenzenes, among others.

(II) PAHs from two to six aromatic rings, obtaining the highest yields for naphthalene, indene, acenapthylene, fluorene and phenanthrene.

(III) Oxygenated compounds, including carboxylic acids like benzoic acid, ethyl and dimethylbenzoic acid, and other compounds such as triethyleneglycol, benzaldehyde, phenol or benzofuran. These two latter compounds are important to emphasize, since they may be precursors from ClPhs and PCDFs, respectively.

(IV) Chlorinated compounds, mainly consisting of chloroalkanes (chlorodecane, chlorododecane and chlorohexadecane), chloronaphthalenes and chloroalkylaromatic compounds (chloromethyl and chloroethylbenzene). ClBzs, ClPhs PCDDs and PCDFs have been also obtained but are not shown here, as previously commented.

Total yield of semivolatile compounds reaches a maximum at 700 °C in pyrolysis, but they keep high yields at 850 °C. If % of total yield decrease is calculated with regard to that obtained in pyrolysis at 700 °C (P7), the results are that yields decrease 78, 19 and 69% in P5, P8 and P10, respectively, and 71, 78, 92 and 99% in C5, C7, C8 and C10, respectively, regarding to P7. So, it can be concluded that combustion at high temperatures has meant destruction of practically all compounds of incomplete combustion, despite the substoichiometric conditions, probably due to an adequate mixing of gases and enough residence time in the second part of the reactor

Only oxygenated compounds were detected in combustion at temperatures higher than 500 °C and no type C or C′ behavior was noted, except in the case of fluoranthene; it is strange that this compound shows a different behavior than the other PAHs. Non-oxygenated compounds that appeared in combustion behave as type A′ and oxygenated compounds as either A′ or B′. Most compounds behave also as type I; type II is mainly observed in oxygenated compounds. Chlorinated compounds present, in general, type A behavior, except chloronaphthalenes and chloromethylnapthalene. Some oxygenated compounds have appeared in pyrolysis, and the most probable explanation is the same as in the case of CO_2: the atmosphere may not have been completely free of oxygen.

Concerning aromatic compounds behavior in pyrolysis, an interesting fact can be noted: substituted monoaromatic compounds and low molecular weight PAHs present both type A and B behavior, and high molecular weight PAHs are practically all type B. But, whereas the maximum in the first ones mainly corresponds to 500 °C (type A) and 700 °C (type B), the latter reached the highest yields at 850 °C. This seems to mean that not only monoaromatic and light PAHs are primary products of thermal degradation of PVC but that they are also precursors of heavier PAHs. So, pyrosynthesis reactions of PAH growth are very likely to occur.

Fig. 4 shows the evolution of the seven probable carcinogenic PAHs detected in pyrolysis runs. The maximum appears at 850 °C, as commented before and 1000 °C is not enough to allow all the compounds to disappear. On the other hand, they have not been detected in combustion runs, except chrysene at 500 °C and only in a very low quantity (10 ppm).

Regarding total levels of the 16 main PAHs, the yields in pyrolysis have been about 2800, 29,000, 35,000 and 21,000 ppm at 500, 700, 850 and 1000 °C, respectively, and 2300 and 40 ppm at 500 and 700 °C, respectively, in combustion. No PAHs were detected at higher temperatures in combustion. The main contribution is due, in all the cases, to naphthalene, which represents between 70% (P10) and 100% (C7) of the total yields of the 16 PAHs, excepting pyrolysis at 850 °C, where it only contributes in 40%.

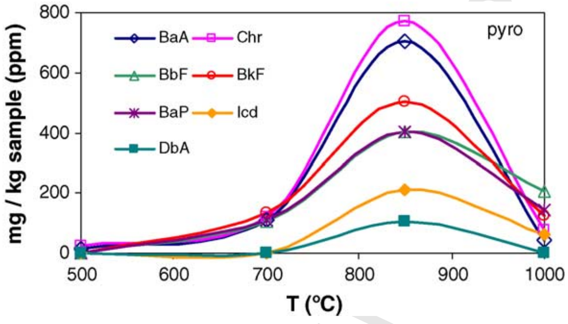

Fig. 4. Seven probable carcinogenic PAHs in pyrolysis.

Wang et al. [12] studied emissions on burning 0.5 g of polyethylene, polystyrene (PS) and PVC in a two-stage, preheated muffle furnace, the primary furnace operating in a temperature range between 500 and 1000 °C with 4 L/min air, and the secondary chamber at 1000 °C adding 2 L/min additional air. Results for PVC showed that PAH emissions were low, they decreased steadily as the temperature of the primary furnace increased (from 6000 to 2000 ppm) and they were reduced by treatment in the afterburner. Naphthalene was the main product obtained.

Instead, Hawley-Fedder et al. [8] obtained in a laboratory furnace that PAHs produced during combustion of 2 g PVC between 800 and 950 °C were greatest at 950 °C, but also a remarkable decrease from 800 to 900 °C was observed. In this case, yields were, approximately, 18,000, 16,000, 5000 and 19,000 ppm at 800, 850, 900 and 950 °C, respectively.

Kim et al. [13] also found an increase of the 16 main PAH yields with temperature during combustion of 0.5 g PVC with 2 L/min air in a downstream vertical tubular furnace at temperatures of 300, 600 and 900 °C: about 800, 3500 and 5000 ppm, respectively. In that work, the high yield for phenanthrene (1400 ppm maximum), higher than that of naphthalene (1100 ppm maximum), was remarkable.

On the other hand, Panagiotou et al. [9] analysed the influence of temperature, residence time, atmosphere and furnace system on the semivolatile compounds from the pyrolysis and combustion of PE, PS and PVC at high temperatures. Results for PVC indicated that conditions in which PAH emissions decreased were: increasing temperature (from 900 to 1200 °C) and residence time (from 1 to 2 s), using air instead of nitrogen and performing the experiments involving dilute clouds of polymer particles in a vertical furnace instead of thick clouds or batch runs in a horizontal furnace. With the best conditions, the yield of napthtalene (the PAH obtained in highest quantities) was 140 ppm, whereas in nitrogen it reached 3000 ppm, and also phenanthrene, anthracene, acenaphtylene, fluoranthene and pyrene were important, as in the present work.

3.3. Chlorobenzenes and chlorophenols

The yields of chlorobenzene are given in Table 5. The different isomers have been individually analysed with corresponding standards in order to find a pattern of formation. Fig. 5 summarizes the total yield of each congener group of ClBzs both in pyrolysis (Fig. 5a) and combustion (Fig. 5b).

From the results obtained, it can be noted that temperature has not much effect on total yields of ClBzs in pyrolysis, whereas the effect is more remarkable in combustion, with a clear maximum at 700 °C. There is a

Table 5
Chlorobenzenes obtained (mg compound/kg sample)

Compound	In mg compound/kg sample							
	P5	P7	P8	P10	C5	C7	C8	C10
Mono	29.8	102.1	202.3	205.5	103.4	89.1	nd	0.41
1,3-	61.4	nd	0.74	0.89	14.0	44.4	nd	nd
1,4-	nd	3.2	3.9	1.7	11.3	41.0	3.3	1.6
1,2-	66.3	1.6	3.0	0.88	31.7	35.4	1.8	0.83
1,3,5-	nd	nd	0.02	0.01	1.4	14.1	nd	0.06
1,2,4-	0.11	0.12	0.15	0.10	10.1	47.2	0.14	0.28
1,2,3-	nd	nd	0.05	0.04	5.7	11.2	0.06	0.10
1,2,3,5- + 1,2,4,5-	0.03	0.04	0.06	0.04	5.0	57.1	0.44	0.30
1,2,3,4-	0.03	0.04	0.06	0.02	3.8	31.6	0.28	0.28
Penta	nd	nd	nd	nd	3.5	124.9	1.6	0.82
Hexa	nd	nd	nd	nd	2.0	233.7	2.8	0.91
Total	157.8	107.1	210.2	209.1	191.7	729.6	10.3	5.6

great predominance of mono- and dichlorobenzenes in pyrolysis, and a temperature higher than 500 °C produces a gradual increase of the first ones at the expense of the latter, which practically disappear. 1,2- and 1,3-Cl_2Bzs greatly predominate over 1,4-Cl_2Bz at 500 °C; then, the yields of the three isomers are similar. On the other hand, no highly chlorinated benzenes have been encountered in pyrolysis.

Now, some discussion has to be presented in order to try to determine the most probable mechanism for chlorobenzenes formation. In principle, the most evident mechanism should be chlorination of benzene, but chlorination of aromatic compounds like benzene with HCl is thermodynamically unfavoured [39,11], i.e., the Gibbs energy is positive:

$$\mathrm{Bz(g)} + 2\mathrm{HCl(g)} \rightleftharpoons \mathrm{Cl_2Bz(g)} + \mathrm{H_2(g)}, \quad \Delta G^\circ = +143.51\,\mathrm{kJ/mol} \qquad (2)$$

However, in the presence of oxygen HCl can be partially converted to Cl_2 through the Deacon process:

$$2\mathrm{HCl(g)} + 1/2\mathrm{O_2(g)} \rightleftharpoons \mathrm{Cl_2(g)} + \mathrm{H_2O(g)}, \quad \Delta G^\circ = -37.95\,\mathrm{kJ/mol} \qquad (3)$$

And, in this case, chlorination of benzene by Cl_2 is thermodynamically favoured:

$$\mathrm{Bz(g)} + \mathrm{Cl_2(g)} \rightleftharpoons \mathrm{Cl_2Bz(g)}, \quad \Delta G^\circ = -46.99\,\mathrm{kJ/mol} \qquad (4)$$

Thus, pyrolysis does not favour chlorine formation because there is no oxygen available to react with HCl, so chlorination reactions are not favoured, either; consequently, alternative pathways previously commented are likely to occur, such as direct scission of partially chlorinated PVC chains.

The formation of chlorobenzenes in combustion is more favoured due to the chlorine formation. The presence of highly chlorinated compounds is much more remarkable in combustion (specifically at 700 °C). Results obtained by Kim et al. [13] also showed dominating congeners to be penta- and hexachlorobenzenes.

However, only thermodynamic considerations like the Deacon process are not probably enough to explain the high yields of chlorobenzenes obtained in combustion, particularly at 700 °C, and kinetic considerations are proposed to be equally important. On the one hand, the thermal equilibrium constant K for this reaction is very sensitive to temperature: K values are $4.17\cdot10^9$ at 300 °C, $3.31\cdot10^1$ at 500 °C and they decrease considerably above 500 °C [40]; this could explain the sharp decrease on yields observed between 700 and 850 °C (as well as taking into account that at higher temperatures thermal and oxidative destruction is greater), but it would not explain the increase on yields from 500 to 700 °C. In this range, kinetics, perhaps, is more important,

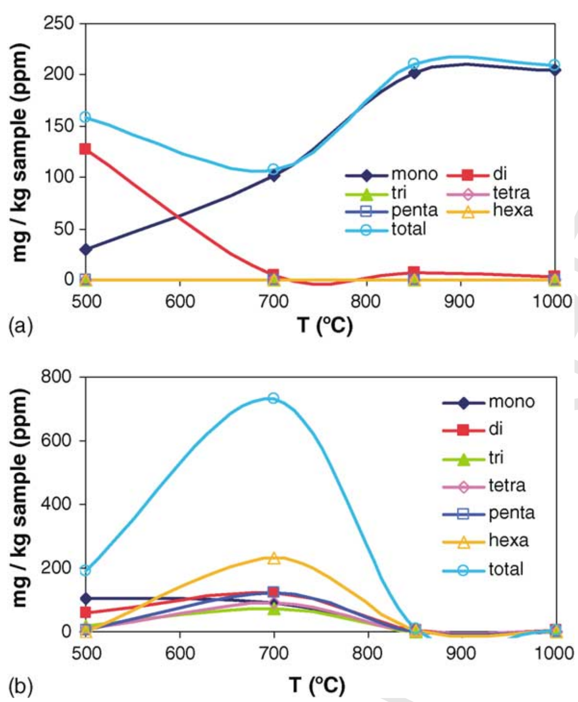

Fig. 5. Chlorobenzenes in pyrolysis (a) and combustion (b).

allowing ClBz formation at 700 °C to be faster than at 500 °C, despite the fact that there is less Cl_2 available. In short, kinetics and thermodinamics show an opposite behavior with temperature and 700 °C is the temperature of maximum ClBz formation because the conditions are the most suitable weighing up the two factors. Anyway, the other previously commented pathways are not rejected.

Another possibility proposed in this work is to consider that certain oxygenated compounds such as benzoic acid, triethylenglycol or benzaldehyde could be precursors of chlorobenzenes. Gibbs energies for the corresponding reactions have been calculated, resulting negative values, what indicates that they are thermodynamically favoured:

$$C_6H_5{-}COOH(g) + HCl(g) + 0.5O_2(g) \rightleftharpoons C_6H_5{-}Cl(g) + CO_2(g) + 0.5H_2O(g), \quad \Delta G^\circ = -103.75\,\mathrm{kJ/mol} \tag{5}$$

$$C_6H_5{-}COH(g) + HCl(g) + O_2(g) \rightleftharpoons C_6H_5{-}Cl(g) + CO_2(g) + H_2O(g), \quad \Delta G^\circ = -450.52\,\mathrm{kJ/mol} \tag{6}$$

$$C_6H_{14}O_4(g) + HCl(g) + 0.5O_2(g) \rightleftharpoons C_6H_5{-}Cl(g) + 5H_2O(g), \quad \Delta G^\circ = -461.22\,\mathrm{kJ/mol} \tag{7}$$

There are not many differences in the yields obtained for the three Cl_2Bz and Cl_4Bz isomers, whereas 1,2,4-Cl_3Bz is the predominant isomer of Cl_3Bzs. It is observed that, in general, the total congener trends are the same as those for the specific isomers.

Regarding chlorophenols, Table 6 shows the different isomers obtained. Fig. 6 also presents the total yield of each

Table 6
Chlorophenols obtained (mg compound/kg sample)

Compound	In mg compound/kg sample							
	P5	P7	P8	P10	C5	C7	C8	C10
2-	nd	0.39	nd	nd	472.2	11.6	nd	nd
3- + 4-	nd	nd	nd	nd	nd	nd	nd	nd
2,3- + 2,4-	nd	nd	nd	nd	258.0	15.7	0.17	0.14
2,5-	nd	nd	nd	nd	nd	nd	nd	nd
2,6-	nd	nd	nd	nd	342.7	7.5	nd	nd
3,5-	nd	nd	nd	nd	nd	nd	nd	nd
3,4-	nd	nd	nd	nd	nd	nd	nd	nd
2,3,5-	nd	nd	nd	nd	3.5	2.0	nd	nd
2,4,6-	nd	nd	nd	nd	528.3	26.0	0.15	0.41
2,3,4-	nd	nd	nd	nd	nd	6.5	nd	nd
2,4,5-	nd	nd	nd	nd	6.0	1.8	nd	nd
2,3,6-	nd	nd	nd	nd	7.8	5.3	nd	nd
3,4,5-	nd	nd	nd	nd	nd	nd	nd	nd
2,3,5,6-	nd	nd	nd	nd	2.2	3.2	nd	nd
2,3,4,5-	nd	nd	nd	nd	nd	nd	nd	nd
2,3,4,6-	nd	nd	nd	nd	34.6	18.9	0.43	0.22
Penta	nd	nd	nd	nd	20.9	49.6	2.13	2.0
Total	nd	0.39	nd	nd	1676	148.0	2.9	2.7

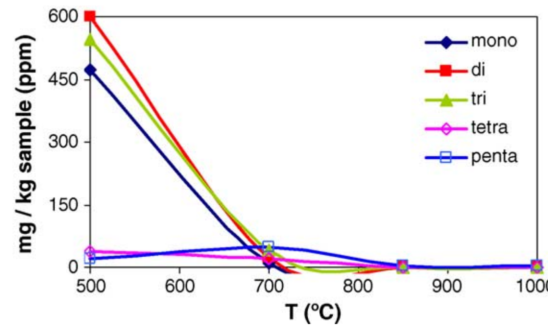

Fig. 6. Chlorophenols in combustion.

congener group of ClPhs in combustion, since in pyrolysis these have not been detected.

Clearly, the highest global yields are obtained in combustion at 500 °C. There is a sharp decrease in total yields when temperature increases. Mono-, di- and trichlorophenols appear in much higher amounts than tetra- and pentachlorophenols, as Kim et al. detected [13]. The predominant ClPh isomers correspond to 2-ClPh, 2,3/2,4- and 2,6-Cl_2Ph, 2,4,6-Cl_3Ph and, in lower yields, 2,3,4,6-Cl_4Ph and 2,3,4,5,6-Cl_5Ph. The decrease in the total yields is the result of ClPh, Cl_2Ph and Cl_3Ph decrease. Cl_4Ph isomers do not account for very much, whereas Cl_5Ph has a different behavior, since it increases with temperature up to 700 °C and then it decreases.

Formation of the different isomers of ClPhs not only can occur by oxidation of the corresponding ClBz precursors, but also by chlorination of lower chlorinated ClPhs or isomerization of other ClPhs. With the results obtained, it can be concluded that formation of isomers with a chlorine atom in *ortho* position with respect to OH is favoured: 2-ClPh, 2,6-Cl_2Ph and 2,4,6-Cl_3Ph are the predominant ones; as well as this, symmetric distribution of chlorine atoms regarding OH predominates among isomers of each congener (2,6-Cl_2Ph, 2,4,6-Cl_3Ph and penta-Cl_5Ph), excepting 2,3,5,6-Cl_4Ph. Those isomers seem to be the most stable ones from a structural point of view.

There is another interesting issue to comment, and this is the fact that ClPh yields are much higher than ClBz ones at 500 °C, whereas at 700 °C trends are reversed. This behavior is, at first sight, difficult to understand, because ClPh are not known to be precursors of ClBzs, but the opposite, and more so in oxidative conditions. A similar trend was observed by Froese and Hutzinger [25] during heterogeneous combustion of acetylene with HCl/air on metal oxides, since ClPhs and PCDFs were reduced when increasing temperature between 300 and 600 °C, whereas ClBzs concentrations were higher. They suggested that this fact could be due to competing formation and reactions and thermodynamic properties and reactivities of the precursors, but it is not clear if this could be applicable to this work, since no catalytic metals supported on ashes are supposed to be involved.

Results obtained by Kim et al. [13] showed a maximum at 600 °C for both ClBzs and ClPhs, but the study was only performed at the three temperatures of 300, 600 and 900 °C, so it is not possible to conclude if the change in trends between 500 and 700 °C reported in the present work could also have occurred but they were unnoticed. The amounts obtained in the previously mentioned work were lower than in this one, with about 2500 ng/g total ClBzs and 180 ng/g total ClPhs, comparing with 730 μg/g ClBzs and 1680 μg/g ClPhs reported in the present work.

3.4. PCDD/PCDFs

Table 7 presents the yields obtained for PCDD/PCDFs in the pyrolysis and combustion experiments carried out at 850 °C, both in pg/g and I-TEQ pg/g. No distinction was possible to make between amounts in gas-phase and in solid-phase on carbonaceous particles, since no filter was placed before the resin in the collection system. Fig. 7 summarizes the total yield of each congener group of PCDFs and PCDDs both in pyrolysis (Fig. 7a) and combustion (Fig. 7b).

Total PCDD/PCDFs content is about 215 pg I-TEQ/g sample in pyrolysis and 4583 pg I-TEQ/g sample in combustion. Results appearing in bibliography are quite dispersed, probably because of the differences in equipment used to run the experiments. McNeill et al. [19], reported total toxicities of 2.6, 6.3 and 42.7 ng I-TEQ/g tar fraction for PVC combustion at 500 °C in air, 1000 °C in air and 500 °C in 11.6% O_2, respectively. PCDD/PCDFs were collected in the tar fraction, which accounted for 24% of the initial PVC. Christmann et al. [18] obtained 19–24 ng I-TEQ/g for pure PVC and <1–41 ng I-TEQ/g for PVC cables in pyrolysis experiments. Results of Kim et al. [13] from combustion of PVC at 300, 600 and 900 °C gave total

Table 7
PCDD/PCDFs obtained (pg compound/g sample)

Compound	pg/g Sample		I-TEQ pg/g Sample	
	pyro 850	comb 850	pyro 850	comb 850
2378-TCDF	4.1	920	0.4	92.0
12378-PeCDF	88.5	1897	4.4	94.9
23478-PeCDF	185	3329	92.4	1665
123478-HxCDF	225	6608	22.5	661
123678-HxCDF	233	4814	23.3	481
234678-HxCDF	267	5419	26.7	542
123789-HxCDF	101	2661	10.1	266
1234678-HpCDF	1457	37531	14.6	375
1234789-HpCDF	215	5806	2.15	58.1
OCDF	1171	35536	1.2	35.5
Total PCDFs	3946	104522	198	4271
2378-TCDD	8.0	91.2	8.0	91.2
12378-PeCDD	6.7	225	3.3	113
123478-HxCDD	15.7	252	1.6	25.2
123678-HxCDD	10.5	240	1.0	24.0
123789-HxCDD	4.2	nd	0.4	nd
1234678-HpCDD	236	4713	2.4	47.1
OCDD	497	11829	0.5	11.8
Total PCDDs	778	17349	17.2	312
Total	4725	121872	215	4583

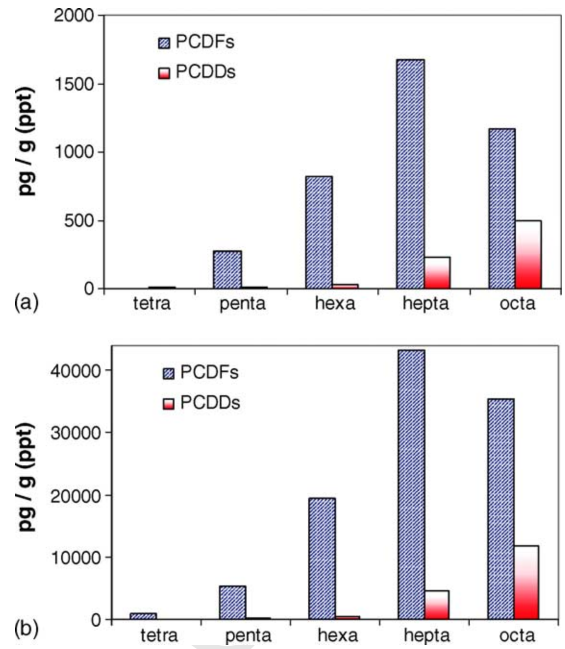

Fig. 7. Total PCDFs and PCDDs in pyrolysis (a) and combustion (b) at 850 °C.

amounts (XAD resin + filter) of 8.95, 163.54 and 0.75 ng/g sample, respectively, compared with 4.7 and 121.9 ng/g sample for pyrolysis and combustion at 850 °C, respectively, obtained in this work. On the other hand, Takasuga et al. [17] obtained a total amount of 15.4 ng/g sample in laboratory incineration of PVC at 900 °C.

PCDFs have been obtained in higher amounts than PCDDs; this is the usual trend. PCDD/PCDF patterns differ if yields are compared in pg/g or in I-TEQ pg/g. In the first case, predominant furans are HxCDF, HpCDF and OCDF (especially 1,2,3,4,6,7,8-HpCDF and OCDF) and predominant dioxins are HpCDD and OCDD, so the higher chlorinated isomers of both PCDDs and PCDFs have been formed in higher amounts than the lower ones, agreeing with previous papers looked up [13,18,19]. In the second case, predominant furans are, however, PeCDF and HxCDF (especially 2,3,4,7,8-PeCDF), whereas predominant dioxins are TCDD and PeCDD (especially TCDD and 1,2,3,7,8-PeCDD). This fact is due to the different relativity toxicity of each isomer.

Furthermore, the PCDF/PCDD ratio varies from 5–6 to 12–14 in pg/g units, if I-TEQ pg/g are used. On the other hand, it can be noted that the patterns obtained in pyrolysis and combustion are quite similar. For this reason, the ratio of total (PCDD + PCDF) yields of combustion to pyrolysis is 26 for pg/g and 21 for I-TEQ pg/g, i.e., there is not much difference.

Tuppurainen et al. [26] studied the correlation between TEQ-related PCDD/Fs to ClPhs from emissions in a pilot-plant incineration process. The results suggested that the coupling of 2,3,4,6- and 2,3,4,5,6-ClPh and/or 2,3,4,6- and 2,3,4,6-ClPh to give hexa-PCDDs and hepta-PCDFs could be the most important route for the formation of PCDD/Fs. This agrees with the results here obtained for these isomers. Instead, the high amounts of octa-congeners should be explained by other mechanisms, and direct chlorination of hexa- and hepta-PCDD/Fs would be the most probable one.

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