



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 CO₂/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.

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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 Cl₂, (iii) cyclization of chloro-C₁/C₂ 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 Cl₂ 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

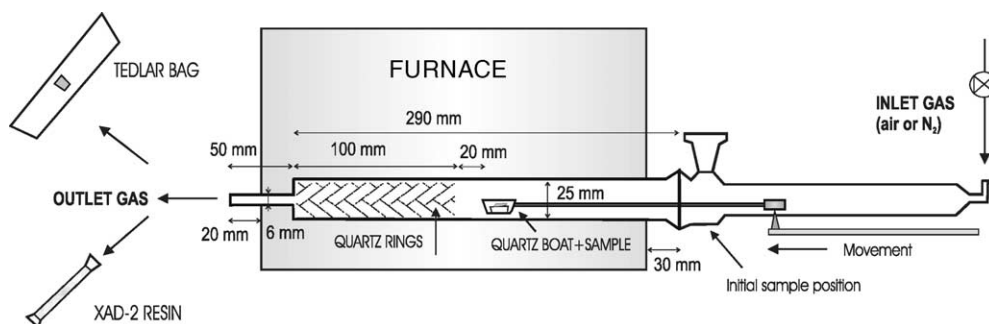


Fig. 1. Scheme of the reactor inside the furnace.

154 2.2. Experiments in furnace

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

167 On the other hand, the sample was placed in a narrow
 168 boat; this was put inside a holder, and a small electric motor
 169 moved it allowing the sample to be introduced through the
 170 reactor at controlled speed (1 mm s⁻¹ in this case). Before
 171 the sample insertion, the furnace nominal temperature had to
 172 be stabilized and the gas flow adjusted. Then, the sample was
 173 moved into the reactor to the first half, where it remained for
 174 100 s, to assure total decomposition of the sample. In the
 175 end, the holder came back out of the furnace. The second
 176 half of the reactor was filled with quartz rings. Thus, the
 177 volatile compounds evolved from the primary decomposition
 178 were here assumed to undergo further reactions because
 179 the packing of quartz rings produced a good local mixing of
 180 the gas, avoiding gas bypass.

181 As previously commented, both pyrolysis and combustion
 182 experiments were conducted at four different tempera-

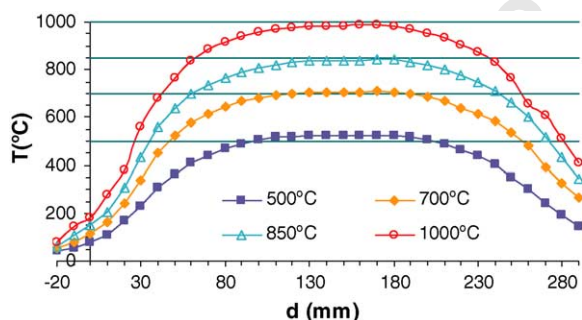


Fig. 2. Temperature profiles.

183 tures (500, 700, 850 and 1000 °C) with about 30 mg of PVC.
 184 Air or nitrogen gas was used in combustion or pyrolysis,
 185 respectively, with a flow of 300 mL/min (measured at 1 atm
 186 and 20 °C). The residence time of gases was calculated both
 187 in the total reactor volume and in the packing for each
 188 nominal temperature considering the measured temperature
 189 profiles, obtaining that the first one ranged from 9 to 17 s
 190 (1000 and 500 °C, respectively) and the latter from 3 to 6 s.
 191 Table 2 presents the eight different conditions performed in
 192 this work. The mass flow of the sample was calculated
 193 assuming that the sample was uniformly distributed along
 194 the boat (2.5 cm) and burnt in a fixed front when entering
 195 the reactor, as well as taking into account the inlet speed, so
 196 the rate of advance of the boat is related with the burning rate of
 197 the sample.

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

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

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-d₄, naphthalene-d₈, acenaphthene-d₁₀, phenanthrene-d₁₀, chrysene-d₁₂ and perylene-d₁₂. 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-d₁₀ 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. ¹³C 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 CO₂, 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 × 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 × 0.25 mm) in PTV injection. Molecular ions monitored were 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 CO₂, CO and light hydrocarbon yields obtained in the experiments. Firstly, it can be observed that CO₂ presents a maximum at 850 °C in combustion, whereas CO does so at 700 °C. Much more CO₂ than CO appears. Fig. 3 gives an idea of combustion efficiency. As temperature rises, CO₂/(CO + CO₂) ratio increases and no CO is detected at 1000 °C. On the other hand, some CO₂ 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 CO₂ observed.

Regarding light hydrocarbons, some comments can be made. Aliphatic hydrocarbons from C₁ to C₆ 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-

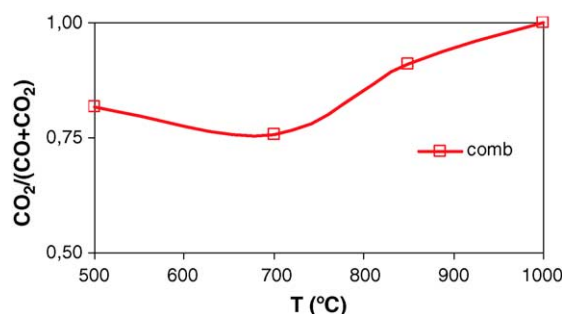


Fig. 3. CO₂/(CO + CO₂) ratio in combustion.

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	<i>n</i> -Butane	768	480	285	nd	532	nd	nd	nd	A, A', I
56	<i>t</i> -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	<i>c</i> -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	<i>n</i> -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	<i>n</i> -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	

414 however, they behave differently; whereas methane yields
415 rise clearly from a relatively low yield at 500 to 1000 °C,
416 benzene is emitted early at 500 °C in a high quantity and
417 then it withstands higher temperatures and even slightly
418 grows. The different behavior can be explained taking into
419 account that methane is a final product from cracking re-
420 actions occurring at high temperatures, while benzene is
421 known to be a primary decomposition product from thermal
422 decomposition of PVC [3–5] and also has a great thermal
423 stability [38]. On the other hand, types A' and I behaviors are
424 almost general, that indicates that the combination of ox-
425 ygen and high temperatures significantly depletes formation
426 of light hydrocarbons.

427 3.2. Semivolatile compounds

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

433 As done with light hydrocarbons, three kinds of
434 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 c-ondensed 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	Type	In mg compound/kg sample								Behavior		
					P5	P7	P8	P10	C5	C7	C8	C10			
C ₈ H ₁₀	106	118.9	Ethyl–benzene	c	1368	527	nd	nd	590	nd	nd	nd	A	A'	I
C ₈ H ₁₀	106	121.2	<i>p</i> -Xylene	c	1091	4286	2773	nd	446	nd	nd	nd	B	A'	I
C ₈ H ₆	102	122.7	Ethynyl–benzene	b	nd	96	1374	579	nd	nd	nd	nd	B		I
C ₈ H ₈	104	127.7	Styrene	b	1004	9311	772	nd	925	nd	nd	nd	B	A'	I
C ₈ H ₁₀	106	128.4	<i>o</i> -Xylene	c	1463	4604	1402	nd	494	nd	nd	nd	B	A'	I
C ₉ H ₁₀	118	143.1	Allylbenzene	d	163	nd	nd	nd	38	nd	nd	nd	A	A'	I
C ₉ H ₁₂	120	145.1	<i>n</i> -Propylbenzene	c	259	nd	nd	nd	40	nd	nd	nd	A	A'	I
C ₇ H ₆ O	106	147.0	Benzaldehyde	c	nd	234	65	36	nd	28	nd	37	B		I
C ₉ H ₁₂	120	147.3	1-Ethyl-3-methylbenzene	d	276	nd	nd	nd	484	nd	nd	nd	A	A'	II
C ₉ H ₁₂	120	148.3	1-Ethyl-4-methylbenzene		nd	nd	37	nd	nd	nd	nd	nd	B		I
C ₆ H ₆ O	94	150.4	Phenol	a	47	86	16	11	197	12	9	5	B	A'	
C ₉ H ₈	116	151.8	1-Ethynyl-4-methylbenzene	b	nd	nd	92	nd	nd	nd	nd	nd	B		I
C ₉ H ₁₂	120	152.1	1,3,5-Trimethylbenzene	c	354	nd	nd	nd	60	nd	nd	nd	A	A'	I
C ₉ H ₈	116	153.3	1-Propynyl–benzene	b	nd	nd	70	nd	nd	nd	nd	nd	B		I
C ₉ H ₁₀	118	155.1	α -Methylstyrene	c	nd	514	168	nd	nd	nd	nd	nd	B		I
C ₉ H ₁₂	120	155.4	1-Ethyl-2-methylbenzene	c	133	514	168	nd	60	nd	nd	nd	B	A'	I
C ₉ H ₁₀	118	156.2	<i>m</i> -Methylstyrene	c	213	566	177	nd	nd	nd	nd	nd	B		I
C ₈ H ₆ O	118	156.7	Benzofuran	c	nd	nd	nd	nd	165	nd	nd	nd	A'		II
C ₇ H ₇ Cl	126.6	160.7	1-Chloro-3-methylbenzene	c	nd	nd	nd	nd	407	nd	nd	nd	A'		II
C ₉ H ₁₀	118	163.2	<i>o</i> -Methylstyrene	c	201	nd	nd	nd	25	nd	nd	nd	A	A'	I
C ₉ H ₁₀	118	166.5	1-Propenylbenzene	c	315	nd	nd	nd	23	nd	nd	nd	A	A'	I
C ₈ H ₉ Cl	140.6	167.2	2-Chloroethylbenzene	c	64	nd	nd	nd	nd	nd	nd	nd	A		I
C ₉ H ₈	116	168.8	Indene	b	1121	16778	4114	55	161	nd	nd	nd	B	A'	I
C ₁₀ H ₁₄	134	170.0	<i>n</i> -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 ₈ H ₈ O	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 ₈ H 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 ₇ H ₆ O 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 ₉ H 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 ₉ H 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 ₆ H 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 ₉ H 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 ₉ H 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 ₉ H 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 ₇ Cl	163	235.9	2-Chloro-naphthalene	b	3	12	40	35	15	5	nd	nd	B		I
C ₁₀ H ₇ Cl	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	b, e	nd	nd	21	nd	nd	nd	nd	nd	B		I
C ₁₂ H ₁₂	156	238.5	2-Ethyl-naphthalene	b, e	159	19	nd	nd	31	nd	nd	nd	A	A'	I
C ₁₂ H ₁₂	156	239.3	1-Ethyl-naphthalene	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 ₉ H ₇ ClO	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		
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
C ₁₃ H ₁₀	166	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	40	nd	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-Ethylidene fluorene	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 ₁₅ 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(<i>d,e,f</i>)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	c	nd	nd	22	nd	nd	nd	nd	nd	B	I
C ₁₆ H ₁₀	202	341.5	Acephenanthrylene/aceanthrylene	c	nd	144	646	50	nd	nd	nd	nd	B	I
C ₁₆ H ₁₀	202	344.2	Acephenanthrylene/aceanthrylene	c	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	<i>m</i> -Terphenyl	c	nd	nd	10	nd	nd	nd	nd	nd	B	I

Table 4 (Continued)

Form	M_w	Calculated Lee	Experiment	Type	In mg compound/kg sample								Behav- ior	
					Compound	P5	P7	P8	P10	C5	C7	C8		C10
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	Benzo(a)fluorene/methylpyrene	b	nd	21	101	nd	nd	nd	nd	nd	B	I
C ₁₇ H ₁₂	216	358.5	Benzo(a)fluorene/methylpyrene	c	22	276	868	nd	nd	nd	nd	nd	B	I
C ₁₇ H ₁₂	216	360.9	Benzo(a)fluorene/methylpyrene	c	19	159	548	nd	nd	nd	nd	nd	B	I
C ₁₇ H ₁₂	216	365.3	Benzo(a)fluorene/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	c	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	Benzanthrene	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	c	nd	nd	130	nd	nd	nd	nd	nd	B	I
C ₂₁ H ₁₄	266	455.0	2,3,6,7-Dibenzofluorene/similar	c	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	c	nd	nd	66	nd	nd	nd	nd	nd	B	I
C ₂₂ H ₁₄	278	483.8	Pentacene/similar	c	nd	nd	39	nd	nd	nd	nd	nd	B	I
C ₂₂ H ₁₂	276	484.7	Cyclopenta(cd)perylene/similar	c	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		

463
464 (I) Substituted monoaromatic compounds, including
465 ethylbenzene, xylenes, dimethylbenzenes, styrene or
466 ethylmethylbenzenes, among others.
467 (II) PAHs from two to six aromatic rings, obtaining the
468 highest yields for naphthalene, indene, acenaphthylene,
469 fluorene and phenanthrene.
470 (III) Oxygenated compounds, including carboxylic acids
471 like benzoic acid, ethyl and dimethylbenzoic acid, and
472 other compounds such as triethyleneglycol, benzalde-
473 hyde, phenol or benzofuran. These two latter
474 compounds are important to emphasize, since they
475 may be precursors from ClPhs and PCDFs, respec-
476 tively.

(IV) Chlorinated compounds, mainly consisting of
480 chloroalkanes (chlorodecane, chlorododecane and
482 chlorohexadecane), chloronaphthalenes and chloro-
483 oalkylaromatic compounds (chloromethyl and chloro-
484 ethylbenzene). ClBzs, ClPhs PCDDs and PCDFs
485 have been also obtained but are not shown here, as
486 previously commented.
487
488

Total yield of semivolatile compounds reaches a max-
489 imum at 700 °C in pyrolysis, but they keep high yields at
490 850 °C. If % of total yield decrease is calculated with regard
491 to that obtained in pyrolysis at 700 °C (P7), the results are
492 that yields decrease 78, 19 and 69% in P5, P8 and P10,
493

494 respectively, and 71, 78, 92 and 99% in C5, C7, C8 and C10,
 495 respectively, regarding to P7. So, it can be concluded that
 496 combustion at high temperatures has meant destruction of
 497 practically all compounds of incomplete combustion, despite
 498 the substoichiometric conditions, probably due to an
 499 adequate mixing of gases and enough residence time in the
 500 second part of the reactor

501 Only oxygenated compounds were detected in combustion
 502 at temperatures higher than 500 °C and no type C or C'
 503 behavior was noted, except in the case of fluoranthene; it is
 504 strange that this compound shows a different behavior than
 505 the other PAHs. Non-oxygenated compounds that appeared
 506 in combustion behave as type A' and oxygenated compounds
 507 as either A' or B'. Most compounds behave also as type I;
 508 type II is mainly observed in oxygenated compounds.
 509 Chlorinated compounds present, in general, type A behavior,
 510 except chloronaphthalenes and chloromethylnaphthalene.
 511 Some oxygenated compounds have appeared in pyrolysis,
 512 and the most probable explanation is the same as in the case
 513 of CO₂: the atmosphere may not have been completely free
 514 of oxygen.

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

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

533 Regarding total levels of the 16 main PAHs, the yields in
 534 pyrolysis have been about 2800, 29,000, 35,000 and
 535 21,000 ppm at 500, 700, 850 and 1000 °C, respectively,
 536 and 2300 and 40 ppm at 500 and 700 °C, respectively, in

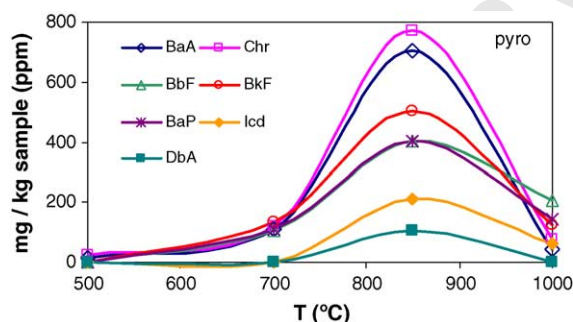


Fig. 4. Seven probable carcinogenic PAHs in pyrolysis.

537 combustion. No PAHs were detected at higher temperatures
 538 in combustion. The main contribution is due, in all the cases,
 539 to naphthalene, which represents between 70% (P10) and
 540 100% (C7) of the total yields of the 16 PAHs, excepting
 541 pyrolysis at 850 °C, where it only contributes in 40%.

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

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

558 Kim et al. [13] also found an increase of the 16 main PAH
 559 yields with temperature during combustion of 0.5 g PVC
 560 with 2 L/min air in a downstream vertical tubular furnace at
 561 temperatures of 300, 600 and 900 °C: about 800, 3500 and
 562 5000 ppm, respectively. In that work, the high yield for
 563 phenanthrene (1400 ppm maximum), higher than that of
 564 naphthalene (1100 ppm maximum), was remarkable.

565 On the other hand, Panagiotou et al. [9] analysed the
 566 influence of temperature, residence time, atmosphere and
 567 furnace system on the semivolatile compounds from the
 568 pyrolysis and combustion of PE, PS and PVC at high
 569 temperatures. Results for PVC indicated that conditions in
 570 which PAH emissions decreased were: increasing tempera-
 571 ture (from 900 to 1200 °C) and residence time (from 1 to
 572 2 s), using air instead of nitrogen and performing the
 573 experiments involving dilute clouds of polymer particles in a
 574 vertical furnace instead of thick clouds or batch runs in a
 575 horizontal furnace. With the best conditions, the yield of
 576 naphthalene (the PAH obtained in highest quantities) was
 577 140 ppm, whereas in nitrogen it reached 3000 ppm, and also
 578 phenanthrene, anthracene, acenaphthylene, fluoranthene and
 579 pyrene were important, as in the present work.

3.3. Chlorobenzenes and chlorophenols

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

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

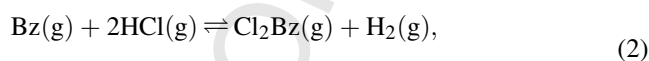
Table 5
Chlorobenzenes obtained (mg compound/kg sample)

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

591 great predominance of mono- and dichlorobenzenes in
592 pyrolysis, and a temperature higher than 500 °C produces a
593 gradual increase of the first ones at the expense of the
594 latter, which practically disappear. 1,2- and 1,3-Cl₂Bzs
595 greatly predominate over 1,4-Cl₂Bz at 500 °C; then, the
596 yields of the three isomers are similar. On the other hand,
597 no highly chlorinated benzenes have been encountered in
598 pyrolysis.

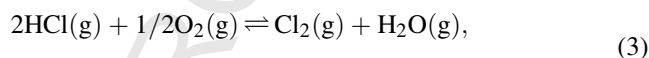
599 Now, some discussion has to be presented in order to try
600 to determine the most probable mechanism for chlorobenzenes
601 formation. In principle, the most evident mechanism
602 should be chlorination of benzene, but chlorination of
603 aromatic compounds like benzene with HCl is thermo-
604 dynamically unfavoured [39,11], i.e., the Gibbs energy is
605

positive:



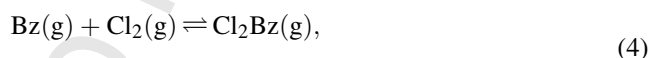
$$\Delta G^\circ = +143.51 \text{ kJ/mol}$$

608 However, in the presence of oxygen HCl can be partially
609 converted to Cl₂ through the Deacon process:



$$\Delta G^\circ = -37.95 \text{ kJ/mol}$$

610 And, in this case, chlorination of benzene by Cl₂ is
613 thermodynamically favoured:



$$\Delta G^\circ = -46.99 \text{ kJ/mol}$$

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

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

628 However, only thermodynamic considerations like the
629 Deacon process are not probably enough to explain the high
630 yields of chlorobenzenes obtained in combustion, particu-
631 larly at 700 °C, and kinetic considerations are proposed to
632 be equally important. On the one hand, the thermal equilibrium
633 constant *K* for this reaction is very sensitive to temperature:
634 *K* values are 4.17·10⁹ at 300 °C, 3.31·10¹ at 500 °C and they
635 decrease considerably above 500 °C [40]; this could explain
636 the sharp decrease on yields observed between 700 and
637 850 °C (as well as taking into account that at higher
638 temperatures thermal and oxidative destruction is greater),
639 but it would not explain the increase on yields from 500 to
640 700 °C. In this range, kinetics, perhaps, is more important,

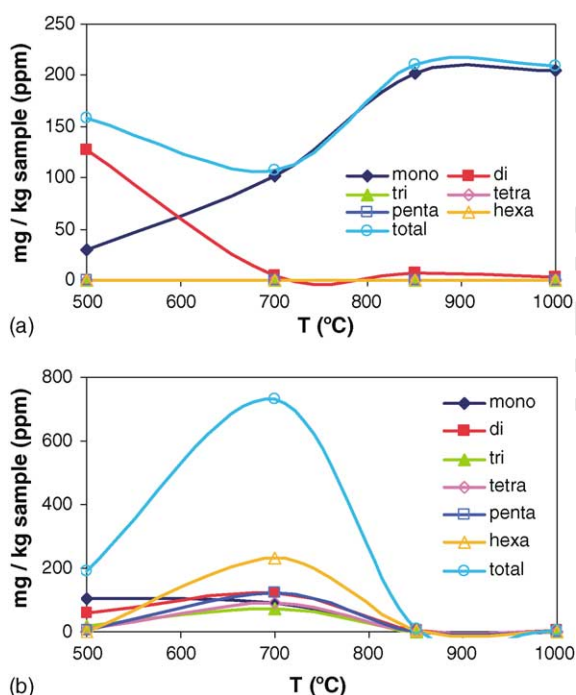
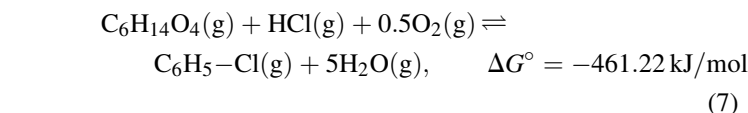
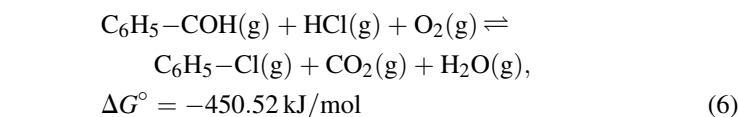
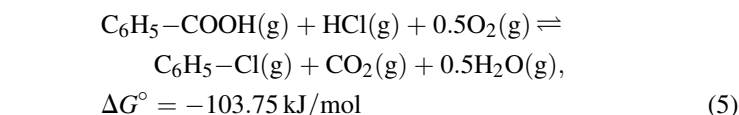


Fig. 5. Chlorobenzenes in pyrolysis (a) and combustion (b).

641 allowing ClBz formation at 700 °C to be faster than at
 642 500 °C, despite the fact that there is less Cl₂ available. In
 643 short, kinetics and thermodynamics show an opposite
 644 behavior with temperature and 700 °C is the temperature
 645 of maximum ClBz formation because the conditions are the
 646 most suitable weighing up the two factors. Anyway, the
 647 other previously commented pathways are not rejected.

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



659 There are not many differences in the yields obtained for
 660 the three Cl₂Bz and Cl₄Bz isomers, whereas 1,2,4-Cl₃Bz is
 661 the predominant isomer of Cl₃Bzs. It is observed that, in
 662 general, the total congener trends are the same as those for
 663 the specific isomers.

664 Regarding chlorophenols, Table 6 shows the different
 665 isomers obtained. Fig. 6 also presents the total yield of each
 666

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

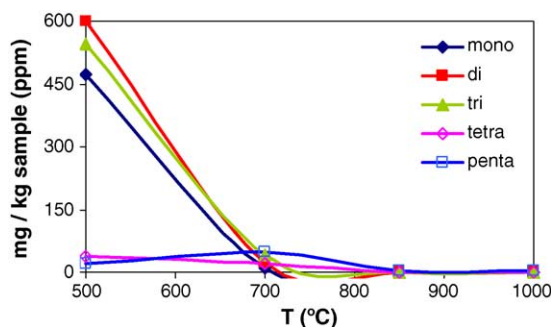


Fig. 6. Chlorophenols in combustion.

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-Cl₂Ph, 2,4,6-Cl₃Ph and, in lower yields, 2,3,4,6-
 Cl₄Ph and 2,3,4,5,6-Cl₅Ph. The decrease in the total yields is
 the result of ClPh, Cl₂Ph and Cl₃Ph decrease. Cl₄Ph isomers
 do not account for very much, whereas Cl₅Ph 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-Cl₂Ph and 2,4,6-Cl₃Ph are the predominant ones;
 as well as this, symmetric distribution of chlorine atoms
 regarding OH predominates among isomers of each
 congener (2,6-Cl₂Ph, 2,4,6-Cl₃Ph and penta-Cl₅Ph), except-
 ing 2,3,5,6-Cl₄Ph. 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 combus-
 tion 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

710 performed at the three temperatures of 300, 600 and 900 °C,
 711 so it is not possible to conclude if the change in trends
 712 between 500 and 700 °C reported in the present work could
 713 also have occurred but they were unnoticed. The amounts
 714 obtained in the previously mentioned work were lower than
 715 in this one, with about 2500 ng/g total ClBzs and 180 ng/g
 716 total ClPhs, comparing with 730 µg/g ClBzs and 1680 µg/g
 717 ClPhs reported in the present work.

718 3.4. PCDD/PCDFs

719 Table 7 presents the yields obtained for PCDD/PCDFs in
 720 the pyrolysis and combustion experiments carried out at
 721 850 °C, both in pg/g and I-TEQ pg/g. No distinction was
 722 possible to make between amounts in gas-phase and in solid-
 723 phase on carbonaceous particles, since no filter was placed
 724 before the resin in the collection system. Fig. 7 summarizes
 725 the total yield of each congener group of PCDFs and PCDDs
 726 both in pyrolysis (Fig. 7a) and combustion (Fig. 7b).

727 Total PCDD/PCDFs content is about 215 pg I-TEQ/g
 728 sample in pyrolysis and 4583 pg I-TEQ/g sample in
 729 combustion. Results appearing in bibliography are quite
 730 dispersed, probably because of the differences in equipment
 731 used to run the experiments. McNeill et al. [19], reported
 732 total toxicities of 2.6, 6.3 and 42.7 ng I-TEQ/g tar fraction
 733 for PVC combustion at 500 °C in air, 1000 °C in air and
 734 500 °C in 11.6% O₂, respectively. PCDD/PCDFs were
 735 collected in the tar fraction, which accounted for 24% of the
 736 initial PVC. Christmann et al. [18] obtained 19–24 ng I-
 737 TEQ/g for pure PVC and <1–41 ng I-TEQ/g for PVC cables
 738 in pyrolysis experiments. Results of Kim et al. [13] from
 739 combustion of PVC at 300, 600 and 900 °C gave total

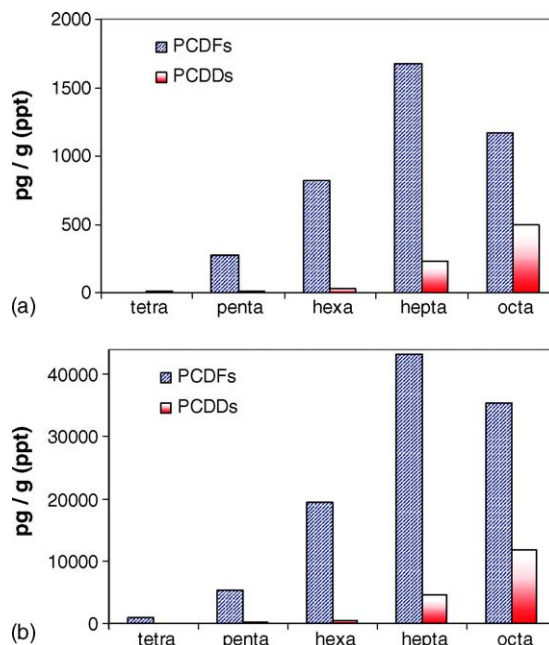


Fig. 7. Total PCDFs and PCDDs in pyrolysis (a) and combustion (b) at 850 °C.

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

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

760 Furthermore, the PCDF/PCDD ratio varies from 5–6 to
 761 12–14 in pg/g units, if I-TEQ pg/g are used. On the other
 762 hand, it can be noted that the patterns obtained in pyrolysis
 763 and combustion are quite similar. For this reason, the ratio of
 764 total (PCDD + PCDF) yields of combustion to pyrolysis is
 765 26 for pg/g and 21 for I-TEQ pg/g, i.e., there is not much
 766 difference.

767 Tuppurainen et al. [26] studied the correlation between
 768 TEQ-related PCDD/Fs to ClPhs from emissions in a pilot-
 769 plant incineration process. The results suggested that the
 770 coupling of 2,3,4,6- and 2,3,4,5,6-ClPh and/or 2,3,4,6- and
 771 2,3,4,6-ClPh to give hexa-PCDDs and hepta-PCDFs could

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

772 be the most important route for the formation of PCDD/Fs.
 773 This agrees with the results here obtained for these isomers.
 774 Instead, the high amounts of octa-congeners should be
 775 explained by other mechanisms, and direct chlorination of
 776 hexa- and hepta-PCDD/Fs would be the most probable one.

777 Acknowledgements

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