

STUDY OF THE EMISSIONS FROM PYROLYTIC AND OXIDATIVE THERMAL DECOMPOSITION OF PVC

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Introduction

Polyvinyl chloride (PVC) is one of the plastics most extensively used due to its versatility. The demand of PVC resin in Europe during 2012 reached 5000 ktonnes¹. PVC waste management is a big problem because of the high volume generated all over the world and its chlorine content. End-of-life PVC is mainly mixed with municipal solid waste (MSW) and one common disposal option for this is waste-to-energy incineration (WtE).

The presence of plastics such as PVC in the fuel mix increases the heating value of the fuel. PVC has two times higher energy content than MSW –around 20 MJ/kg vs 10 MJ/kg, respectively. However, the high chlorine content in PVC resin, 57 wt.%, may be a source for the formation of hazardous chlorinated organic pollutants in thermal processes. Chlorine present in the feedstock of WtE plants plays an important role in the formation of (i) chlorine (Cl₂) and (ii) hydrochloric gas (HCl), both of them responsible for corrosion, and (iii) chlorinated organic pollutants².

In this work, pyrolytic and oxidative thermal degradation of PVC resin were carried out in a laboratory scale reactor at 500 °C in order to analyze the influence of the reaction atmosphere on the emissions evolved. Special emphasis was put on the analysis of chlorinated organic pollutants such as polychlorodibenzo-*p*-dioxins (PCDDs), polychlorodibenzofurans (PCDFs) and other related compounds like polychlorobenzenes (PCBzs), polychlorophenols (PCPhs) and polycyclic aromatic hydrocarbons (PAHs). Another objective of this work was to compare the results with those of a previous work³ in which emissions at different temperatures in both pyrolysis and combustion of another PVC resin had been studied; in that case, experiments for PCDD/Fs emissions had been performed only at 850 °C.

Materials and methods

PVC resin

Experiments were carried out with virgin PVC resin Etinox 650, a powdery free of additives vinyl chloride homopolymer obtained by suspension polymerization. *Table 1* shows the results from the characterization of this resin.

Table 1. PVC Etinox 650 characterization

PVC Etinox 650 characterization									
N	C	H	S	O	Cl	Ash	Moisture	LHV ¹	dp ²
wt. %								kJ/kg	µm
nd	37.6	4.59	nd	0.78	55.1	0.18	0.65	18930	115

nd: non detected ; ¹LHV: Low Heating Value; ²dp: particle diameter

Lab scale reactor

All the experiments were performed in a horizontal quartz tube-type reactor, which is already described in a previous paper³. Four parameters can be controlled in this reactor: speed at which the sample is introduced in the reactor, furnace temperature, atmosphere of reaction (N₂/air) and gas flow rate. Two different sets of experiments were performed to collect different compounds. On one hand, gases and volatile compounds were collected in Tedlar® bags placed at the outlet of the reactor. On the other hand, semivolatile compounds such as PAHs, PCBzs, PCPhs and PCDD/Fs were adsorbed in a XAD-2 resin also placed at the outlet of the reactor.

About 30 mg of PVC resin were used for each experiment. Air ($\lambda = m_{\text{used}}/m_{\text{stoichiometric}} = 0.71$) and N₂ were used in combustion and pyrolysis respectively, with a flow rate of 300 mL/min and a furnace temperature equal to 500 °C. Samples were introduced in the furnace at 1 mm/s.

Analysis

CO and CO₂ collected in Tedlar® bags were analyzed in a TCD Shimadzu GC-14A equipped with a concentric packed column *Alltech CRT 1₂*, while the analysis of light hydrocarbons, benzene, toluene and xylenes from Tedlar® bags was carried out in a FID Shimadzu GC-17A with a capillary Alumina/KCl column.

The XAD-2 resin used in the experiments was pre-cleaned with dichloromethane by solid-liquid extraction in an ASE 100 (*Dionex*) extractor. After each experiment where semivolatile compounds (boiling point above 130 °C) were collected, resins were extracted with dichloromethane/hexane 50 v/v% in the extractor and afterwards concentrated firstly in a rotary evaporator and secondly with a gentle stream of N₂. Finally, the samples were analyzed by HRGC-MS on a *DB-624* (30 m x 0.25 mm) column, while PCBzs and PCPhs were analyzed on a *HP-5MS* (30 m x 0.25 mm) column. The samples were spiked with standards used for the identification and quantification of semivolatile compounds including PAHs with 10 µL of a 4000 ng/mL solution of six deuterated aromatic compounds. In the case of PCBzs and PCPhs, two solutions containing five ¹³C-labelled PCBzs and PCPhs each one were employed as internal standards. The concentration of both solutions was 100 µg/mL, and the samples were spiked with 10 µL of each one. Finally, 5 µL of a 200 mg/mL solution of anthracene-d₁₀ were spiked in the vials as a recovery standard.

The resins corresponding to PCDD/Fs were extracted with toluene in an ASE 100 (*Dionex*), cleaned-up in an automated PowerPrep™ and concentrated with a rotatory evaporator and a gentle stream of N₂. PCDD/Fs were analyzed according to the US EPA 1613 method by HRGC/HRMS on a Micromass AutoSpec-Ultima NT coupled to a *DB-5MS* (60 m x 0.25 mm) column. The standards used for PCDD/Fs were 10 µL EPA 1613 LCS and 10 µL of the internal standard EPA 1613 ISS.

Results and discussion

Gases and volatile compounds

CO₂ yield was 64,320 ppm in combustion vs 7,190 ppm in pyrolysis. Before performing pyrolysis experiments, the furnace was purged with nitrogen. However, the fact that CO₂ was produced in the pyrolysis means that some oxygen may have remained in the furnace, so there would not have been strict pyrolytic conditions in that case. Toluene and o-, p- and m-xylene were obtained also in a high amount. Most of the compounds increased their yields under oxidative conditions. At the low temperatures at which these experiments were performed, the presence of oxygen favors the formation of free radicals, which leads to higher pyrolytic reaction rates and, as a consequence, higher hydrocarbons yields.

Semivolatile compounds and PAHs

Up to 40 semivolatile compounds –excluding targeted polychlorinated aromatic compounds– were identified in gas samples from combustion and pyrolysis experiments. Chlorotoluene was the only chlorinated hydrocarbon found.

Concerning PAHs, the total yield was higher in

Table 2. PAHs yields

	PAHs	
	Pyrolysis	Combustion
	<i>mg compound/kg sample (ppm)</i>	
naphthalene	2770	3650
acenaphthylene	100	115
acenaphthene	140	80
fluorene	550	nd
phenanthrene	860	700
anthracene	370	270
fluoranthene	290	nd
pyrene	80	nd
benzo(a)anthracene	190	100
chrysene	180	nd
benzo(b)fluoranthene	nd	nd
benzo(k)fluoranthene	nd	nd
benzo(a)pyrene	nd	nd
indeno(1,2,3-cd)pyrene	nd	nd
di-benz(a,h)anthracene	nd	nd
benzo(g,h,i)perylene	nd	nd
Sum 16 PAHs	5530	4915

nd: non detected

pyrolysis than in combustion (5530 vs 4915 mg/kg, respectively), although no much difference was observed, which agrees with the results for low temperatures of the previously referred work with another PVC resin obtained by emulsion polymerization³. Ten of the sixteen PAHs characterized by USEPA as priority pollutants were detected (*Table 2*). The main contribution was due, both in pyrolysis and combustion, to naphthalene which represented 50% of the total yield of the 16 PAHs in pyrolysis and 75% in combustion. All PAHs presented lower yields in oxidative than in pyrolytic conditions, except naphthalene and acenaphthylene.

PCBzs and PCPhs

The yields of PCBzs and PCPhs are given in *Table 3*. Regarding PCBzs, the highest global yield was obtained in pyrolysis, 9.2 mg/kg, vs 2.7 mg/kg in combustion. PeCBz was the predominant isomer in pyrolysis (7.2 mg/kg), while 1,2,4-TriCBz was the one in combustion (1.9 mg/kg). These results differ from the ones obtained in a previous work for another PVC resin, in which PeCBz was not detected in pyrolysis and MoCBz was much more important in combustion³. From the results obtained it can be noted that the total yield of PCPhs was much higher in combustion than in pyrolysis, 128 mg/kg vs 3.4 mg/kg, as it could be expected since formation of PCPhs is favored by the presence of oxygen. There was a great predominance of MoCPh in combustion (59.5 mg/kg), which represented 47% of the total PCPhs yield.

Table 3. PCPhs and PCBzs yields

	PCPhs		PCBzs	
	Pyrolysis	Combustion	Pyrolysis	Combustion
	<i>mg compound/kg sample (ppm)</i>			
2-MoCPh	0.14	59.5	MoCBz	0.89
3-+4-MoCPh	nd	nd	1,3-DiCBz	nd
2,4-DiCPh	nd	nd	1,4-DiCBz	nd
2,5-DiCPh	nd	11.9	1,2-DiCBz	nd
2,3-DiCPh	nd	33	1,3,5-TriCBz	0.37
2,6-DiCPh	nd	3.3	1,2,4-TriCBz	nd
3,5-DiCPh	3.3	18	1,2,3-TriCBz	nd
3,4-DiCPh	nd	nd	1,2,3,5-+1,2,4,5	nd
2,3,5-TriCPh	nd	nd	1,2,3,4-TeCBz	0.72
2,4,6-TriCPh	nd	nd	PeCBz	7.2
2,4,5-TriCPh	nd	1.1	HxCBz	nd
2,3,4-TriCPh	nd	0.2	Sum PCBzs	9.2
2,3,6-TriCPh	nd	0.1		2.7
3,4,5-TriCPh	nd	nd	<i>nd: non detected</i>	
2,3,5,6-TeCPh	nd	0.01		
2,3,4,5-TeCPh	nd	0.3		
2,3,4,6-TeCPh	nd	0.2		
PeCPh	nd	0.1		
Sum PCPhs	3.4	128		

PCDD/Fs

Table 4 presents the yields obtained for PCDD/Fs in the pyrolysis and combustion experiments carried out. Much higher yields of PCDD/Fs were obtained in combustion than in pyrolysis. In the combustion experiment, the yields of PCDDs and PCDFs were similar –4995 and 4620 pg/g, respectively–, being 1,2,3,7,8,9-HxCDD (4520 pg/g) the most abundant dioxin, whereas 2,3,7,8-TCDF and 2,3,4,7,8-PeCDF were the predominant furans

obtained with the highest yields –950 pg/g and 930 pg/g, respectively. Only three congeners were obtained under pyrolytic atmosphere: 2,3,4,7,8-PeCDF, 1,2,3,7,8-PeCDD and 1,2,3,7,8,9-HxCDD, being the last one the most predominant congener (170 pg/g) in this experiment. The ratio PCDDs/PCDFs was about 1 in combustion, both in pg/g and pg WHO-TEQ/g units, whereas in pyrolytic conditions this ratio varied from 9.5 to 6 in pg/g and pg WHO-TEQ/g, respectively. On the other hand, results for another PVC resin at 850 °C showed PCDD/PCDFs ratios around 0.1 or even lower³, with a very different pattern to that showed in the present work.

It can be concluded that high levels of emissions were produced from combustion at 500 °C, around 990 pg WHO-TEQ/g, whereas in pyrolysis the values were much lower, around 44 pg WHO-TEQ/g. These results are, however, below those obtained for another PVC at 850 °C –3960 and 180 pg WHO-TEQ/g for combustion and pyrolysis, respectively³.

Table 4. PCDD/Fs yields

	PCDD/Fs			
	Pyr		Comb	
	pg/g _{sample}	pg WHO ₂₀₀₅ -TEQ/g _{sample}	pg/g _{sample}	pg WHO ₂₀₀₅ -TEQ/g _{sample}
2378-TCDF	nd	950	nd	95
12378-PeCDF	nd	420	nd	12
23478-PeCDF	20	930	6	280
123478-HxCDF	nd	330	nd	33
123678-HxCDF	nd	270	nd	27
234678-HxCDF	nd	280	nd	28
123789-HxCDF	nd	150	nd	15
1234678-HpCDF	nd	470	nd	4.7
1234789-HpCDF	nd	110	nd	1.1
OCDF	nd	710	nd	0.2
Total toxic PCDFs	20	4620	6	490
2378-TCDD	nd	40	nd	42
12378-PeCDD	20	nd	21	nd
123478-HxCDD	nd	nd	nd	nd
123678-HxCDD	nd	90	nd	9
123789-HxCDD	170	4520	17	452
1234678-HpCDD	nd	345	nd	nd
OCDD	nd	nd	nd	nd
Total toxic PCDDs	190	4995	38	503
Total toxic PCDDs/Fs	210	9615	44	992

Combustion: $\lambda=0.71$; nd:non detected;

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