

Influence of Chlorine and Oxygen on the Formation of Chlorobenzenes during PVC Thermal Decomposition

Ignacio Aracil¹, Andres Fullana¹, Juan Conesa¹, Sukh S Sidhu²

¹Department of Chemical Engineering. University of Alicante

²Environmental Engineering. University of Dayton

Introduction

Polyvinyl chloride (PVC) is a widely used chlorinated polymer present in many applications of daily life such as pipes, window frames, cables, flooring, packaging, medical products or car under-floor protection. In 1999, 4.1 million tons of PVC waste were generated in the European Community, and this is predicted to increase 80% up to 7.3 million tons in 2020¹. Currently, most of PVC waste is landfilled, a small fraction is mechanically recycled and incineration accounts for about 15% of total PVC waste. New technologies are also being developed that will make pyrolysis+combustion treatments (with initial dehydrochlorination) economically viable².

Thermal decomposition of PVC can be represented by two main steps. In the first one, dehydrochlorination takes place and as soon as hydrogen chloride starts to be generated, benzene is produced through intramolecular cyclization of polyene radicals formed from direct scission of the remaining polyene chains. In the second step, the polyene chains are believed to react through intermolecular reactions and these crosslinked chains undergo further reactions to form alkyl aromatic hydrocarbons and char residue^{3,4}.

Incineration presents some advantages compared to other options, such as energy recovery and great volume reduction. Several disadvantages are also involved, like heavy metal and toxic chloroaromatic compounds emissions (PCDDs, PCDFs, PCBs, chlorobenzenes, chlorophenols,...) due to the chlorine-containing waste. In spite of this, it has been proven that disturbances in the combustion conditions are much more important than the chlorine content of the fuel or the chlorine source (PVC, NaCl,...) for the formation of some of these compounds^{5,6}. PCDDs, PCDFs and PCBs cannot be easily monitored in industrial incinerators, therefore other compounds like chlorobenzenes (CBzs), that are present in higher quantities, have been proposed as indicators⁷. Chlorobenzenes have been chosen as indicator since they have shown good correlation with PCDD/F emissions and are known precursors in PCB formation. This laboratory study deals with the formation of chlorobenzenes during PVC thermal decomposition and the effect of different operating parameters on their formation.

Materials and Methods

Experiments were performed with PVC resin Etinox-450 free of additives obtained by emulsion polymerization, which is commonly used in low viscosity plastisols. It is a white powder with a medium molecular weight and a very small particle size ranging from 1.4 to 24.4 μ m. Table 1 shows the chemical composition of the PVC obtained by elemental analysis (C, H, S) and X-ray fluorescence.

Table 1

Chemical composition of PVC resin

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

Fly ash obtained from the US EPA was used as catalyst in some of the experiments. This fly ash, denoted as OX fly ash, had been collected from an electrostatic precipitator of a grate-fired MSW incinerator and thermally treated at 500°C in air for 24h, and its organic carbon content (equals the total carbon content) was 0.03%. All the chemical properties of this fly ash can be found elsewhere ⁸.

Figure 1 shows a drawing of the system designed to conduct the experiments. For each experiment, 25 mg of PVC were placed in a tubular glass reactor (100 mm length, 7 mm ID) and heated to 500°C at 30°C/min in a 25 mL/min helium (He) stream. In the reference experiment, the compounds evolved entered the second reactor at 750°C, where high-temperature reactions among compounds occurred. A 25 mL/min of He flow was added to the second reactor exit gas stream before it entered the low-temperature zone (300°C). The products were then trapped in an adsorptive (XAD-2) trap. Simultaneously, using a 1 mL/min split, products were also monitored on-line with a mass spectrometer. Six deuterated aromatic compounds (dichlorobenzene-d₄, naphthalene-d₈, acenaphthene-d₁₀, phenanthrene-d₁₀, chrysene-d₁₂ and perylene-d₁₂) were added to the XAD-2 resin before starting the experiments and these were later used as internal standards to quantify the reaction products. All the compounds trapped in the resin were extracted with methylene chloride and analyzed by GC/MS. Major products (aromatic hydrocarbons) were identified using MS spectral library matches, while standards of CBz isomer were used to quantify CBz yields.

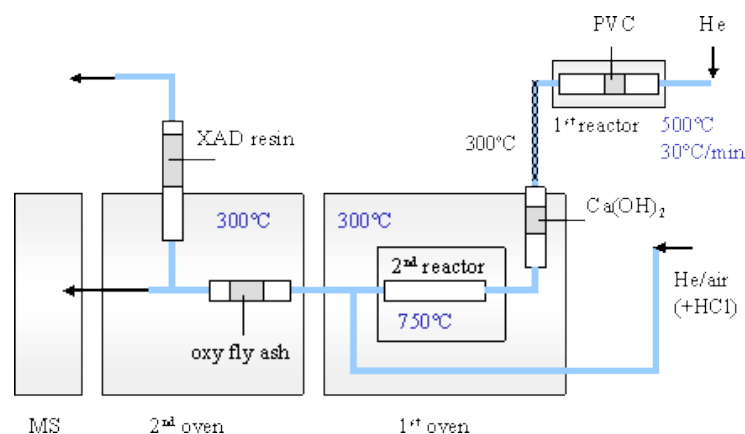


Figure 1. Schematic drawing of the system designed for the experiments.

In some of the experiments, calcium hydroxide (75 mg) was placed after the first reactor to trap the hydrogen chloride coming from PVC thermal decomposition. The effect of the oxygen (about 11% v/v in the total flow) in the low-temperature zone was studied by changing the secondary flow from He to air. Several experiments were conducted where hydrogen chloride gas was added to the secondary flow in the same quantity (10 mL) and during the same time interval in which HCl was generated during PVC decomposition. Finally, some experiments were performed where the gas stream in the low-temperature zone was passed through a fixed bed of OX fly ash (100 mg).

This experimental design enabled us to investigate the impact of the following four parameters:

- 1) The presence/absence of HCl in the high-temperature zone.
- 2) The presence of oxygen in the low-temperature zone.
- 3) The addition of hydrogen chloride to affect only reactions in the low-temperature zone.
- 4) The presence of OX fly ash in the low-temperature zone to act as catalyst.

By combining these four parameters, a total of sixteen experiments were performed.

Results and Discussion

Figure 2 shows the total yields of non-chlorinated aromatics detected. The major ones were, in this order, benzene,

toluene, naphthalene, indene, phenanthrene, 2-methylnaphthalene and 1-methylnaphthalene. There was no significant difference in the total yields and no clear trend could be observed. This indicates that the parameters investigated in this study have little effect on the formation of non-chlorinated aromatic compounds. However, the behavior of chlorobenzenes was influenced by the parameters investigated in this study. It can be noted from Figure 3 that oxygen was the most important parameter enhancing CBz formation; the only case in which this did not occur is when neither fly ash nor HCl were present (this only happened when $\text{Ca}(\text{OH})_2$ was present after 1st reactor and no additional HCl was injected after 2nd reactor). This is logical, since if no chlorine source is present (HCl or fly ash), no difference should be expected on the total CBz yields in the presence or absence of oxygen. When oxygen was present, chlorination of benzene was higher in the presence of metals (OX fly ash). This is probably due to conversion of HCl to Cl_2 (metal catalyzed Deacon reaction) or the presence of metal hypochlorites (Cu_2OCl_2), both of which are highly efficient chlorinating agents⁹. Table 2 details the results of the different congeners of chlorobenzenes in each experiment and the conditions in which they were formed.

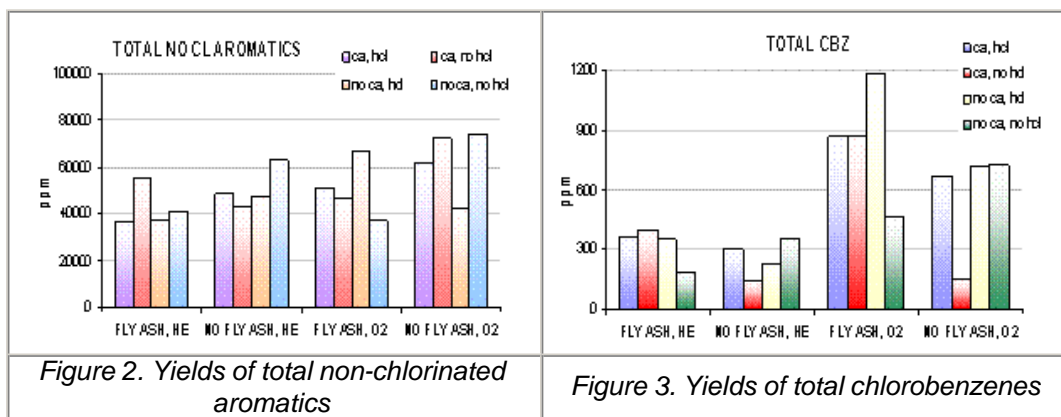


Figure 3. Yields of total chlorobenzenes

Table 2

Yields (in ppm) of the different CBz congeners for each experiment and conditions

Experiment	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
+ $\text{Ca}(\text{OH})_2$	x	x	x	x	x	x	x	x								
+HCl	x	x	x	x					x	x	x	x				
+OX fly ash	x	x			x	x			x	x			x	x		
+ O_2		x		x		x		x		x		x		x		x
monoCBz	95	112	65	97	97	71	41	92	196	449	125	290	116	210	333	321
total diCBz	64	66	42	52	79	54	19	16	36	54	25	31	11	24	14	87
total triCBz	88	138	62	113	90	123	27	25	39	92	27	63	13	31	5	105
total tetraCBz	68	212	63	146	69	214	28	9	43	197	21	110	16	60	2	82
pentaCBz	38	214	45	193	48	248	18	9	29	289	18	130	17	90	2	95
hexaCBz	13	124	23	71	17	156	9	2	8	109	15	95	9	52	2	39
total	366	866	300	672	400	865	142	153	352	1190	230	719	183	469	359	729

When comparing two by two the yields of total chlorobenzenes in experiments which only differed in one parameter between them, some interesting results arise, although it was not always easy to interpret that because the behavior of the congeners was different. Thus, oxygen clearly rises CBz yields, as mentioned above, but according to the results, this effect is almost independent on the presence of fly ash as long as HCl is present in the low-temperature zone, which seems to contradict the mechanism by which oxychlorination reaction is catalyzed by metals. Maybe the explanation is that oxygen was equally able to react with HCl on the walls of the tubes.

The addition of HCl in the secondary flow resulted in an increase of total chlorobenzenes only when there was Ca

(OH)₂ but no fly ash, and when there was fly ash but no Ca(OH)₂. This means that, in the presence of fly ash, CBz yields increased when HCl was present at the highest concentration (no Ca(OH)₂ and HCl addition). On the other hand, when no fly ash was present, the addition of HCl only increased total yields when chlorobenzenes had not been previously formed at high temperatures (Ca(OH)₂ present), so in this case, the rise in the yields appeared at intermediate concentrations. In general, the presence of fly ash increased total yield of chlorobenzenes, but the opposite occurred when there was no Ca(OH)₂ and no HCl was added. This suggests that fly ash can dechlorinate chlorobenzenes at intermediate HCl concentrations.

The amount of data generated makes it difficult to study product trends for each CBz congener. To resolve this problem, Principal Component Analysis (PCA) was used. This is a statistical method that provides a group of new variables (principal components or PCs) whose linear combination generates the original variables. Figure 4 shows the representation of the different CBz congeners, total chlorobenzenes and the four parameters studied versus the two PCs that most contribute to the data variance. In this study, five PCs explain 96% of this variance. The distribution with respect to the two axes gives an idea of the relationship between variables. For example, in this case, monochlorobenzene and Ca(OH)₂ are situated in opposite directions along the PC2, for which it is deduced that this congener was mainly produced when no Ca(OH)₂ was present; i.e., in the high-temperature zone by the reaction of benzene and hydrogen chloride. The rest of the congeners (hexa-, penta-, tetra- and a bit further, tri- and dichlorobenzene), together with total chlorobenzenes, are located in a cluster near the PC1 axis where the oxygen is also present. Thus, it is expected that the presence of oxygen enhances the yields of these chlorobenzenes. Finally, both fly ash and additional HCl are very close and just over the PC1 axis, which indicates that the effect of these two variables is very similar; for example, monochlorobenzenes were hardly affected by the two.

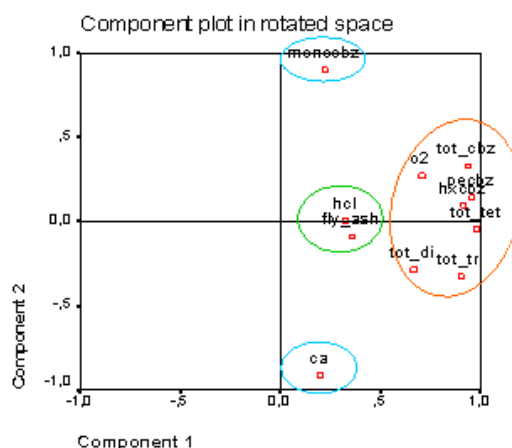


Figure 5. Loading plot from PCA showing the relationship among chlorobenzenes and the parameters studied

Several correlations were investigated, and a linear correlation between total chlorobenzenes and total chlorinated compounds detected was found. However, no correlation was found between the different CBz congeners and benzene. Other major chlorinated compounds apart from chlorobenzenes were chloronaphthalenes, chloroanthracenes and tetrachloroethene.

Despite some difficulties when interpreting certain results, some important conclusions can be drawn from this work:

- Ca(OH)₂ trapped HCl but this did not completely inhibit CBz formation. The chlorobenzenes were either formed directly from the PVC chain during thermal decomposition or were formed from a reaction between HCl and benzene in tubes prior to Ca(OH)₂.
- The highest yields of chlorobenzenes appeared when OX fly ash, oxygen and additional HCl were present and no Ca(OH)₂ was used; i.e. most chlorinating conditions.

- c) The presence of HCl in the high-temperature zone (750°C); i.e. when no Ca(OH)₂ was used, enhanced monochlorobenzene formation, which suggests gas-phase formation.
- d) Oxygen in the low-temperature zone promoted the formation of higher chlorinated benzenes except in the absence of both HCl and OX fly ash.
- e) OX fly ash and additional HCl enhanced the formation of higher chlorinated benzenes.

Acknowledgements

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