

FORMATION OF PCDDs AND PCDFs DURING LOW-TEMPERATURE PYROLYSIS OF PVC IN AN INERT AND OXIDATIVE ATMOSPHERE.

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ABSTRACT

The formation of PCDDs and PCDFs during pyrolysis and oxidative degradation of two different PVC samples at 675 K was studied in a fluidized bed reactor. During pyrolysis in an inert atmosphere, formation of PCDDs and PCDFs appeared to be low, at ppt level. In an air atmosphere formation of PCDDs and PCDFs was 10 to 1000 times higher. Freeboard configuration has a significant influence on the emission levels during oxidative degradation, but not during pyrolysis. The congener profiles for all samples show a predominance towards dibenzofurans.

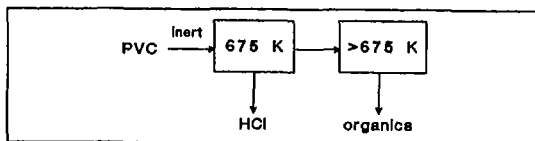
KEYWORDS

Pyrolysis, oxidative degradation, PCDD, PCDF, PVC, fluidized bed.

INTRODUCTION

In the manufacturing of daily commodities, plastics are increasingly superseding metals. After use or discarding of the commodity, these plastics, attached to metal surfaces or not, return as waste. Besides dumping, waste is processed by means of incineration. Some plastics, like polyvinylchloride (PVC), substantially consist of a halogen fraction. During the incineration of PVC, the chlorine fraction is released as hydrogen chloride (HCl). However, polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) might also be formed.

Pyrolysis offers an alternative process for treatment of waste. An efficient route for pyrolysis is a two-step process, in which the first step at low temperature is used to obtain a concentrated HCl stream. The model process is as follows:



The optimal conditions of the first step are a temperature of 675 K and a residence time of 1200 s.; under these conditions, over 90 wt% of the chlorine is removed as HCl [1].

However, part of the organic fraction of PVC is also released in the low temperature step. In the case

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of flexible PVC, the plasticizer is almost entirely released in the temperature range 425–525 K. The chlorine content of the organic fraction, released with the HCl in the first step, was found to be in the range of 100 ppm, which consists mainly of chlorobenzene and chlorotoluene [1].

The aim of this study was to determine whether PCDDs and PCDFs are formed in the low temperature step. These compounds are not to be expected in an inert atmosphere. On the other hand, for a flexible PVC formation of PCDDs and PCDFs is in principle possible, as it contains considerable amounts of oxygen-containing plasticizer. To determine the necessity of working in a totally inert atmosphere, degradation experiments with PVC samples were also performed in air.

EXPERIMENTAL

The study was carried out with a virgin PVC (Cl-content 57 wt.%) and with a flexible PVC (Cl-content 36 wt.%). The flexible PVC contains 33 wt.% plasticizer (DEHP) and 1.5 wt.% stabilizers (Ba and Cd oxides). The experiments were performed in a fluidized bed reactor (i.d.: 28 mm; u_{mf} : 10 mm/s; operating temperature: 675 K), which is a convenient gas–solid contacting system. A diagram of the set-up is shown in figure 1.

For each experiment PVC powder (particle size .100 μm) was fed into the reactor at constant mass flow (1.5–3 mg/s) with a specially designed solid feeding system. Because of the difference in the softening properties of the two PVC samples, two injectors were used. For the virgin PVC a water-cooled stainless steel injector (i.d.: 2 mm; o.d.: 15 mm) was used with the injector tip just above the bed. This injector could not be used for the flexible PVC. The plasticizer released in the reactor, condenses on the tip of the cooled injector, leading to blockage. In this case a much smaller quartz injector (i.d.: 2 mm; o.d.: 4 mm) was used, which was placed with its tip in the freeboard, 100 mm above the hot bed. Because of the difference in size and temperature of the injectors, the freeboard volume and temperature are different. Solid particles were removed from the gas stream in a cyclone. Organics were trapped in a scrubber filled with high purity n-hexane. After each experiment the entire system was thoroughly cleaned with hexane, and care was taken to work as quantitatively as possible. This hexane fraction and the scrubber fraction were mixed. The hexane was spiked with ¹³C-labelled standards (toxic PCDDs and PCDFs, summarised in table 1), and then purified and concentrated [2]. The final isomer-specific analysis was performed on a GC–MS system (HP–5980, HP MSD 5970B) in EI-mode using Supelco 2331 capillary column with on-column injection.

Table 1: Overview of the PCDDs and PCDFs measured.

2,3,7,8-TCDD	2,3,7,8-TCDF
1,2,3,7,8-PCDD	2,3,4,7,8-PCDF
1,2,3,6,7,8-H ₆ CDD	1,2,3,4,7,8-H ₆ CDF
1,2,3,4,6,7,8-H ₇ CDD	1,2,3,4,6,7,8-H ₇ CDF
1,2,3,4,6,7,8,9-OCDD	1,2,3,4,6,7,8,9-OCDF

RESULTS AND DISCUSSION

The yields of the PCDDs and PCDFs, formed during pyrolysis in N₂ of virgin and flexible PVC are given in figure 2. The emission levels show a complex pattern and are for both samples in the ppt range. Although the oxygen content of the flexible PVC is much higher than that of virgin PVC, the influence is not reflected on the emission patterns. In figure 3 and 4, the emission levels for pyrolysis in an inert atmosphere are compared with the ones in air. In an air atmosphere, PCDD and PCDF emissions are 10 to 1000 times higher. The emission levels of flexible PVC are an order of magnitude higher than those of virgin PVC. This can be explained by the difference in injector/freeboard configuration. In the case of the water-cooled injector the hot gas is quenched, resulting in lower

emission levels. This result confirms that the formation of PCDDs and PCDFs is due to secondary reactions of organics with HCl.

The congener profiles for all experiments show a predomination of dibenzofurans. This can be explained by the formation of biphenyl as one of the organic pyrolysis products. Biphenyl may react with oxygen radicals and HCl to a chlorinated dibenzofuran.

These results are in contrast with the work of Giugliano et. al. [3], where no detectable amounts of PCDDs and PCDFs were found during incineration of waste containing PVC, but in agreement with the work of Tysklind et. al. [4] and Theisen et. al. [5] in which more or less the same complex patterns were reported.

CONCLUSIONS

PCDDs and PCDFs are formed only at ppt-level during pyrolysis of PVC at 675 K. No influence of the presence of oxygen-containing plasticizers has been observed. During oxidative degradation of PVC, emission levels are 10 to 1000 times higher than in an inert atmosphere. Under these conditions quenching of the reactant gas leads to a significant decrease in PCDD and PCDF emissions.

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FIGURES

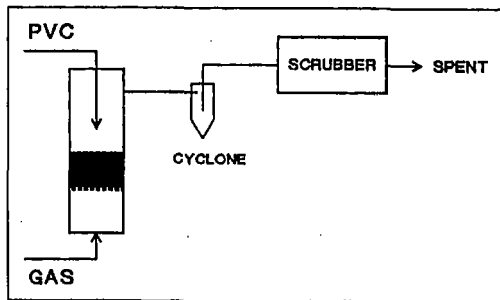


Figure 1: Diagram of experimental set-up.

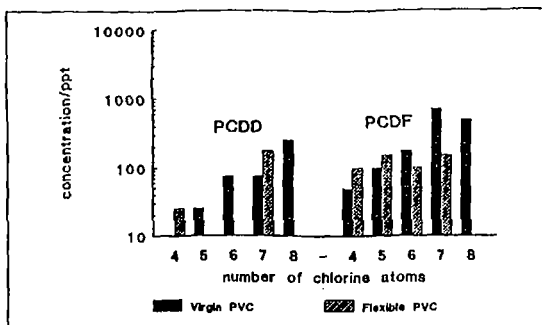


Figure 2: Isomer profile of PCDDs and PCDFs after pyrolysis at 675 K; comparison of virgin and flexible PVC. Note that the y-axis is a log scale and starts with 10 ppt, which is the detection limit of the analysis.

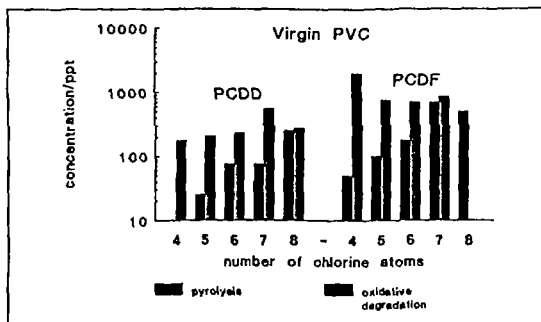


Figure 3: Isomer profile of PCDDs and PCDFs. Comparison of pyrolysis and oxidative degradation at 675 K for virgin PVC. Note that the y-axis is a log scale and starts with 10 ppt, which is the detection limit of the analysis.

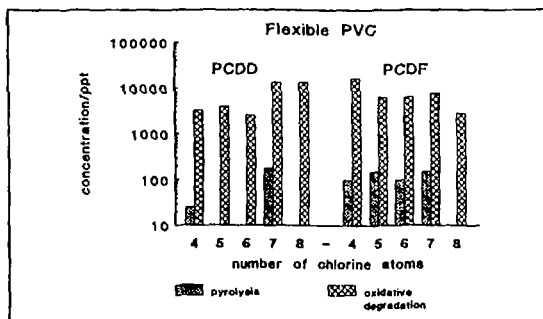


Figure 4: Isomer profile of PCDDs and PCDFs. Comparison of pyrolysis and oxidative degradation at 675 K for flexible PVC. Note that the y-axis is a log scale and starts with 10 ppt, which is the detection limit of the analysis.