

FORMATION OF PCDD/FS FROM THE PYROLYSIS OF POLYETHYLENE WITH INORGANIC CHLORINE

Ming-Hui Zheng¹, Peng-Yan Liu^{1,2}, Ming-Jun Piao¹, Zhang Bing¹, Xiao-Bai Xu¹

¹Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P.O. Box 2871, Beijing 100085, China

²Department of Chemistry, Hebei University, Baoding 071002, China

Introduction

Formation of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in combustion processes of chlorine containing organic materials have been frequently studied¹. Chlorine, catalysts and organic compounds are essential for these reactions. Although copper chloride has been reported to have a significant catalytic role on PCDD/Fs formation via the Deacon process, the function of inorganic chlorine in these reactions is not known in detail².

The purpose of this study was to investigate the effect of inorganic chlorine on formation of PCDD/Fs from pyrolysis or combustion of polymer in absence of organic chlorine. PE (Polyethylene) was selected in this study because it is the leading plastic in total production in the world, and also the major one in municipal solid wastes.

Methods and Materials

Polyethylene (HDPE 5000S) in pellet form was the product of Yanshan Co..

Polymer pyrolysis and combustion was conducted in a tube-type furnace. The combustion apparatus was shown in Figure 1. The combustion chamber consisted of a quartz tube (80 cm×4 cm i.d.). Following the quartz tube was the collecting system, which included a glass wool fiber, a glass filter membrane to keep the particles, a XAD-2 adsorbents vessel, and two liquid nitrogen cold traps. The air was introduced in front of the quartz tube with 2 L/min. Glass wool fiber, glass fiber membrane, and the sample boat were heated at 500°C in a muffle furnace for 2 h just before using, in order to remove the possible organic compounds contaminants.

2.0 g PE was melted in a sample boat and mixed with different kinds of metal chlorides. The sample was cooled at room temperature. A complete experimental matrix was given in Table 1. At first, the furnace was heated to 400°C and the air was introduced in. Then the sample boat containing PE was pushed into the combustion zone of the furnace. After the combustion, took out the boat, stopped the air, and turned off the furnace.

Glass wool fiber, glass fiber membrane, XAD-2 adsorbents, solid residues on the wall of the quartz tube and sample boat were spiked with a mixture of ¹³C-labelled PCDD/Fs (Cambridge Isotope Laboratories) prior to their 24 h Soxhlet extraction with toluene. The extracts were washed with concentrated sulfuric acid following concentration by rotary evaporation. The bulk of the co-

FORMATION AND SOURCES I -POSTER

extracted organic material was removed by successively passing the extract through the following series of chromatographic columns: silica, acid-base silica multilayer, and basic alumina. Just prior to GC-MS analysis, two ^{13}C -labelled recovery standards (Cambridge Isotope Laboratories) were added for the quantification of surrogated recovery. The analyses were carried out by Agilent 6890 GC/ 5973N MS using a 60 m HP-5 ms fused-silica column. Quantification of PCDD/Fs was performed in selected-ion monitoring mode. For each congener two most abundant ions of molecular ion clusters were measured.

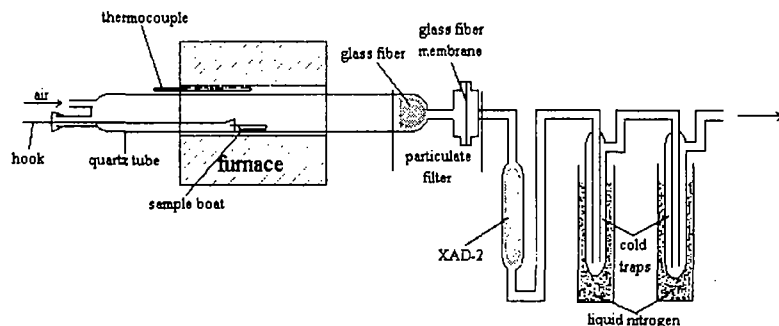


Figure 1. Schematic of the combustion and collection system

Table 1 Inorganic chlorine variation in the experiment

Experiment no.	Inorganic chlorine
1	no
2	40 mg NaCl
3	20 mg ZnCl_2
4	20 mg CuCl_2
5	40 mg FeCl_3
6	40 mg CuCl_2
7	20 mg NaCl+20 mg ZnCl_2
8	20 mg NaCl+20 mg CuCl_2
9	20 mg ZnCl_2 +20 mg CuCl_2

Results and Discussion

No PCDD/Fs were detected in experiment no.1, which did not contain any chlorine sources. No detectable PCDD/Fs were observed in experiment no.2, which only contained NaCl as chlorine sources. PCDD/Fs formation was confirmed in other experiments with transition metal chlorides. The homologue profiles of PCDD/Fs in the experiments were shown in Table2.

Leonir et al. have reported no difference in emission of PCDD/Fs were found between the combustion experiments with or without NaCl in the fuel³. As it could be seen from Table 2, NaCl was an effective chlorine source in these experiment conditions, but it was not observed to have any effects on PCDD/Fs formation without catalysts.

PCDFs were more dominant than PCDDs, and higher chlorinated PCDD/Fs were more formed preferentially from experiment no.3 to no.9. This is a typical PCDD/Fs profile in the combustion

FORMATION AND SOURCES I -POSTER

experiments using the wastes with chlorine sources and Cu catalyst⁴. It has been found that an increase in the PCDD/Fs formation with increasing amount of metal chlorides.

Table 2 The homologue profiles of PCDD/Fs in the experiments (ng/g PE)

Compounds	3#	4#	5#	6#	7#	8#	9#
2378-TCDF	1.11	0.11	ND	18.72	0.86	2.43	24.66
Σ TCDF	5.43	0.11	4.20	43.03	1.90	7.19	90.52
2378-TCDD	ND	ND	ND	ND	ND	ND	ND
Σ TCDD	ND	ND	ND	ND	ND	ND	7.27
12378-PCDF	ND	ND	0.72	1.10	ND	0.31	7.92
23478-PCDF	0.56	ND	0.27	7.86	ND	1.30	15.56
Σ PCDF	4.43	0.16	5.18	84.49	3.07	8.81	166.72
12378-PCDD	ND	ND	ND	1.02	ND	ND	3.21
Σ PCDD	ND	ND	ND	18.29	5.48	ND	40.36
123478-H ₆ CDF	ND	ND	0.84	ND	ND	2.81	48.00
123678-H ₆ CDF	ND	0.11	0.47	8.56	ND	0.67	16.67
123789-H ₆ CDF	0.53	ND	ND	22.29	ND	1.40	22.69
234678-H ₆ CDF	ND	ND	ND	ND	ND	ND	7.52
Σ H ₆ CDF	3.88	0.20	3.68	97.54	ND	10.02	186.92
123478-H ₆ CDD	ND	ND	ND	1.17	ND	ND	ND
123678-H ₆ CDD	ND	ND	ND	1.60	ND	ND	4.26
123789-H ₆ CDD	ND	ND	ND	7.70	ND	ND	18.78
Σ H ₆ CDD	ND	ND	ND	34.60	ND	ND	45.98
1234678-H ₇ CDF	3.14	1.00	4.62	112.56	7.74	26.59	402.40
1234789-H ₇ CDF	ND	ND	0.80	32.98	2.89	3.62	104.59
Σ H ₇ CDF	3.93	1.00	7.59	215.84	10.63	41.26	646.75
1234789-H ₇ CDD	ND	ND	ND	24.42	ND	1.85	41.29
Σ H ₇ CDD	3.93	ND	0.77	44.02	ND	3.42	80.01
OCDD	ND	ND	ND	37.50	ND	9.89	109.41
OCDF	0.73	0.64	1.75	128.37	2.96	33.10	283.08

ND<0.05 ng/g PE

Acknowledgments

This study was supported by National Natural Science Foundation of China. Grant no. 29707003. The authors are grateful to Agilent Tech. Co. Lab. for apparatus supports.

References

1. Tuppurainen K.A., Ruokojarvi P.H., Asikainen A., Aatamila A.H., Ruuskanen J. (2000) Environ Sci Technol. 34,4958
2. Wikstrom E., Lofvenius G., Rappe C. Marklund S. (1996) Environ Sci Technol. 30,1637
3. Leonir D., Kaune A., Hutzinger O., Mutzenich G., Horch K. (1991) Chemosphere 23,1491
4. Hatanaka T., Imagawa T., Takeuchi M. (2000) Environ Sci Technol. 34,3920