

Formation of Polychlorinated Aromatic and Aliphatic Compounds on Fly Ash in the Presence of Sulfur

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1. Introduction

A large variety of organohalogen compounds are formed during the metal-catalyzed decomposition of carbon on fly ash of municipal waste incinerators (MWI). The de-novo-synthesis¹⁾ (formation on fly ash from particulate carbon) is an important pathway to explain this formation. In this paper the behaviour of fly ash is discussed to which 1% elemental sulfur was added before thermal treatment. The objective of this work is to identify reaction products of instable chloroaromatic intermediate compounds with sulfur. S. Sinkkonen and J. Koistinen found tetra- and pentachlorodibenzothiophenes in fly ash of waste incinerators⁷⁾, and also in fly ash of an aluminium-smelter and a metal-reclamation plant⁸⁾. We know from the chemistry of coal, that a big variety of structures are formed by destruction. R. Moliner¹⁰⁾ reports the formation of methyl- and ethyl-derivates from naphthalene and benzothiophene after distillation of coal at 700°C. B. Ahling, A. Björseth, G. Lunde³⁾ found, that chlorobenzenes and octachlorostyrene are formed during the destruction of PVC at 570-1130°C. R. Luijk⁴⁾ report about the formation of hexachlorobutadiene and octachlorostyrene by the metal-catalyzed oxidation of residual carbon on fly ash. Generally for the formation mechanism in incinerators currently two path ways are discussed:

- the homogeneous gas phase reaction of small organic structures and the build-up of larger compounds by cyclisation, such as by Diels-Alder reaction above 600°C, mainly from butadiene and propene^{5,6)}
- the gas-solid interaction on the surface of organics with chloride, sulfur and oxygen. As organic reaction partners may be considered either volatile components from the gas phase, or the residual organic carbon from the fly ash.

In addition to the compounds already identified, the formation of other species, especially caused by the presence of elemental sulfur, was studied. First results are presented here as a contribution to the de-novo-synthesis of organics from carbon of fly ash.

2. Experimental

Fly ash from an electrostatic precipitator of a MWI-plant was used in this study. The inhomogeneous material was ground and refluxed five times with cyclohexane and benzene, filtered and dried under reduced pressure (0,15 mbar) at room temperature for 48 hours. Then 1% sulfur was added to the fly

ash and thermal treatment was performed for two hours in a vertical quartz tube with a frit at the bottom using an ascending flow of wet synthetic air at 250°, 300°, 350°, 400°, 450°, 500° C. Two washing bottles (benzene, cyclohexane) were used for collecting volatile organic compounds. The residue was extracted for 24 hrs. with carbon tetrachloride under reflux, the clean-up of the extract and of the solution of the washing bottles was done separately. For removing the sulfur, the solutions were extracted with TBAH (tetrabutylammonium hydrogensulfate) and natriumsulfite.⁹⁾ Further sample preparation is described elsewhere^{1,2)}. First, the samples were analyzed for sulfur-compounds with a combination of gaschromatograph-atomic emission spectrograph, HR-GC/AED^{11, 12)}, (HP 5921A-5890 series), DB-5 (30m, i.d. 0,32 mm, d_f 0,25 µm), splitless injection (1 µl carbontetrachloride), T-program 60°C (2 min.), then 5°/min. to 280°C, 280°C (20 min.). Because, there are no ¹³C-standards for all sulfur compounds, thianthren was selected as internal standard for quantification, since there is no formation of thianthren at thermal treatment of fly ash. Quantification of the organohalogen-sulfur-compounds with GC/AED was carried out using the sulfur-channel at 181 nm (figure 1). The response of the GC/AED, however, is a factor of 100 lower than with HR-GC/MSD-SIM-mode (HP 5890-5970 series). At trace level the samples were analyzed with HR-GC/MSD in the -SIM-mode (HP 5890-5970 series) with thianthren as internal standard, after determining the substance specific response factors of the respective compounds relative to thianthren.

3. Results and Discussion

After thermal treatment and clean-up of the fly ash, a series of compounds was identified and quantified such as tetrachlorothiophene, polychlorinated benzothiophenes and dibenzothiophenes, octachlorophenylthiophene, decachlorobisbutadienylsulfides, hepta- and octachlorostyrene, decachlorovinyl-naphthalenes, decachlorophenylbutadiene, decachlorooctatetraene and the dodecachlorobisphenyl-ethenes. The polychlorinated benzothiophenes were the compounds with the highest concentrations, by polychlorinated dibenzothiophene. The maximum of formation of polychlorinated benzothiophenes (PCBT's) is at 350°C similar to the polychlorinated dioxins and furans, and the trichloro- to the pentachloro- isomers being dominant. The data are given in table 1.

Table 1: Formation of polychlorinated benzothiophenes (PCBT's) on fly ash with 1 % sulfur, (concentrations in ng/g fly ash)

	Σ PCBT	Σ Cl ₂ BT	Σ Cl ₃ BT	Σ Cl ₄ BT	Σ Cl ₅ BT	Σ Cl ₆ BT
250°C	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.
300°C	737,03	141,01	137,10	145,46	204,07	109,39
350°C	3327,77	272,95	1004,51	1194,91	543,51	311,89
400°C	1865,55	381,47	653,49	464,03	243,95	122,61
450°C	883,16	85,98	208,06	316,51	203,24	69,37
500°C	532,54	42,06	155,31	182,91	101,71	50,55

For the polychlorinated dibenzothiophenes (PCDT's), the maxima of formation are shifted to higher temperatures. Compared with the polychlorinated benzothiophenes are the amounts 10 to 30 times lower. The highest concentrations for the Cl₄DT's and the Cl₅DT's are founded at 400°C, for the Cl₆DT's and Cl₇DT's even at 450°C (table 2). Table 3 is shows, that the maximum of formation for the tetrachlorothiophene is at 300°C. The decachlorooctatetraene (Cl₁₀OT), the octachlorodihydro-benzothiophene (Cl₈DHBT), the chlorostyrenes (Cl₇STY, Cl₈STY), the octachlorophenylthiophene (Cl₈PT) and the decachlorophenylbutadiene (Cl₁₀PB) have all their maximum of formation at 400°C (table 3). The amounts found for the styrenes are altogether very low. Differently from those, the

amounts of the Cl₁₀OT and Cl₁₀BBS's are one to two scales higher. It is interesting to know (table 3), that for the decachlorobisbutadienylsulfides (Cl₁₀BBS's), the decachlorovinyl-naphthalenes (Cl₁₀VN's) and the dodecachlorobisphenylethenes (Cl₁₂BPE's), the maximum is shifted to 450°C, also as for the Cl₆DT's and the Cl₇D's.

Table 2: Formation of polychlorinated dibenzothiophenes (PCDT's) on fly ash with 1% sulfur, (concentrations in ng/g fly ash)

	Σ PCDT	Σ Cl4DT	Σ Cl5DT	Σ Cl6DT	Σ Cl7DT	Σ Cl8DT
250°C	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.
300°C	56,83	16,74	25,95	11,34	2,80	n.n.
350°C	92,41	30,50	30,45	14,19	2,96	n.n.
400°C	132,79	57,31	43,35	18,82	4,16	n.n.
450°C	83,79	20,71	33,77	24,29	6,70	n.n.
500°C	75,86	15,40	32,15	23,95	4,36	n.n.

Table 3: Formation of organohalogen compounds on fly ash with 1 % sulfur, (concentrations in ng/g fly ash)

	250°C	300°C	350°C	400°C	450°C	500°C
Cl4T	n.n.	81,40	46,25	30,32	5,98	7,59
Cl10OT	n.n.	1,67	11,34	93,96	17,21	10,53
Cl8DHBT	n.n.	0,50	5,04	44,97	11,56	6,33
Cl10BBS	n.n.	n.n.	2,45	12,00	20,14	11,81
Cl10VN	n.n.	5,98	0,71	17,14	18,27	15,31
Cl7STY	n.n.	0,78	0,85	5,55	1,71	0,61
Cl8STY	n.n.	0,19	4,01	9,85	2,14	1,86
Cl8PT	n.n.	1,74	1,83	4,14	3,13	1,30
Cl12BPE	n.n.	2,38	0,84	4,03	4,92	6,24
Cl10PB	n.n.	0,23	0,12	1,35	0,84	1,13

4. Conclusions

- The macromolecular carbon structure of the fly ash is a source for the formation of polychlorinated aromatic structures (i.e. polychlorinated dioxins, furans, benzothiophenes) during the metal-catalyzed degradation of the carbon. In these reactions aromatic structures with carbon-chlorine bonds may react with sulfur with formation of stable organosulfur compounds. A second possibility of forming chlorinated sulfur compounds is the gasphase reaction of instable cracking products of the carbon with sulfur, e.g. by cyclization with simultaneous input of sulfur. So the sulfur may be involved in cyclization reactions of polychlorinated butadienes, styrenes, biphenyls and phenylbutadiene which react to thiophenes, benzothiophenes, dibenzothiophenes and phenylthiophenes. The maxima of formation of the polychlorinated organosulfur-compounds occurs at higher temperatures compared with corresponding oxygen-compounds. The stability is probably higher, because of a lower rate of destruction.
- The maximum of formation for the tetrachlorothiophene is at 300°C. At higher temperatures other compounds, i.e. decachlorobisbutadienylsulfides (Cl₁₀BBS's), decachloroocta-tetraene (Cl₁₀OT) are preferably formed. This fact may indicate a common precursor compound.
- Generally chlorinated aromatic compounds have a maximum of formation at lower temperatures as chlorinated aliphatic compounds.
- The metal-catalyzed destruction of macromolecular carbon on fly-ash in dependence on the temperature between 250°C and 500°C leads to other compositions of the crack-products and the formation of other compound classes is preferred, in the presence of sulfur.

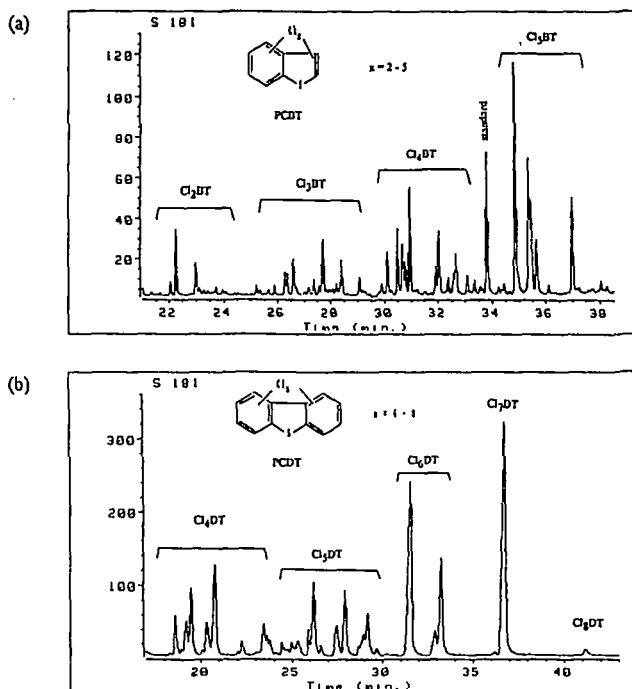


Figure 1: Sulfur specific detection with a combination of GC-atomic emission detector (GC-AED) at 181 nm (sulfur channel), (a) polychlorinated benzothiophenes (PCBT) from fly ash with 1% sulfur at 350 °C/2h, (b) polychlorinated dibenzothiophenes (PCDT) from chlorination of dibenzothiophene with CuCl_2 at 350 °C/2h.

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