



Effect of temperature and oxygen on the formation of chlorobenzene as the indicator of PCDD/Fs

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Abstract

Sampling and analysis of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are both time-consuming and expensive. In principle, real-time monitoring of chlorobenzene (CBz) as an indicator for PCDD/Fs could be useful to control and optimize incinerator operating conditions. To test this strategy, CBz was analyzed together with PCDD/Fs in flue gas samples collected from a hospital waste incinerator. Moreover, lab experiments were conducted to investigate the effect of temperature and oxygen on CBz formation from fly ash from the same incinerator. The experimental results demonstrate that chlorobenzene (in particular PeCBz) correlate well with PCDD/Fs, in line with previous research. The optimum temperature of CBz formation is in a range of 350 to 400°C and CBz yield increases significantly with oxygen, in line with PCDD/Fs formation. This study is useful for confirming the de novo mechanism and defining correlations between CBz and PCDD/Fs.

Key words: PCDD/Fs; indicator; chlorobenzene; oxygen; temperature

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Introduction

Chlorobenzene (CBz), polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) could be formed and emitted from the post combustion of waste incinerators (municipal solid waste and hospital waste) (Olie et al., 1977; Huang and Buekens, 1995; Gao et al., 2009). More than hundred countries signed the Stockholm Convention on Persistent Organic Pollutants (POPs) to limit such pollutant emission. Since 2007, China National Implementation Plan (NIP) for the Stockholm Convention on Persistent Organic pollutants (NIP, 2007) was performed. According to NIP, 10.23 kg I-TEQ PCDD/Fs was emitted in 2004, of which 1.18 kg I-TEQ from hospital waste incineration, i.e., 11.5% of the total PCDD/Fs emission.

Numerous researchers have tried to elucidate the formation mechanisms of PCDD/Fs including two major routes: (1) PCDD/Fs formation by heterogeneous catalysis condensation reaction of direct precursors as chlorobenzene and chlorophenol; (2) PCDD/Fs formation through an oxidative breakdown of macromolecular carbon structures namely de novo synthesis from simple hydrocarbon and chlorine (Addink et al., 1995b; Huang and Buekens, 1995; Stanmore, 2004; Li et al., 2007; Altarawneh et al., 2009). Key parameters affecting PCDD/Fs emission during thermal process include: precursor, chlorine in feed, temperature, residence time and oxygen availability (Addink

et al., 1995a; McKay, 2002). The optimum temperature zone of PCDD/Fs formation in the flue gas is 300 to 400°C (Addink and Olie, 1995a; Huang and Buekens, 2001; McKay, 2002). Gaseous oxygen is required for the de novo reaction in order to initiate carbon gasification and rearrangement. Several authors propose an optimum oxygen content in the flue gas for the PCDD/Fs formation (Addink and Olie, 1995b; Ryan and Altwicker 2000; Yin et al., 2008; Zhang et al., 2008). They show that the rate of PCDD/Fs formation increase when the oxygen concentration was varied from 1% to 10%. Pekárek et al. (2001) found the concentration of PCDD/Fs was distinctly decreasing during transition from oxygen rich atmosphere to pure nitrogen. In China, the content of oxygen in the flue gas needs to remain within the range of 5%–10% according the pollution control standard of hazardous wastes incineration (GB18484-2001).

Conventional measurements of PCDD/Fs are time-consuming, expensive and require advanced skill. Combustion conditions could be optimized by means of primary measures using suitable real-time monitoring of indicators for PCDD/Fs (Everaert and Baeyens, 2002; USEPA, 2004; Lavric et al., 2005). Many compounds were analyzed together with PCDD/Fs to identify the suitable surrogates including carbon monoxide, total of hydrocarbon, chlorinated aromatic and even the single isomers of PCDD/Fs (Blumenstock et al., 1999; Weber et al., 2002; USEPA, 2004). Among the possible surrogates, CBz shows ideal potential as an indicator for PCDD/Fs

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(Lavric et al., 2005). In 1985, a strong relation between hexa-chlorobenzene (HxCBz) and PCDD/Fs was first observed (Öberg and Bergström, 1985). This supports the idea of using chlorobenzene as the indicator parameter for PCDD/Fs, enabling both rapid sampling and a relatively simple analytical procedure. Various alternative instruments for predicting PCDD/Fs emission levels have been proposed (Blumenstock et al., 2001; Yamada et al., 2004; Yin et al., 2007). The resonance enhanced multiphoton ionization mass spectrometry (Jet-REMPI) (Oser et al., 1998) was applied to detect CBz and low chlorinated PCDD/Fs. Time of flight mass spectrometry combined with vacuum ultraviolet photo-ionization (TOFMS/VUV) (Yin et al., 2007) was applied to on-line measurement of polynuclear aromatic hydrocarbon (PAHs) and PCDD/Fs precursor in simulated flue gas. Taylor and Lenoir (2001), after reviewing the formation of chloroaromatic formation in incineration, conclude that chlorination and condensation of aliphatic hydrocarbon compounds lead to the formation of chlorobenzenes, chlorinated polycyclic aromatic hydrocarbon, as well as PCDD/Fs. The CBz could be formed via oxidation, condensation and chlorination of the carbon matrix from fly ash (Taylor and Lenoir, 2001), as the de novo synthesis of PCDD/Fs. However, a detailed mechanistic explanation for the correlation between PCDD/Fs and CBz is presently not developed.

In the present study, CBz and PCDD/Fs were analyzed in flue gas samples collected from a hospital waste incinerator (HWI). Then, experiments were conducted on a fixed-bed of fly ash to elucidate the effect of temperature and oxygen on CBz formation and compare these to their influence on PCDD/Fs formation.

1 Materials and methods

The daily disposal capacity of the HWI in Huzhou City, China, is 10 tons per day. The combustion system features a rotary kiln, followed by burnout in a fluidized bed. The air pollution control system consists of a semi-dry scrubber and a fabric filter. Five flue gas samples were collected at the exit of the cooling tower, just before the gas cleaning system. Kaune et al. (1996, 1998) investigated the influence of gas clean system and other various facilities on the correlation between CBz and PCDD/Fs, the sampling points suggested be performed at the same location and before the flue gas cleaning system to develop the correlation. Fly ash was collected from the exit of the fabric filter at the HWI. The fly ash was Soxhlet extracted with hexane for 24 hr to remove CBz, then nitrogen-dried. The key metal content of fly ash also been detected by ICP-MS (Thermo Scientific XII, USA), Fe was 0.28 wt.%, and Cu was 0.06 wt.%.

Experiments were carried out at atmospheric pressure in a tubular furnace (Fig. 1). A metered gas flow passes through a pre-heater, continuing upwards through the fixed bed of fly ash in the tubular. Tubular furnace has self-governed heater and temperature controller. Experimental conditions are reported in Table 1. The fly ash was 2 g and gas flow was 300 mL/min for 30 min in all of the

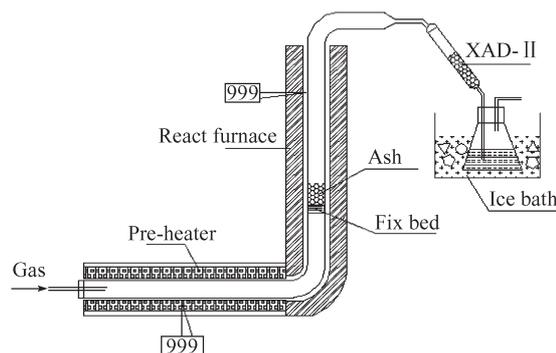


Fig. 1 Schematic drawing of experimental apparatus.

Table 1 Experimental condition in laboratory

Exp no.	Temperature (°C)	Gas	Exp no.	Temperature (°C)	Gas
T1	200	Air	A1	350	N ₂
T2	250	Air	A2	350	5% O ₂
T3	300	Air			
T4	350	Air	A3	350	10% O ₂
T5	400	Air			
T6	450	Air	A4	350	15% O ₂
T7	500	Air			
T8	550	Air	A5	350	Air

experiments. Organics in the flue gas was absorbed on XAD-2 and in hexane in an ice bath. The solid-(fly ash) and gas-phase samples (XAD trap and hexane absorber) were separately analyzed.

After the clean up procedure according the EPA23 method, high-resolution gas chromatography with high-resolution mass spectrometry (HRGC/HRMS) (JMS-800D, JEOL, Japan) with a DB-5MS column (60 m × 0.25 mm × 0.25 μm) was applied to analyze the PCDD/Fs concentration. All isotope standards were purchased from the Cambridge Isotope Laboratories. The target compounds were tetra- to octa-CDD/Fs (in principle, 136 isomers). All concentrations are normalized to dry air, 11% O₂, 1.01 × 10⁵ Pa and 273 K.

The CBz analysis was conducted using GC-ECD (GC 6890N, Agilent, USA) with a DB-5 column (30 m × 0.25 mm × 0.25 μm). The temperature program for GC oven was as follows: initial temperature 80°C, held for 4 min; increased at 5°C/min to 106°C, held for 0.5 min; increased at 8°C/min to 250°C and held for 15 min. The chlorinated benzenes standards were from Aldrich (Milwaukee, USA). Pretreatment was according to the state standard method of HJ/T74-2001 and GB 7492-87, in China, consisting of extraction and a clean-up procedure (H₂SO₄ treatment, multi-layer silica gel column and florisil). The average recovery of high chlorinated compound was above 80%.

2 Results and discussion

2.1 Pollutant emission and correlation between PCDD/Fs and CBz

While measuring organic pollutants, the key operation parameters were measured at the exit of the cooling tower:

the oxygen level was in the range of 6.65%–13.68%, the water content 30%–46%, and temperature window was 180–200°C. Water was injected into the quench tower to cool the flue gas from around 800 to 200°C.

The organic pollutants concentrations are shown in Table 2. The CBz concentration was 2 to 3 orders of magnitude higher than the value of PCDD/Fs. This is an essential advantage for CBz as the indicator for PCDD/Fs. In the flue gas, PCDFs formation is more favored than that of PCDDs: especially for Te- to HxCDF homologues, the ratio of PCDFs/PCDDs ranged from 5.9 to 14.0. The ratio of PCDFs/PCDDs produced by de novo synthesis is generally higher than 3, while the ratio is much smaller than 1 in precursor formation (Huang and Buekens, 1995; Stanmore, 2004; Zhang et al., 2008). Therefore, de novo synthesis possibly dominated PCDD/Fs formation in the post combustion in line with previous research (Huang and Buekens, 1995). The typical homologue distribution could be seen in the Fig. 2. The coefficient of determination R^2 is applied to estimate the correlation between TEQ and PCDD/Fs with total and individual CBz. The analytical results are shown in Fig. 3a and Table 3. They demonstrate that PeCBz and HxCBz are suitable indicators of PCDD/Fs in flue gas; this relation between CBz and PCDD/Fs also was observed in other incinerators as Fig. 3b (Öberg and Bergström, 1987). Correlation between CBz and low chlorinated congeners (e.g., HxCBz to TeCDD, $R^2 = 0.967$) were better than those with high chlorinated species (HxCBz to OCDD, $R^2 = 0.727$). An excellent relation was also found between HxCBz and PeCBz ($R^2 = 0.99$).

2.2 Effect of temperature on CBz formation from fly ash

Temperature is the most influential factor on PCDD/Fs formation and emission (Karasek and Dickson, 1987; Stieglitz and Vogg, 1987; Addink and Olie, 1995a; Leclerc et al., 2006). Fly ash contains macromolecular carbon

Table 2 Pollutant concentration in the flue gas before the gas clean system (unit: $\mu\text{g}/\text{Nm}^3$)

Sample no.	PeCBz	HxCBz	I-TEQ	PCDDs	PCDFs
F1	1.83	1.24	0.016	0.08	0.61
F2	3.58	2.17	0.030	0.14	1.04
F3	2.97	1.50	0.035	0.18	1.27
F4	8.29	4.86	0.065	0.44	2.59
F5	9.59	5.75	0.055	0.37	5.25

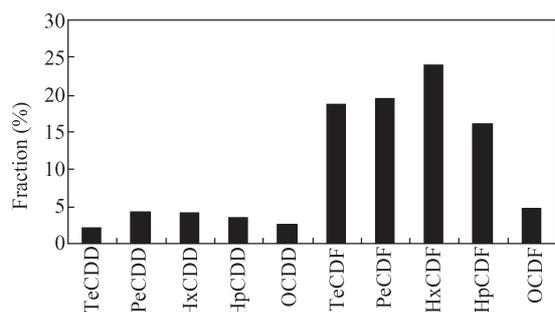


Fig. 2 Homologue profile of PCDD/Fs in flue gas of the HWI.

Table 3 Correlation between CBz and PCDD/Fs in the flue gas samples

No.	Correlation	R^2
1	$C_{I-TEQ} = 0.0053C_{PeCBz} + 0.0126$	0.856
2	$C_{I-TEQ} = 0.0086C_{HxCBz} + 0.0136$	0.810
3	$C_{PCDD/F} = 0.5014C_{PeCBz} - 0.4837$	0.845
4	$C_{PCDD/F} = 0.8405C_{HxCBz} - 0.4591$	0.846
5	$C_{TeCDD} = 0.006C_{PeCBz} + 0.0103$	0.981
6	$C_{TeCDD} = 0.0099C_{HxCBz} + 0.0108$	0.967
7	$C_{TeCDF} = 0.0545C_{PeCBz} + 0.0844$	0.960
8	$C_{TeCDF} = 0.0906C_{HxCBz} + 0.0893$	0.948
9	$C_{PeCDD} = 0.0111C_{PeCBz} + 0.007$	0.953
10	$C_{PeCDD} = 0.0184C_{HxCBz} + 0.008$	0.941
11	$C_{PeCDF} = 0.0503C_{PeCBz} + 0.094$	0.963
12	$C_{PeCDF} = 0.0829C_{HxCBz} + 0.1011$	0.932
13	$C_{HpCDF} = 0.0657C_{HxCBz} + 0.0155$	0.823
14	$C_{OCDD} = 0.0072C_{PeCBz} - 0.0055$	0.777
15	$C_{OCDD} = 0.0117C_{HxCBz} - 0.0039$	0.727
16	$C_{OCDF} = 0.0108C_{PeCBz} + 0.0018$	0.648
17	$C_{OCDF} = 0.0173C_{HxCBz} + 0.0048$	0.595

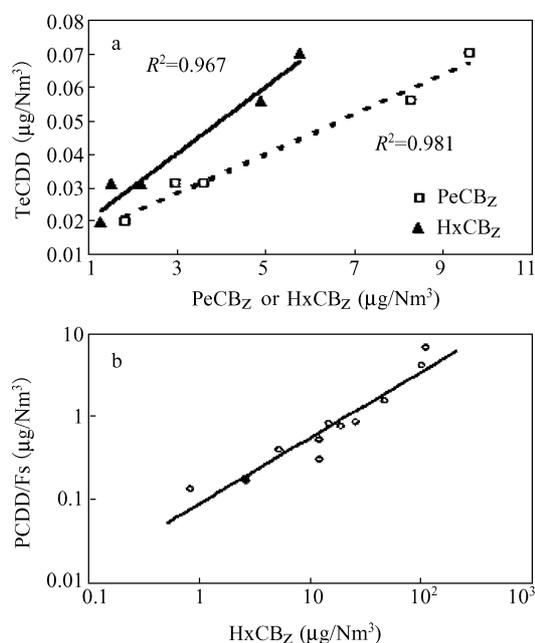


Fig. 3 Correlation between PCDD/Fs and CBz: (a) correlation in this study; (b) data are cited from the publication (Table 1) by Öberg and Bergström (1987).

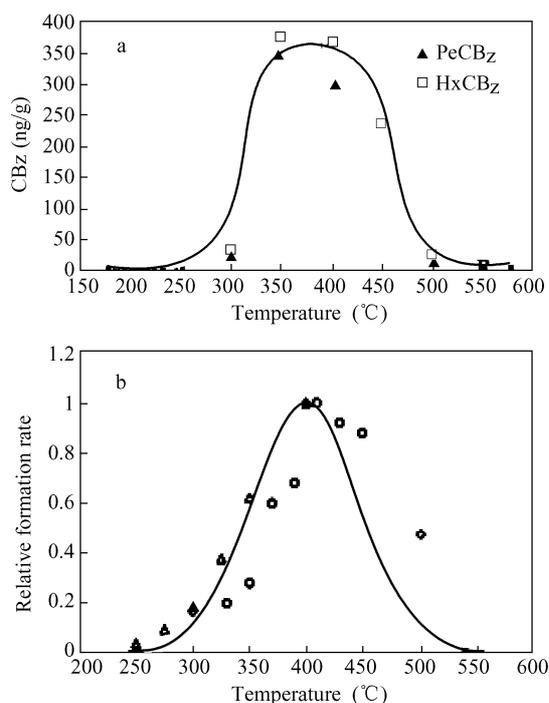
or residual carbon, various organic compounds, chloride and metal ions. A variety of chloroaromatic compounds forms, through a heterogeneous mechanism taking place on the fly ash (Stieglitz and Vogg, 1987; Addink and Olie, 1995a; Kakuta et al., 2007). The temperature influence on surrogate formation is studied, to test the correlation between CBz as an indicator and PCDD/Fs.

The experimental results are present in Table 4 and Fig. 4a. The highest yield occurred at 350 and 400°C. The major part of CBz, formed above 300°C, evaporates rather than remaining on the solid phase (> 90%). Milligan and Altwickler (1995) showed that above 325°C most of the PCDD/Fs stayed in the gas phase. In our experiments (Fig. 4a), the yield of PeCBz and HxCBz peaks around 400°C, an optimum temperature for CBz formation from fly ash. The trend with temperature of CBz is consistent with that of PCDD/Fs (Fig. 4b) (McKay, 2002), and have a similar

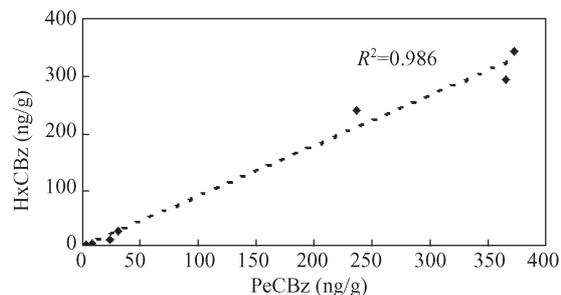
Table 4 CBz yield in the experiments with different temperature (unit: ng/g)

Exp no.	1235TeCBz	1245TeCBz	1234TeCBz	PeCBz	HxCBz
TS1	0.11	8.68	0.84	1.87	0.87
TS2	0.46	1.42	1.19	1.49	1.24
TS3	0.73	8.51	6.76	6.49	6.41
TS4	4.99	3.14	12.09	20.98	25.70
TS5	5.38	9.22	1.91	4.62	8.56
TS6	1.78	1.08	4.19	6.24	7.56
TS7	2.41	1.19	2.52	3.10	3.61
TS8	0.66	0.74	1.30	1.14	2.06
TG1	0.23	0.43	0.43	0.81	0.84
TG2	0.48	1.53	1.39	2.46	2.23
TG3	6.76	4.51	24.32	25.12	22.41
TG4	76.26	19.49	245.84	351.72	317.87
TG5	119.85	73.88	251.00	360.71	284.49
TG6	51.00	24.75	146.76	230.45	233.24
TG7	14.01	11.50	22.16	20.99	10.02
TG8	8.92	9.72	9.79	8.49	3.55

TS: the solid phase yield in the experiments with different temperature; TG: the gas phase yield in the experiments with different temperature.

**Fig. 4** Effect of temperature on the formation of organic aromatics: (a) CBz yield in this study; (b) PCDD/Fs yield (relative to 400°C case) in the reported literature (McKay, 2002).

optimum temperature window. This ensures a steady correlation between CBz and PCDD/Fs in the flue gas with varying temperature. The good correlation between PeCBz and HxCBz (Fig. 5, $R^2 = 0.986$) also appears as that among the flue gas samples in HWI ($R^2 = 0.994$), demonstrating that even under various conditions a robust correlation can exist among compounds with similar formation routes. As in previous research (Taylor and Lenoir, 2001), both CBz and PCDD/Fs could be formed via the similar routes.

**Fig. 5** Correlation between PeCBz and HxCBz in laboratory experiments.

2.3 Effect of oxygen on CBz formation from fly ash

Excess air is a key operation parameter for effective combustion, influencing upon organic pollutant formation (Leclerc et al., 2006; Zhang et al., 2008). Zhang et al. (2008) investigated the effect of O_2 level on PCDD/Fs formation in a municipal solid waste (MSWI); increasing O_2 concentration from 6.0% to 10.5% led to a higher yield of PCDD/Fs (16.9 to 34.3 ng/Nm³) (Fig. 6b). The solid- and gas-phase of CBz concentration were analyzed separately, as shown in Table 5. The concentration of solid-phase CBz almost keeps constant, suggesting that oxygen did not markedly influence CBz distribution up to 10% from 5%, the gas-phase HxCBz yield increased significantly, from 24.32 to 160.15 ng/g, suggesting that a lower O_2 level in flue gas was favorable for limiting organic pollutant formation and emission. There is an optimum oxygen concentration for CBz formation (Fig. 6b). Considering the limit emission of organic pollutant, it is therefore important to limit the oxygen concentration within a suitable value range.

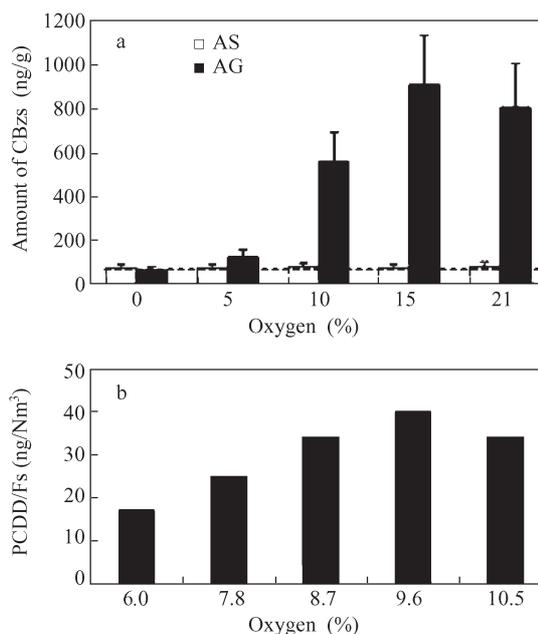
**Fig. 6** Effect of oxygen on the formation of organic aromatics: (a) CBz yield in the present study; (b) PCDD/Fs collected in the bag filter of a MWI (Zhang et al., 2008).

Table 5 CBz yield in the experiments with different atmosphere (unit: ng/g)

Exp no.	1235TeCBz	1245TeCBz	1234TeCBz	PCBz	HxCBz
AS1	7.58	13.78	12.80	18.27	18.60
AS2	7.59	13.81	12.83	18.31	18.64
AS3	5.39	18.59	16.55	17.14	17.92
AS4	5.35	9.80	14.62	19.16	23.07
AS5	6.34	10.16	17.07	21.83	25.29
AG1	5.06	21.71	9.31	15.07	10.88
AG2	10.92	25.47	30.05	34.38	24.32
AG3	39.87	55.63	125.30	174.63	160.15
AG4	54.93	67.93	196.21	281.59	306.45
AG5	50.55	50.46	179.17	252.55	270.91

AS: the solid-phase yield in the experiments with different atmosphere; AG: the gas-phase yield in the experiments with different atmosphere.

3 Conclusions

The experimental results indicate that HxCBz and PeCBz are the probable surrogate for PCDD/Fs. The effect of temperature on CBz and PCDD/Fs is similar, and CBz formation from fly ash enhanced markedly with rising oxygen content. In order to minimize the organic pollutant formation and emission, flue gas should be rapidly cooled from 450°C to below 200°C by quench cooling tower with a short residence time for particulates in optimum temperature zone (350–450°C) and the excess oxygen levels should be kept lower than 10% (V/V) while ensuring effective combustion.

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References

Addink R, Bakker W C M, Olie K, 1995a. Influence of HCl and Cl₂ on the formation of polychlorinated dibenzo-*p*-dioxins/dibenzofurans in a carbon/fly ash mixture. *Environmental Science & Technology*, 29(8): 2055–2058.

Addink R, Cnubben P A J P, Olie K, 1995b. Formation of polychlorinated dibenzo-*p*-dioxins/dibenzofurans on fly ash from precursors and carbon model compounds. *Carbon*, 33(10): 1463–1471.

Addink R, Olie K, 1995a. Mechanisms of formation and destruction of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in heterogeneous systems. *Environmental Science & Technology*, 29(6): 1425–1435.

Addink R, Olie K, 1995b. Role of oxygen in formation of polychlorinated dibenzo-*p*-dioxins/dibenzofurans from carbon on fly ash. *Environmental Science and Technology*, 29(6): 1586–1590.

Altarawneh M, Dlugogorski B Z, Kennedy E M, Mackie J C, 2009. Mechanisms for formation, chlorination, dechlorination and destruction of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs). *Progress in Energy and Combustion Science*, 35(3): 235–274.

Blumenstock M, Zimmermann R, Schramm K W, Kaune A, Nikolai U, Lenoir D et al., 1999. Estimation of the dioxin emission (PCDD/FI-TEQ) from the concentration of low chlorinated aromatic compounds in the flue and stack gas of a hazardous waste incinerator. *Journal of Analytical and Applied Pyrolysis*, 49(1-2): 179–190.

Blumenstock M, Zimmermann R, Schramm K W, Kettrup A, 2001. Identification of surrogate compounds for the emission of PCDD/F (I-TEQ value) and evaluation of their on-line real-time detectability in flue gases of waste incineration plants by REMPI-TOFMS mass spectrometry. *Chemosphere*, 42(5-7): 507–518.

Everaert K, Baeyens J, 2002. The formation and emission of dioxins in large scale thermal processes. *Chemosphere*, 46(3): 439–448.

Gao H, Ni Y, Zhang H, Zhao L, Zhang N, Zhang X et al., 2009. Stack gas emissions of PCDD/Fs from hospital waste incinerators in China. *Chemosphere*, 77(5): 634–639.

Huang H, Buekens A, 1995. On the mechanisms of dioxin formation in combustion processes. *Chemosphere*, 31(9): 4099–4117.

Huang H, Buekens A, 2001. Chemical kinetic modeling of de novo synthesis of PCDD/F in municipal waste incinerators. *Chemosphere*, 44(6): 1505–1510.

Kakuta Y, Matsuto T, Tojo Y, Tomikawa H, 2007. Characterization of residual carbon influencing on de novo synthesis of PCDD/Fs in MSWI fly ash. *Chemosphere*, 68(5): 880–886.

Karasek F W, Dickson L C, 1987. Model studies of polychlorinated dibenzo-*p*-dioxin formation during municipal refuse incineration. *Science*, 237(4816): 754–756.

Kaune A, Lenoir D, Schramm K W, Zimmermann R, Kettrup A, Jaeger K et al., 1998. Chlorobenzenes and chlorophenols as indicator parameters for chlorinated dibenzodioxins and dibenzofurans in incineration processes: Influences of various facilities and sampling points. *Environmental Engineering Science*, 15(1): 85–95.

Kaune A, Schramm K W, Henkelmann B, Kettrup A, Nikolai U, Zimmermann R et al., 1996. Pentachlorobenzene as indicator for PCDD/F emissions from a hazardous waste incinerator: Effect of using active carbon in the flue gas cleaning. *Organohalogen Compounds*, (27): 159–162.

Lavric E D, Konnov A A, Ruyck J D, 2005. Surrogate compounds for dioxins in incineration: A review. *Waste Management*, 25(7): 755–765.

Leclerc D, Duo W L, Vessey M, 2006. Effects of combustion and operating conditions on PCDD/PCDF emissions from power boilers burning salt-laden wood waste. *Chemosphere*, 63(4): 676–689.

Li X D, Zhang J, Yan J H, Cen K F, Ryan S P, Gullett B K et al., 2007. Experimental and modeling study of de novo formation of PCDD/PCDF on MSW fly ash. *Journal of Environmental Sciences*, 19(1): 117–122.

McKay G, 2002. Dioxin characterisation, formation and minimisation during municipal solid waste (MSW) incineration: Review. *Chemical Engineering Journal*, 86(3): 343–368.

Milligan M S, Altwickler E R, 1995. Mechanistic aspects of the se-novo synthesis of polychlorinated dibenzo-*p*-dioxins and furans in fly-ash from experiments using isotopically labeled reagents. *Environmental Science & Technology*, 29(5): 1353–1358.

Öberg T, Bergström J G T, 1985. Hexachlorobenzene as an indicator of dioxin production from combustion. *Chemosphere*, 14(8): 1081–1086.

Öberg T, Bergström J G T, 1987. Emission and chlorination pat-

- tern of PCDD/PCDF predicted from indicator parameters. *Chemosphere*, 16(6): 1221–1230.
- Olie K, Vermeulen P L, Hutzinger O, 1977. Chlorodibenzo-*p*-dioxins and chlorodibenzofurans are trace components of fly ash and flue gas of some municipal incinerators in The Netherlands. *Chemosphere*, 6(8): 455–459.
- Oser H, Thanner R, Grotheer H H, 1998. Continuous monitoring of ultratrace products of incomplete combustion during incineration with a novel mobile Jet-REMPI device. *Chemosphere*, 37(9-12): 2361–2374.
- Pekárek V, Grabic R, Marklund S, Pun ochá M, Ullrich J, 2001. Effects of oxygen on formation of PCB and PCDD/F on extracted fly ash in the presence of carbon and cupric salt. *Chemosphere*, 43(4-7): 777–782.
- NIP (China National Implementation Plan), 2007. China national implementation plan for the stockholm convention on persistent organic pollutants. April 2007. <http://www.pops.int>.
- Ryan S P, Altwicker E R, 2000. The formation of polychlorinated dibenzo-*p*-dioxins/dibenzofurans from carbon model mixtures containing ferrous chloride. *Chemosphere*, 40(9-11): 1009–1014.
- Stanmore B R, 2004. The formation of dioxins in combustion systems. *Combustion and Flame*, 136(3): 398–427.
- Stieglitz L, Vogg H, 1987. On formation conditions of PCDD/PCDF in fly ash from municipal waste incinerators. *Chemosphere*, 16(8-9): 1917–1922.
- Taylor P H, Lenoir D, 2001. Chloroaromatic formation in incineration processes. *The Science of the Total Environment*, 269(1-3): 1–24.
- USEPA, 2004. The use of surrogate compounds as indicators of PCDD/F concentrations in combustor stack gases. <http://www.epa.gov/appcdwww/aptb/EPA-600-R-04-024.pdf>.
- Weber R, Sakurai T, Ueno S, Nishino J, 2002. Correlation of PCDD/PCDF and CO values in a MSW incinerator-indication of memory effects in the high temperature/cooling section. *Chemosphere*, 49(2): 127–134.
- Yamada M, Waki I, Sakairi M, Sakamoto M, Imai T, 2004. Real-time-monitored decrease of trichlorophenol as a dioxin surrogate in flue gas using iron oxide catalyst. *Chemosphere*, 54(10): 1475–1480.
- Yin X F, Li X D, Lu S Y, Luo J S, Gu Y L, Yan J H et al., 2007. On-line real-time monitoring of trace organic pollutant formation in the simulated flue gas. *Proceedings of the Chinese Society of Electrical Engineering*, 27(17): 29–33.
- Yin X F, Li X D, Luo J S, Lu S Y, Gu Y L, Yan J H et al., 2008. Influences of temperature and atmosphere on PCDD/Fs formation from PAHs via de novo synthesis reaction. *Journal of Combustion Science and Technology*, 14(2): 117–121.
- Zhang H J, Ni Y W, Chen J P, Zhang Q, 2008. Influence of variation in the operating conditions on PCDD/F distribution in a full-scale MSW incinerator. *Chemosphere*, 70(4): 721–730.