Effect of temperature and oxygen on the formation of PCDD/Fs surrogate

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Abstract

The correlation between chlorobenzenes (CBzs) and PCDD/Fs in the flue gas of a hospital waste incinerator, and effect of temperature and oxygen on the CBzs formation from fly ash were investigated through experiments. The results showed pentachlorobenzene and hexachlorobenzene are good indicators for PCDD/Fs. The optimum temperature of CBzs formation was in the range between 350°C – 450°C, and CBzs yield increased significantly when oxygen content was over 10%, which are very similar with the impact of such parameters on PCDD/Fs formation.

Introduction

In the post combustion of waste incinerator, chlorobenzenes (CBzs), polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) are formed and emitted. The key parameters affecting PCDD/Fs emission from thermal process are: chlorine in feed, temperature, residence time and oxygen availability[1]. The general view for the optimum temperature zone of PCDD/Fs formation is 300 °C to 500 °C[1] in the flue gas. Meanwhile, optimum oxygen content exists during the PCDD/Fs formation process[2]. The work[3] showed that the rate of PCDD/Fs formation increased and a maximum formation was found at ≥ 5%, when the oxygen concentration was varied between 1 and 10%. Recent developments focus on the optimization of the primary combustion process and the limit emission of contaminants. For improving the knowledge about the process, time-resolved flue gas analysis has to be performed. The conventional methods for PCDD/Fs determination are time consuming and high cost. The control and optimization of the varying combustion conditions could be done by monitoring indicator for PCDD/Fs. Many researches have been done and various components were analyzed together with PCDD/Fs to identify the suitable surrogate, and various alternative methods for estimating the PCDD/PCDF emission levels in a shorter time have been proposed. Amongst the possible surrogates, CBzs showed real possibilities to be good indicator for PCDD/Fs[4].

The measurements of CBzs and PCDD/Fs were carried out in a hospital waste incinerator (HWI). The affecting factors on the surrogate formation is not so widely investigated as the parameters of PCDD/Fs, so the experiments were conducted on a fix-bed furnace to elucidate effect of temperature and oxygen on the CBzs formation from fly ash.

Materials and Methods

The disposal capacity of the HWI is about 15 tons medical waste per day. The combustion technology adopts a rotary kiln combined with a fluidized bed as a burnout element. Kuane[5,6] investigated the influence of gas cleaning system on the connection between CBzs and dioxin, and the sampling points suggested be performed at the same location and before the flue gas cleaning system to develop the correlation. Five flue gas samples were collected in front of the gas cleaning system. Fly ash was collected from a fabric filter exit at the HWI. The fly ash was Soxhlet extracted with hexane for 24 h to remove existing CBzs, finally nitrogen-dried. Experiments were carried out at atmospheric pressure in a tubular furnace (Fig.1). Gas flowed into the tubular reactor through a flow meter, passing a pre-heater, upwards through the fix bed covered fly ash. Experiments are reported in Table 1. The flue gas was absorbed in the XAD-2 and hexane in ice bath. The solid- (fly ash) and gas- phase samples (XAD trap and hexane absorber) were separately analyzed. High-resolution gas chromatography with high-resolution mass spectrometry (HRGC/HRMS) (JEOL JMS-800D) was applied to analyze the PCDD/Fs concentration. The CBzs analysis was conducted in the GC-ECD (Agilent 6890N GC).

Results and Discussion

Tatlor and Lenoir[7] have done a review on chloroaromatic formation in incineration process, studies of the chlorination and condensation of aliphatic hydrocarbon compounds lead to the formation of chlorinated benzenes and chlorinated polycyclic aromatic hydrocarbon at low temperature.

Pollutants emission and correlation between PCDD/Fs and CBzs

The organic pollutant concentration was showed in Table 2. The CBzs concentration was 2-3 orders of magnitude than the PCDD/Fs. This is the principal advantage for the surrogate compound. In the flue gas, the PCDFs formed favor than the PCDDs, the ratio of PCDFs/PCDDs ranged from 5.9 to 14.0. The ratio of PCDFs/PCDDs produced by de novo synthesis is generally bigger than 3, but in precursor formation the PCDFs/PCDDs ratio is much smaller than 1. So de novo synthesis possibly dominated the dioxin formation, thus produces much PCDFs. The coefficient of determination R^2 is applied to estimate the correlation between TEQ, PCDD/Fs and congener with CBzs. The analysis results are presented in Table 3. The results demonstrated that PeCBz and HxCBz are good indicators of PCDD/Fs in the flue gas. There is a better correlation between CBzs and low chlorinated congener (HxCBz to TeCDD, R^2=0.97) than that between CBzs and high chlorinated species (HxCBz to OCDD, R^2=0.78).

Effect of temperature on the CBzs formation from fly ash

Temperature is the most influential factor on PCDD/Fs formation, the study of temperature influence on surrogate formation is important to elucidate the correlation and mechanism. The experimental results are reported in Table 4 and Fig.2 (A). It can be found that T4 and T5 experiments (350°C, 400°C) have the maximal yield. The gas-phase CBzs predominated CBzs amount in the temperature zone of 350 to 450 °C (>90%), the reasonable explanation is that the major part of formed CBzs evaporates rather than remains in the solid phase at high temperature above 350 °C. Milligan and Altwicker[8] showed that most of the PCDD/Fs stayed in the gas phase at temperature above 325°C. In fig.2 (A), effect of temperature on PeCBz and HxCBz is so obvious that CBzs formation had a peak at 350°C in our experimental condition, so there must be an optimum temperature for CBzs formation. Compare to effect of temperature on PCDD/Fs formation Fig.2 (B), the yield trend with temperature is so consistent with each other and almost have the same optimum temperature window[1]. This ensures a steady correlation between high chlorinated benzenes and PCDD/Fs.

Effect of oxygen on the CBzs formation from fly ash

Excess air coefficient is a key operation parameter for effective combustion, also influence the organic pollutant formation and emission. Huai-Jun Zhang, et al.[9] investigated the effect of O_2 level on PCDD/Fs formation in a municipal solid waste (MSWI), increasing O_2 supply from 6.0% to 10.5% essentially led to a higher yield of PCDD/Fs (16.9 to 34.3 ng/Nm^3). The solid- and gas- phase concentration were analyzed respectively. Considering the solid concentration of CBzs, the oxygen did not markedly influence the CBzs distribution in fly ash (Fig.3). However, when the oxygen content was over 10%, the gas-phase CBzs yield increased significantly, from 125.13 to 555.59 ng/g, suggested lower O_2 level in flue gas was favorable for reducing organic pollutant formation. In order to control the organic emission, it is therefore important to limit the oxygen concentration in the flue gas.

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Table 1 Experimental condition in lab

Exp no.	Temp. °C	Gas	Exp no.	Temp. °C	Gas
T1	200	air	A1	350	N_2
T2	250	air	A2	350	5% O_2
T3	300	air	A3	350	10% O_2
T4	350	air	A4	350	15% O_2
T5	400	air	A5	350	air

T6	450	air	The fly ash was 2 g and gas flow was 300 ml/min for 30 min in all of the experiments.
T7	500	air	
T8	550	air	

Table 2 Pollutant concentration in the flue gas before the gas cleaning system, μg/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

Table 3 Correlation between CBzs and dioxin in the stack gas samples, μg/Nm^3

No.	Correlation	R^2
1	[I-TEQ] = 0.0053[PCBz] + 0.0126	0.8561
2	[I-TEQ] = 0.0086[HCBz] + 0.0136	0.8104
3	[PCDD/F] = 0.5014[PCBz] - 0.4837	0.8445
4	[PCDD/F] = 0.8405[HCBz] - 0.4591	0.8463
5	[TeCDD] = 0.006[PCBz] + 0.0103	0.9806
6	[TeCDD] = 0.0099[HCBz] + 0.0108	0.9672
7	[TeCDF] = 0.0545[PCBz] + 0.0844	0.9604
8	[TeCDF] = 0.0906[HCBz] + 0.0893	0.9476
9	[PeCDD] = 0.0111[PCBz] + 0.007	0.9531
10	[PeCDD] = 0.0184[HCBz] + 0.008	0.9408
11	[PeCDF] = 0.0503[PCBz] + 0.094	0.9632
12	[PeCDF] = 0.0829[HCBz] + 0.1011	0.9318
13	[OCDD] = 0.0072[PCBz] - 0.0055	0.7767
14	[OCDD] = 0.0117[HCBz] - 0.0039	0.7272
15	[OCDF] = 0.0108[PCBz] + 0.0018	0.6482
16	[OCDF] = 0.0173[HCBz] + 0.0048	0.595

Table 4 CBzs yield in the experiments with different temperature, ng/g

Exp no.	1235TeCBz	1245TeCBz	1234TeCBz	PeCBz	HxCBz
TS[a]1	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
TG[b]1	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

[a] TS, the solid phase yield with different temperature; [b] TG, the gas phase yield.

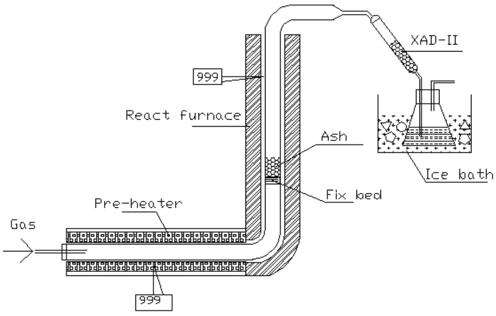

Fig. 1 Schematic drawing of experimental apparatus

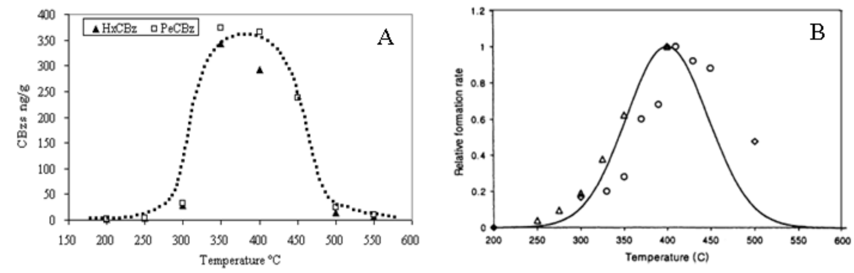

Fig.2 A: CBzs amount (TG+TS) in the experiment with different temperature; B: Relative formation rates of PCDD/Fs from the literature[1]

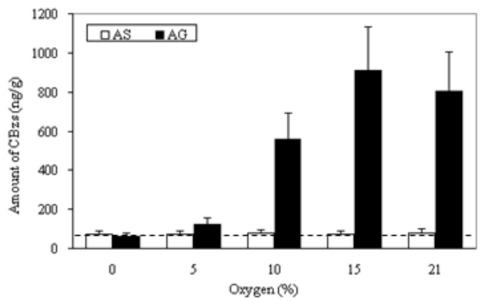

Fig.3 CBzs amount with different oxygen content: AS, the solid- phase yield; AG, the gas- phase yield.