STUDY ON EFFECT OF WATER ON CATALYZED FORMATION OF PCDD/FS

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Introduction

There are many studies focusing on the influencing factors including temperature, catalysts, chlorine sources, residence time on the formation mechanism of Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) during the waste incineration process[1-3]. Besides the above mentioned factors, the moisture was also paid attention by the researchers[4-6]. The waste to incinerators contains a certain content of moisture and an amount of water is injected to air pollution control devices to cool the flue gas in some cases, which can ultimately affect the formation of PCDD/Fs. Jay and Stieglitz[4] reported that in the presence of water vapor considerably less PCDD and PCDF were detected. Briois C. [5] reported in the presence of 1% water was observed to considerably reduce the yield of all PCDD/Fs formed. Meanwhile, Stieglitz indicated the homologue patterns shifted to lower chlorinated homologues[6], and increased the yield of PCDDs from oxidized fly ash at 300 ℃, after water was introduced. Ross found that water in the gas stream enhanced the catalytic activity of fly ash, at the typical moisture levels found in incinerators (approximately 15%)[7]. The author of this paper in the primary research found the water vapor promotes the formation of PCDD/Fs from de novo synthesis pathway by activating fly ash[8].

However, it is still necessary to further investigation to understand the effect of water. The purpose of this study is to elucidate the effect of water on PCDD/Fs formation from precursor compounds by doing experiments as the surface-catalyzed reactions and metal-catalyzed reactions with different moisture contents.

Material and methods

The fly ash was collected from the fabric filter of a mechanical stocker for treating municipal solid waste in China and the sample was heated for 6 hours at 350℃ to reduce the carbon concentration. The main element contents of the ash are shown in Table 1. The BET ash surface area is 3270 cm^2g^{-1} and the average particle size is 18.35μm. Then the sample was soxhelt extracted with toluene for 24 hours to remove contaminants. The fly ash was mixed with 1, 2, 3-TrCBz for 24 hours in churn-dasher (Ash/ TrCBz, 50:1). Experiments were carried out at atmospheric pressure in a tubular quartz furnace of 21.6 mm inner diameter, at 350℃ for 30min. The total length of tube was 1.6 m. The carried gas with 90% Nitrogen (N_2) and 10% oxygen (O_2) was induced into the tubular reactor through a calibrated capillary flow meter. The gas flow was constant with 200ml/min. The reactive water was injected by a Harvard apparatus pump with constant flow rate. Flow rate range can be adjusted from 0.0014 μl/hr to 26.56 ml/min. The flue gas was absorbed in the XAD-2 and toluene in an ice bath. The series of experiments were the mixture of 1,2,3-TrCB and $CuCl_2$, the mixture of 1,2,3-TrCB and fly ash with different moisture. All PCDD/Fs measurements were conducted on high-resolution gas chromatography with high-resolution mass spectrometry (HRGC/HRMS) (JEOL JMS-800D). The experimental runs and PCDD/Fs emission results are shown in Table 2.

Results and discussion

Effect of water on non-catalyzed formation

According to our primary experimental research[8], when no catalyst was added in the reactants (fly ash), the introduction of water enhanced the yield of PCDDs and PCDFs. Although the promotion effect of 6% and 12% appeared almost the same, the more content of water (18%) presented relatively reactive for the total production of PCDDs and PCDFs. In fact, this promotion mainly resulted from the increase of HpCDD, along with a slight decrease of OCDD compared to that at the content of 12%.

Effect of water on copper (Ⅱ)-catalyzed formation

According to results of 1, 2, 3-TrCB plus $CuCl_2$ experimental, the high water content can dramatically suppress the yield of PCDD/Fs (shown in Table 2). The reduction mainly resulted from the decrease of the high chlorinated homologue components (Fig. 1). With the presence or absence of water, PCDDs were markedly less formed than PCDFs in the experimental conditions, even the average ratio of PCDF/PCDD up to 7. This result was the nearly same as that of Hatanaka[9]. With the increase of the water content from 6% to 20%, the ratio of PCDF/PCDDs was increased from 6.4 to 6.7. The major contribution of the total PCDD/Fs yield was high chlorinated species, which indicated $CuCl_2$ was not only a catalyst but also the chlorine source and the major formation mechanisms between PCDDs and PCDFs were different and furthermore the formation of PCDDs was suppressed by water more effectively than PCDFs in these. The chlorination degree at different moisture conditions was reduced from 6.2 to 5.8, which revealed de-chlorination reactions seemed to be slightly enhanced in presence of the water. However, due to the increase of 2, 3, 4, 7, 8-PeCDF, it was found the I-TEQ value increased when the content of moisture was 6% compared to no water condition. Considering the above result, it should be assumed that the compounds formed at first were lower chlorinated species as TrCDF or PeCDF and then the strong oxidizing power of elementary chlorine converted the compounds to the final product, for example, OCDF. This should explain why 2, 3, 4, 7, 8-PeCDF and the I-TEQ value was increased simultaneously when the content of moisture was 6%.

Effect of water on surface-catalyzed formation

According to results of the 1,2,3-TrCB plus fly ash experimental, both the PCDD/Fs yield and I-TEQ value reduced significantly with the presence of water. The major products were the low chlorinated species as Tetra-CDD/Fs due to a lack of more chlorine supply (Fig. 2). When the water content was increased from 6% to 10%, the I-TEQ was reduced and this reduction mainly resulted from the decrease of the 2, 3, 4, 7, 8- PeCDF yield. At the same time, although the moisture was changed, the ratio PCDF/PCDD only slightly increased from

1.1 to 1.6, which pointed out that the fly ash as catalyst had weak selective catalysis for PCDDs or PCDFs. The change trend of PCDD/Fs ratio was the same as that of Briois's[5]. The major isomers of tetra-, penta- chlorinated homologue were 1368-T4CDD, 12469- P5CDD, 2367- T4CDF, 13469- P5CDF. With the increasing of water content, the amount of H6CDF, H7CDF, and O8CDF decreased continuously. The amount of T4CDF and P5CDF slightly increased with the water content and decreased when the water content was larger than 10% (Fig.2). The chlorination degree was decreased from 5.3 to 4.8 at different moisture conditions because of the introduction of water, which expressed that water on ash had a various influence on de-chlorination compared to the 1, 2, 3-TrCB + $CuCl_2$ experiments.

Compared to the above results of different kind experiments, it could indicate that water enhances the de-chlorination reactions, suppresses the total yield of PCDD/Fs but the inhibition was limited.

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Table 1 Elemental analysis of fly ash (unit, wt%)

Element	Si	Ca	Al	Cu	C	P	O	S	Cl	K	Mg	Fe	Zn
Wt%	7.55	17.21	4.49	0.30	0.73	1.29	34.3	5.21	12.25	6.31	1.87	3.57	1.87

Table 2 PCDD/Fs yield and TEQ with different water content

No.	Water (vol %)	The mixture of reactant	ΣPCDD/Fs (μg/gTrCB)	I-TEQ (μg/ gTrCB)
C1	0	1,2,3-TrCB(10mg) + $CuCl_2$(20mg)	36.6	0.41
C2	6	1,2,3-TrCB(10mg) + $CuCl_2$(20mg)	25.0	0.54
C3	15	1,2,3-TrCB(10mg) + $CuCl_2$(20mg)	9.7	0.15
C4	20	1,2,3-TrCB(10mg) + $CuCl_2$(20mg)	8.9	0.14
F1	0	1,2,3-TrCB(10mg) + ash(500mg)	29.8	0.31
F2	3	1,2,3-TrCB(10mg) + ash(500mg)	22.6	0.28
F3	6	1,2,3-TrCB(10mg) + ash(500mg)	24.0	0.29
F4	10	1,2,3-TrCB(10mg) + ash(500mg)	22.4	0.23

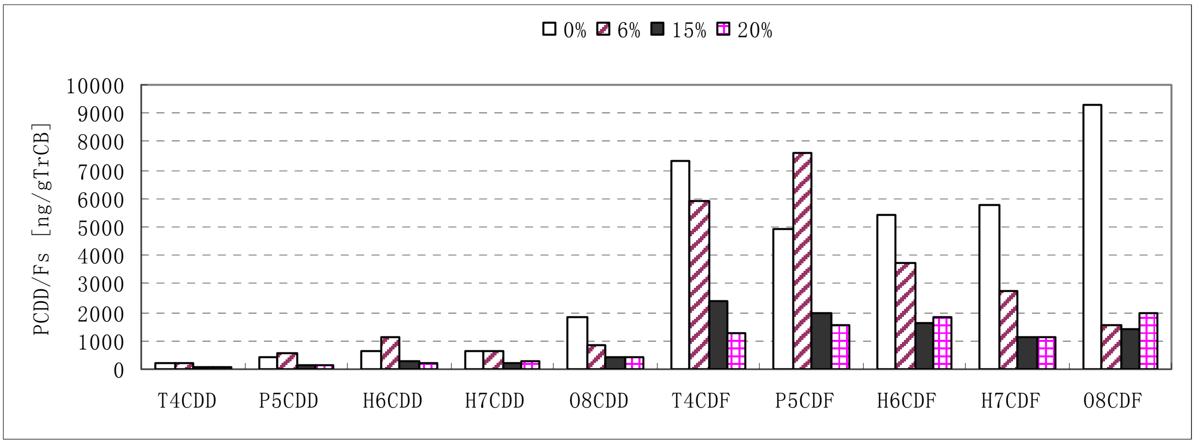

Fig.1Homologue profile of PCDD/Fs in the experiments of 1,2,3-TrCB + $CuCl_2$ reactions

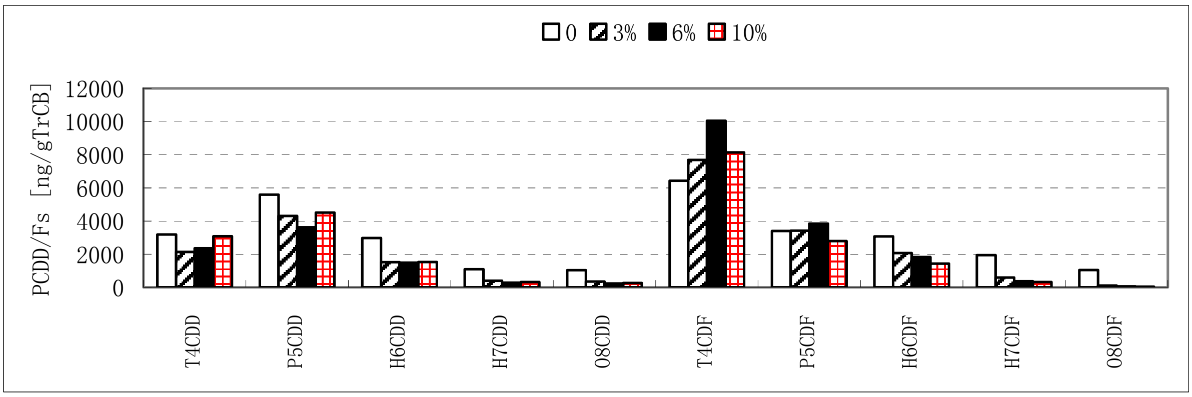

Fig.2 Homologue profile of PCDD/Fs in the experiments of 1,2,3-TrCB + fly ash reactions