

Effect of water on catalyzed de novo formation of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans

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Abstract

The effect of water vapor on catalyzed de novo formation of polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) was investigated through experiments conducted on a fixed-bed apparatus. The results indicated that water vapor could promote the formation of PCDD and PCDF. The dominant pathway was activating fly ash in this work, while water also reacted with chlorine to change the equilibrium of Deacon reaction, which influenced the final yield of PCDD/PCDF. Also a suppression effect of water on CuCl₂ was found according to the values of the catalysis indicator. It is possible that water reduced the catalysis of CuCl₂ or prevented its direct chlorination. But the overall effect of water on the formation of PCDD and PCDF was promotion rather than inhibition.

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1. Introduction

In the post combustion zone of a MSW incinerator, polychlorinated dibenzo-*p*-dioxins (PCDD)/polychlorinated dibenzofurans (PCDF) can be formed via a de novo reaction, which has been considered as a major pathway for the final dioxin yields [1,2]. Numerous researches have been carried out in both lab and full scale to investigate various parameters that determine the final yield of PCDD/PCDF and to understand the mechanism of de novo formation. Some key parameters were studied including temperature [3], carbon [4], chlorine [5], oxygen [6], and catalysts among which copper was considered to be extremely active during the de novo synthesis [7,8].

In full-scale MSW incinerator operation, the incoming refuse contains a certain content of moisture [9], which may ultimately affect the formation or destruction of PCDD/PCDF. The presence of water probably plays a role in the formation of PCDD/PCDF. The research of Sakurai et al. [10] and Ross et al. [11] indicates that water enhances the final yield of PCDD/PCDF. However, Jay and Stieglitz [12] showed that in the presence of water considerably less PCDD and PCDF was detected. Meanwhile, it was found that water vapor had little

effect on the dioxin formation in the dry zone of an iron ore sintering bed [13]. On the other hand, the homologue patterns shift to lower chlorinated homologues when water is added into the reacting gas phase [5,14]. However, the effect of water on the de novo formation within catalyst has not been clarified, due to the complex pathways and complex influences during de novo synthesis.

The potential effect of water on the de novo formation of PCDD and PCDF may include the following pathways: water vapor (a) activates the reaction sites on fly ash through reacting with carbon to promote the final yield [11]; (b) changes some key reaction equilibrium to influence the total yield, for example, that of the Deacon reaction [5]; (c) provides additional hydrogen which may lower the chlorination of final yield [15]; and (d) provides additional oxygen.

It should be noted that Ross et al. [11] used pentachlorophenol to produce PCDD/PCDF on fly ash surface, which is normally regarded as a heterogeneous precursor reaction. A more recent research indicates that water may influence the emission of hydrogen chloride (HCl) [16], which is the major form of chlorine in full-scale incinerators. The radical •OH was much active in the model research [17], and a recent theoretical research was carried out to investigate the reaction of •OH with PCDD [18], but it needs further experimental verification especially under low temperature (300–400 °C).

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

Element	Ca	P	Si	Fe	Cu	Al	Zn	K	C	Na	Mg	Cl
EX FA1	12.45	0.55	14.27	3.06	0.11	4.82	0.86	4.17	1.25	3.56	1.31	0.99
EX FA2	4.01	0.59	8.54	0.95	0.17	2.67	4.97	NA	1.0	NA	0.41	5.7

^a EX FA1 was the fly ash in this paper, EX FA2 was the fly ash in Wikström et al. [5].

With respect to model research, water vapor was included in a simple kinetic model [19]; however, it was only taken into consideration in the reaction with solid carbon. It was also reported that water modified the rate of reaction [20]; however, this study was mainly derived from the dechlorination of OCDD and OCDF. Generally, comprehensive kinetic models might oversimplify the reactions in which water was present, whereas micro kinetic models could not be applied in moist conditions without the basic understanding of the role of water.

From this literature review, it was found that the effect of water on a catalyst like CuCl_2 was not investigated yet and this effect may be important. The relative importance of the above pathways has not been elucidated. Therefore, a further clarification of the role of water on de novo formation is needed. In this paper, a series of experiments were conducted in a fixed-bed reactor so that a better understanding of the mechanisms involving water could be obtained. Furthermore, the effect of water on the catalyst and the relative importance of potential reaction pathways is discussed.

2. Materials and methods

The fly ash was collected from a mechanical stoker MSW incinerator and was Soxhlet extracted for 24 h to remove organic compounds from the fly ash. Results of an elementary analysis of the ash through energy dispersive X-ray analysis (EDXA) and IRIS IntrepII XSP (Thermo Finnigan Flash EA1112) are shown in Table 1.

The experiments were conducted in a tubular furnace (the length of heating zone was 800 mm), while the distance between the reacting materials and the entrance of the tube was 600 mm (Fig. 1). The length and inner diameter of the quartz tube was 1150 and 24 mm, respectively. Nitrogen (99.999%) and oxygen are induced into a temperature-controlled water-bath so

that a typical moisture percent in the gas flow could be generated, mixed with chlorine gas and introduced into the quartz tube. Several pre-experiments were conducted to ensure the reproducibility of the moisture content. A proportional integral derivation (PID) temperature controller was employed to adjust the reacting zone temperature. XAD-2 resins and toluene in ice bath absorbed dioxins from the flue gas. The reactor system was rinsed with toluene and acetone to clean the inner surface of tube and pipeline, and the tube was heated at 350 °C with nitrogen for over 10 min between the individual runs.

All experimental reaction runs were conducted at the temperature of 350 °C for 30 min. There were a lot of research on the optimum temperature of de novo formation due to the difference of fly ash, reaction time or experiment apparatus [1]; however, the general view for the temperature window is 300–400 °C. Our previous experiments indicated that 350 °C was the best temperature for the fly ash to produce PCDD/PCDF. The flow gas contains nitrogen 170 ml/min; oxygen 25 ml/min; chlorine (900 ppm in nitrogen) 25 ml/min; and different content of water. The volume percentage for each gas in dry flow gas is nitrogen 88%; oxygen 11%; chlorine 102 ppm. The chlorine gas is regarded as a much stronger oxidant and chlorinating agent than HCl to form PCDD/PCDF [3]. The reactants were shown in Table 2. In each experiment, 2 g fly ash was used. In the M series experiments, 0.25 g $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was added as catalyst.

Sample pretreatment was performed according to USEPA method 8280B. All analyses were conducted using a high-resolution gas chromatograph (HRGC)/low-resolution mass spectrometer (LRMS) (Finnigan Voyager Thermal Trace 2000). Chromatographic separation was carried out on a 60 m DB-5 quartz capillary column. The temperature program for GC oven was initial temperature 100 °C, held for 2 min; 100–200 °C at 25 °C/min; 200–280 °C held for 20 min. Carrier gas, helium (99.999%), 1.2 ml/min. Manual splitless sample injection was the sampling option, and the temperature of injector is 250 °C. Each sample volume is 1 μl . Mass spectrum condition: electron impact ionization 70 eV; electron multiplier voltage 420 V; ion source temperature 220 °C; interface temperature 250 °C; selected ion monitoring mode (SIM). All isotope standards were purchased from Wellington laboratories, Canada.

3. Results and discussion

Isotope standards including sample, internal and recovery standards were added in all experiment samples. The recovery ratio of isotope standards varied from 50 to 120%, which showed acceptable reliability of the series of experiments according to USEPA Method 8280B. The formation of PCDD and PCDF is

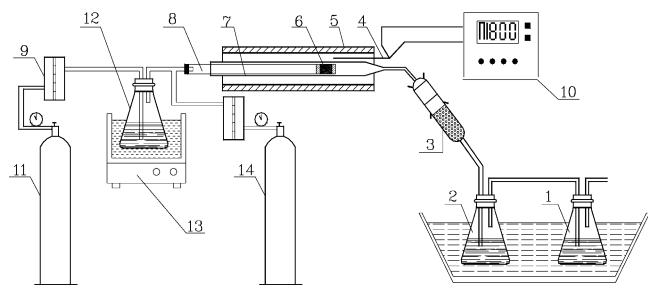


Fig. 1. Schematic drawing of experimental system (not to scale). 1, 2, toluene; 3, XAD-2 resin; 4, thermocouple; 5, oven; 6, ceramic-boat; 7, quartz tube; 8, handspike; 9, gas container; 10, control panel; 11, nitrogen or oxygen gas; 12, bubbler; 13, electrical water-bath; and 14, chlorine gas.

Table 2
PCDD/PCDF yield with different water content via EX FA or catalyzed EX FA

No.	Water (vol%)	Fly ash	Σ PCDD (ng/g)	Σ PCDF (ng/g)	Chlorine degree	Catalysis indicator (F_c)
H1	0	EX FA	20.08	0.38	7.93	N
H2	6	EX FA	42.49	2.44	7.78	N
H3	12	EX FA	47.42	0.53	7.93	N
H4	18	EX FA	55.54	2.56	7.62	N
M1	0	EX FA + $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	121.82	56.73	6.65	8.73
M2	6	EX FA + $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	118.71	69.85	6.52	4.2
M3	12	EX FA + $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	124.04	57.00	6.65	3.77
M4	18	EX FA + $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	226.92	90.62	6.81	5.47

For H1–H4, EX FA: 2 g. For M1–M4, EX FA: 2g; $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 0.25 g. The volume distribution of dry gas flow is nitrogen 88%; oxygen 11%; chlorine 102 ppm. The reaction temperature in all runs is 350 °C.

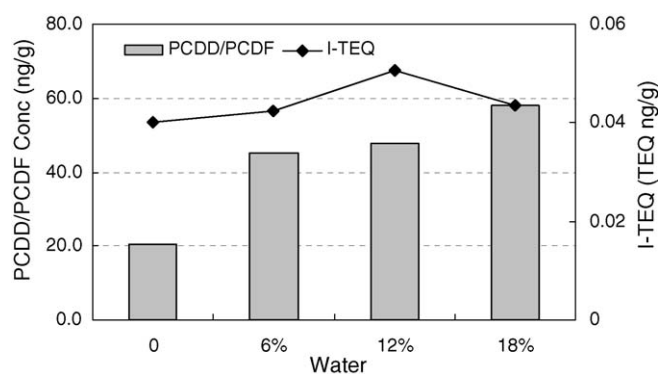


Fig. 2. Total PCDD/PCDF yield and I-TEQ with different moisture when no catalyst was added.

shown in Table 2. Neither TCDD nor OCDF was detected in all the runs.

3.1. Effect of water on non-catalyzed formation

When no catalyst is added to the reactants, the introduction of water markedly enhances the yield of PCDD/PCDF (Fig. 2). In fact, at an addition level of 18%, such promotion mainly results from an increase of the HpCDD yield, along with a slight decrease of OCDD compared to that at the moisture content of 12% (Fig. 3). In all runs without a catalyst OCDD almost accounted for the total yield, which is to be explained by the addition of a strong chlorinating agent, i.e. chlorine gas. The

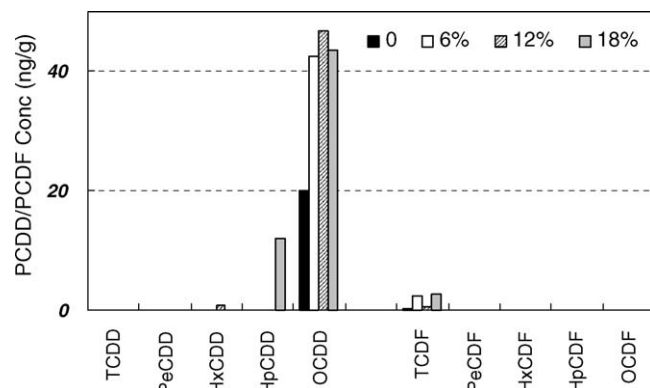


Fig. 3. PCDD/PCDF homologue with different moisture when no catalyst was added.

repeat experiments with new quartz tube and fresh fly ash presented the same homologue pattern and the Soxhlet extraction of fly ash before use guaranteed the exclusion of organic compounds. It should be noted that the PCDD/PCDF production without using a catalyst was much lower and that the formation of PCDD was higher than PCDF, even in the presence of catalyst. Assuming that the compounds formed at first were PCDD, regardless of the level of chlorination, the strong oxidizing power of elementary chlorine in the reacting gas phase then converted these compounds to the final product, OCDD. This explains why OCDD accounts for most of the total production.

On the other hand, the addition of water did not change much to the homologue pattern since the major product was OCDD only. However, when addition of water reached 18%, the major contribution of the total yield derived from HpCDD, whereas OCDD slightly decreased. Considering the Deacon reaction, it was possible that 6 and 12% of water was not enough to change the equilibrium of the reaction, or that the change of the reaction equilibrium did not reach the extent to influence the reactivity of chlorine in the gas phase and consequently did not decrease the chlorination of PCDD. When the content of water reached a significant level (18%), the active elementary chlorine might be consumed by Deacon reaction, which reduced the chlorination capability. Thus, it can be inferred that the addition of water only influences the chlorination pattern by changing reaction equilibrium (pathway b) when the content of water reached a critical point to consume chlorine required for the higher chlorination.

3.2. Effect of water on catalyst

A catalysis indicator (F_c) is defined as following to discuss the effect of water on catalysis of formation:

$$F_c = \frac{V_c}{V_n}$$

where V_c and V_n are the average reaction rate of catalytic reaction and the corresponding non-catalyzed reaction, respectively. The catalysis indicator (F_c) was calculated at different levels of water addition in Table 2. According to its definition, F_c refers to the relative effect of certain parameters on the catalyst of a reaction.

The addition of water dramatically decreased the catalysis indicator. When no water is added to the flowing gas, the intensive effect of catalysis could be illustrated by the highest

catalysis indicator of 8.73. Meanwhile, the indicator reached its minimum at a moisture content of 12%, after which it increased to 5.47 with the further rise of moisture in the gas phase. Considering the catalysis indicator, the addition of water suppressed the effect of CuCl_2 as a catalyst of de novo formation of PCDD and PCDF. In previous research, CuCl_2 was identified as active catalyst of Deacon reaction [21], and was regarded to facilitate the chlorination [22]. Therefore, the reaction of water with active catalyst may result in a suppressing effect on the catalyst. However, this suppressing effect was limited as shown in the rise of indicator from 12 to 18%. Bearing in mind that water itself also stimulated the total yield of PCDD and PCDF, it was reasonable that the higher content of water (18%) had a larger indicator compared to relatively less water (6 and 12%). Thus, it can be concluded that the water may suppress the copper-based catalyst of de novo formation but owns its limitation.

3.3. Effect of water on catalyzed formation

When CuCl_2 was employed as a catalyst, the total PCDD/PCDF yield did not increase dramatically until the water reached 18%. The I-TEQ value even slightly decreased when the content of moisture was 6 and 12%, compared to the no water run (Fig. 4). With respect to chlorination degree from 6.65 to 6.81, water addition slightly stimulates a transition from lower chlorinated homologues to higher chlorinated ones, which is not consistent with the result of Wikström et al. [5]. This may result from a difference of reactant materials and experimental apparatus. A comparison of fly ash elements is shown in Table 1. The lack of Cl in EX FA1 was compensated by the addition of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, through which the final percentage of Cl in the reactant reached 4.62%. Moreover, in our experiments fly ash was fixed in the tube allowing enough time to be activated.

Neither did the relatively low addition of water (6 and 12%) produce dramatic influence on the homologue pattern, whereas 18% water promoted the formation of HpCDD, OCDD and HxCDF (Fig. 5). However, other homologues such as HxCDD, TCDF, PeCDF generally appeared stable regardless of the variation of moisture content. Concerning the effect of activating (pathway a), it is reasonable assuming that when active sites are increased, the favorable homologues are promoted more than the others, which is similar to the precursor formation catalyzed by

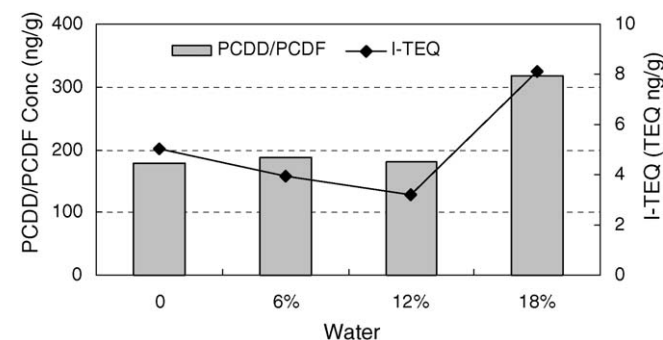


Fig. 4. Total PCDD/PCDF yield and I-TEQ with different moisture when $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was added.

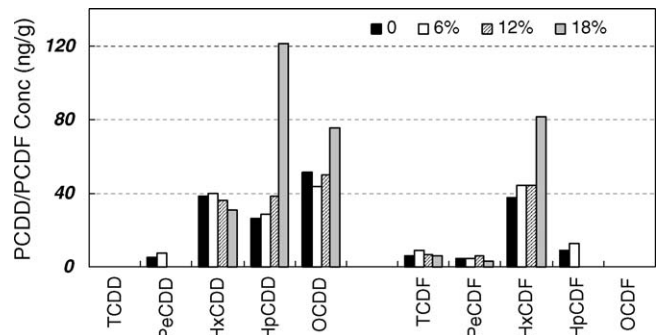


Fig. 5. PCDD/PCDF homologue with different moisture when $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was added.

fly ash at low temperature [10]. The selectivity of catalyst may account for this trend. In other word, the predominant homologues produced in a dry gas will also account for the major products in a moist gas phase, no matter whether this dominance refers to high-chlorinated homologues or low-chlorinated ones. The results of Sakurai et al. [10] indicate that the addition of water promotes TCDD most, inferring that certain homologues were favored in certain active sites. Concerning the promotion effect at 18% water and combining the above discussion, it can be concluded that the pathway of activating fly ash dominates the effect of water on the de novo formation of PCDD/PCDF.

Due to the property of MSW fuel, water cannot be thoroughly removed from the fuel in full-scale incinerators. Especially in China, high content of water is one of the characteristics of MSW [23]. While the field research indicated a weak correlation between water and PCDD/PCDF formation [24], it may produce the trend of lower chlorination, which could increase the total TEQ value. For one thing, the low content of water can facilitate the combustion in chamber, which benefits the emission control including dioxins. For another thing, less water in flue gas can be effective in re-producing PCDD/PCDFs through de novo formation. We will continue our experiments in full-scale incinerators to further our sight on the effect of water and develop corresponding PCDD/PCDF control technology.

4. Conclusion

Different pathways by which water affects de novo formation of PCDD/PCDF are examined through a series of experiments on a fixed-bed reactor. During the reaction, water may activate the fly ash, providing more reactive sites for the formation of favored homologues, regardless of chlorination degree. Thus, the formation of PCDD/PCDF can be promoted with the addition of water. The active sites vary in different fly ash, resulting in different PCDD/PCDF patterns. This confirms the view that the characteristics of fly ash is key to PCDD/PCDF formation. Meanwhile water changes equilibrium conditions of Deacon reaction and influences the final yield but this influence is minor compared to the effect of activating. When the content of water reached 18%, the chlorine can be dramatically consumed so that the pattern of PCDD/PCDF was changed to lower chlorination homologues. The catalysis indicator reached the lowest when water content was 12%, and when water content increased to 18% the indicator

still maintained less than the value of no water run. This means water suppresses copper-based catalyst such as CuCl_2 , but the inhibition is limited due to the promotion effect of water. It is possible that water is involved in the reaction with CuCl_2 , preventing it from catalyzing the Deacon reaction or directly chlorinating precursors of PCDD/PCDF. The overall effect of water on the formation of PCDD/PCDF is promotion rather than inhibition.

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