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Pyrolysis of MWI fly ash – Effect on dioxin-like congeners

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HIGHLIGHTS

- Shows the effects of temperature, time and addition of lime.
- Temperature is important, but time is surprisingly little.
- Dechlorination makes lower TEQ removal compared with mass removal.
- Unexpectedly, addition of lime results in lower PCDD/F removal efficiency.

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ABSTRACT

Removal and destruction of dioxin-like congeners, including polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs) and biphenyls (PCBs), from fly ash were investigated at varying pyrolysis temperatures and reaction times and using calcium-based additives. Destruction efficiencies based on TEQ and mass both increase with rising treatment temperature. However, additional low chlorinated PCDD/Fs were formed significantly by dechlorination of high chlorinated PCDD/Fs, at pyrolysis temperatures of 250 and 300 °C. Surprisingly, lower destruction efficiencies were realized in the presence of Ca-based additive, compared with those without additive, and TEQ values of fly ash into which CaO was introduced increased, compared with the raw ash, due to significant formation of low chlorinated PCDD/Fs (4–5 Cl). However, complex interactions among unburned carbon, sulfur and metals in the fly ash collected in this study make it difficult to pinpoint the exact causes. The results obtained in this study indicate that degradation and formation of dioxin-like congeners take place simultaneously in pyrolysis process, such as formation of low chlorinated PCDD/Fs via dechlorination of highly chlorinated PCDD/Fs.

1. Introduction

Dioxin-like congeners include polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs) and biphenyls (PCBs); these can be formed in thermal processes in each environment containing carbon, chlorine and catalyst (Buekens et al., 2001; Suzuki et al., 2004). In Taiwan, activated carbon injection (ACI) followed by baghouse filtration (ACI+BF system) has been adopted in 23 large-scale municipal waste incinerators (MSWIs) for controlling the emission of dioxin-like congeners. In 2011 about 3000 tons of activated carbon were consumed by these MSWIs for PCDD/F removal. Although ACI+BF technology can effectively reduce PCDD/F emissions and meet the stringent emission standard (0.1 ng I-TEQ/Nm^3) for large-scale MSWIs in Taiwan, previous study indicates that it may actually increase the total PCDD/F discharge (i.e., including that in fly ash and flue gas) from MSWIs (Chi et al., 2005). As a result, since 2006 Taiwan EPA has started to regulate the PCDD/F content in fly ash with the allowable limit of 1.0 ng I-TEQ g^{-1}. In 2011, 6505 thousand tons of wastes including 4235 thousand tons of municipal waste and 2270 thousand tons of nonhazardous industrial wastes were incinerated in 24 large-scale MSWIs in Taiwan. As high as 1 080 000 tons and 280 000 tons of bottom ash and fly ash were also generated, respectively, in 2011. The volume of waste is effectively reduced with incineration, but toxic compounds (such as PCDD/Fs and PCBs) and heavy metals (such as lead, mercury and cadmium) are concentrated in residues. Therefore, the development of an effective technology for proper treatment and disposal of PCDD/F-containing fly ash is urgently needed.

Although some innovative technologies including biodegradation and acid extraction have been investigated for the treatment of fly ash, the availability of these techniques are limited and some bottlenecks need to be overcome (Ecke et al., 2000; Nam et al., 2005). Nowadays, thermal processes including incineration, pyrolysis, and gasification/melting are still commonly adopted for the treatment of hazardous wastes. Destruction of organic pollutants via combustion is an intuitive way. However, previous study indicates that formation and distruction of PCDD/Fs in fly ash coexist

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with 10% O_2 content and destruction rate may be higher than formation rate as temperature is increased to 400–450 °C (Weber et al., 1999). Therefore, high temperature (>450 °C) is needed for PCDD/F destruction in the O_2-containing condition, but PCDD/F may be formed in tail gas. Compared with oxygen-rich combustion and taking into account the high operating cost of the gasification/melting process, a pyrolysis system can be operated with lower cost and lower potential of PCDD/F formation. Addink and Olie (1995) indicates that PCDD/Fs in fly ash can be degraded in a pyrolysis system operating at the temperature of 300–400 °C. Therefore, energy consumption of pyrolysis is also lower, due to the lower operating temperatures needed. Interestingly, studies indicate that dioxin-like congeners including PCDD/Fs and PCBs may be formed in pyrolysis system (Weber and Sakurai, 2001; Shibata et al., 2003; Joung et al., 2006). In contrast, Altarawneh et al. (2009) indicates that PCDD/F formation is not observed under non-oxidative conditions. Therefore, pyrolysis with oxygen-free condition is evaluated as a potential process for degrading dioxin-like congeners in fly ash collected from the BF hopper in a large-scale MSWI in Taiwan. Moreover, the effect of calcium-based additives on dioxin-like congeners removal is also evaluated in this study.

2. Materials and methods

2.1. Laboratory-scale module of pyrolysis and operating parameters

A laboratory-scale (lab-scale) pyrolysis module was designed for this study. 1 g of raw ash collected from MSWI with the size between 75 and 125 μm was placed in a quartz tubular reactor with 15 mm of inner diameter and 300 mm of tube length. The bed height of raw ash in quartz tubular reactor was 11 mm. Oxygen is an important element for PCDD/F formation. PCDD/Fs may be significantly formed if oxygen is present, even with only 0.5% oxygen content in thermal process (Weber and Sakurai, 2001). On the other hand, previous study indicates that water vapor may cause PCDD/F formation via *de novo* synthesis (Shao et al., 2010). Therefore, applying N_2 gas stream with high temperature can help to expel water vapor in fly ash and reduce its effects. Carrier gas is nitrogen (N_2) and the gas flow rate is controlled at 0.1 slpm with a mass flow controller. For fully understanding the characteristics of PCDD/F degradation with pyrolysis, XAD-2 resin was connected after a lab-scale module for adsorbing gas-phase dioxin-like congeners formed or vaporized from raw ash during the pyrolysis at high temperature. Before starting the experiment of each batch, the reactor was purged with N_2 for 5 min in room temperature to completely eliminate any residual O_2 from the lab-scale system. The effects of pyrolysis temperature and reaction time for PCDD/F degradation were evaluated in this study. The operating parameters of pyrolysis system include three temperatures (250, 300 and 350 °C) and three reaction times (1, 2 and 3 h). On the other hand, calcium-based (Ca-based) compounds including $Ca(OH)_2$ and CaO are commonly applied to absorb acidic gases (SO_2 and HCl) from flue gas of MSWI. For understanding the effects of Ca-based compounds on PCDD/F removal, $Ca(OH)_2$ and CaO were introduced into raw fly ash collected from BF of MSWI in this study, respectively. $Ca(OH)_2$ and CaO were applied as additives and introduced into raw fly ash with 5% or 10% of additive content.

2.2. PCDD/F analysis

The ash samples after pyrolysis and gas-phase PCDD/Fs adsorbed by XAD-2 resin were Soxhlet extracted immediately. Before extraction, the samples were spiked with known amounts of labeled standard solution with Method 1613 for PCDD/F analysis and Method 1668a for dioxin-like PCB analysis, respectively, following isotope quantification standards. After extraction and clean-up procedures, seventeen 2,3,7,8-substituted PCDD/Fs and 12 dioxin-like PCBs were analyzed with high resolution gas chromatography (HRGC) (Thermo Trace GC)/high resolution mass spectrometry (HRMS) (Thermo DFS) using a fused silica capillary column DB-5 MS (60 m × 0.25 mm × 0.25 μm, J&W). The mean recoveries of the standards for all $^{13}C_{12}$-2,3,7,8-substituted PCDD/Fs and $^{13}C_{12}$-PCBs were 66–109% and 51–98%, respectively. The recoveries were all within the acceptable 40–130% and 25–150% range set by the U.S. EPA in Method 1613 and 1668a, respectively.

In this study, destruction and removal efficiencies of PCDD/Fs were calculated including gaseous PCDD/Fs vaporized or desorbed from fly ash at high temperature and adsorbed by XAD-2 resin and solid-phase PCDD/Fs remained on fly ash. The formula for calculating the destruction efficiency is shown as below:

$$\text{Destruction efficiencies}\ (\%) = \left\{1 - \frac{[(\text{Amount of dioxin-like congeners adsorbed by XAD-2 resin}) + (\text{Amount of dioxin like congeners in fly ash after pyrolysis})]}{(\text{Amount of dioxin-like congeners in raw fly ash})}\right\} \times 100\%$$

3. Results and discussion

3.1. Property of fly ash tested this study

The fly ash tested in this study was collected from the hopper of a BF in a large-scale MSWI in Taiwan. The capacity of the MSWI is 600 ton/d with two stoker furnaces. In 2011, about 3×10^9 kWh of energy was generated in this MSWI and 80.2% of total energy generated was sold to Taiwan Power Company, however, 9600 tons of fly ash and 29 000 tons of residues were also generated. Average TEQ concentration of PCDD/Fs in the BF ash of this MSWI in 2011 was 3.66 ng I-TEQ g^{-1}, reported by Taiwan EPA. Therefore, the fly ash generated from BF of this MSWI is categorized as hazardous waste. The particle size ranges mainly from 45 to 212 μm (70–325 mesh). Fly ash with particle size between 75 and 125 μm was selected as matrix for pyrolysis in this study. Table 1 shows the chemical components of raw matrix. Significant chloride was found due to the absorption of $HCl_{(g)}$ with injected lime within semi-dry absorber. The WHO toxicity equivalent factor (WHO-TEF) published in 2005 is adopted in this study for calculating the toxicity. Removal and Destruction characteristics of 17 toxic PCDD/Fs and 12 dioxin-like PCBs (dl-PCBs) were investigated on the BF ash. Total TEQ concentration of raw BF ash was measured

Table 1
The chemical composition of raw fly ash tested.

Non-metal element		Metal element		Others	
Item	Content (ppm)	Item	Content (ppm)	Item	Content (ppm)
C	29 000	As	0.564	Chloride	280 000
N	510	Ba	2580	Sulfate	28 200
H	29 500	Cd	200		
S	18 100	Cr	92.5		
		Cu	904		
		Hg	8.22		
		Pb	4460		