Effect of water washing on POPs concentration during pyrolysis of MSWI fly ash

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Introduction:

Effective management of municipal solid waste (MSW) has become an urgent issue that has attracted increasing public attention. In Taiwan, MSW treated by incineration increased from 71.5% in 2003 to 97.7% in 2017. For each ton of MSW that is incinerated in a mass burn unit, 15–40 kg of fly ash (FA) is produced, requiring further treatment and landfill[1]. Fly ash generated from MSW incineration contains three major pollutants: heavy metals, chloride salts and toxic organic components which pose serious threats to the environment and human health. For better treating and disposal of these residues, various technologies have been investigated and adopted to reduce the hazardous characteristics of FA, including thermal stabilization (e.g. sintering and vitrification), accelerated carbonation, and chemical stabilization using additives. However, these methods only stabilize the pollutants to prevent the leaching of dissolved chloride salts or heavy metals but cannot effectively destroy toxic organic pollutants. Therefore, reusability of FA is still limited due to these concerns and most of treated FA commonly ends up in sanitary landfill. Among the persistent organic pollutants (POPs) present in FA, polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) have attracted increasing concern due to their adverse effects on environment and human health. Pyrolysis with oxygen-free condition is evaluated as a potential process for degrading PCDD/Fs congeners in fly ash. In addition, washing processes are generally applied to remove soluble chloride in fly ash for reuse of fly ash as construction materials. Yang et. al. (2017)[2] investigated the effect of a water-washing process on the removal of harmful chlorides and found that over 70 wt.% of chlorides in FA could be removed by water washing using liquid/solid (L/S) ratio of 3 mL:1 g in 5 minute. In this study, we will investigate the effect of water washing on the PCDD/Fs removal efficiency from FA via pyrolysis process.

Materials and methods:

The raw FA samples were collected from baghouse of an MSWI located in central Taiwan. FA was washed with DI water (ratio of 1 g: 5 mL) at room temperature by magnetic stirring (100 rpm) for 5 min. Then, FA was filtrated by silica fiber filter and dried at 105^{o}C for 24 hour prior to pyrolysis. Chloride contents of raw FA and washed FA were determined by titration with NH_4SCN (Volhard's method). A laboratory-scale pyrolysis module was designed and applied for this study as described in Figure 1. Approximately 5g FA (including "raw fly ash", "washed fly ash" and "washed + catalyst fly ash") was placed in a quartz tubular reactor with 15 mm of inner diameter and 300 mm of tube length. Carrier gas was nitrogen (N_2) and the gas flow rate was controlled at 1.2 slpm by a mass flow controller and was preheated at 200^{o}C before entering the pyrolysis chamber. 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 system. The effects of pyrolysis temperature for PCDD/F degradation were evaluated in this study. To better understand the characteristics of PCDD/F degradation with pyrolysis, XAD-2 resin was connected after a lab-scale module for adsorbing gas-phase pollutant formed or released from fly ash during the pyrolysis. Then, seventeen 2,3,7,8-substituted PCDD/Fs congeners in fly ash and XAD-2 samples were extracted, cleaned up and analyzed individually with GC/MS.

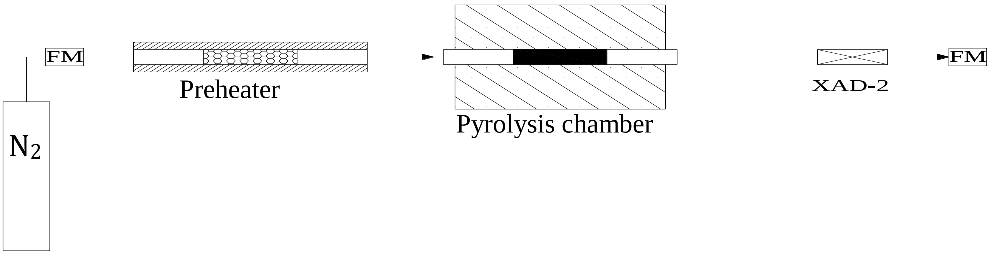

Figure 1. Schematics of the pyrolysis system

Results and discussion:

After being washed with water, chloride content in MWSIs fly ash was reduced from 23.4% to 7.1%, which equals to a 69.5% reduction (Table 1). However, PCDD/Fs concentration in fly ash was increased from 0.96 to 1.89 ng I-TEQ/g after washing which is higher than the level regulated by Taiwan EPA (1.0 ng I-TEQ/g). Possible reason for the increase level of PCDD/Fs in fly ash could be the reduction of fly ash mass after washing. Initially, 20g of fly ash was weighed prior to water washing experiment in order to determine how much fly ash would be washed out and the results indicate that around 40 ± 1% of total fly ash mass was washed out. Therefore, the enhancement of PCDD/Fs level in fly ash after washing with water is attributed to the fact that soluble contents including CaO, NaO, CaCl and NaCl were washed out after experiment.

Table 1. Chloride contents and PCDD/Fs concentrations in raw and washed fly ashes

Samples	Chloride content (%)	PCDD/Fs concentration (ng/g)	PCDD/Fs concentration (ng I-TEQ/g)
Raw fly ash	23.4	32.7	0.96
Washed fly ash	7.1	65.7	1.89

The effect of water washing on PCDD/Fs concentration in fly ash was evaluated by pyrolyzing raw and washed fly ashes continuously from 200^{o}C to 350^{o}C in 1 hour (15 min at 200^{o}C, 15 min at 250^{o}C and 30 min at 350^{o}C) and the results are reported in Table 2. Water discharged from washing process was also analyzed and no PCDD/Fs was detected. The PCDD/Fs removal efficiencies of raw and washed fly ash were 85.2% and 89.1%, respectively. However, PCDD/Fs are found in gas stream of the system during the pyrolysis of raw fly ash. With sampling volume of 0.072 Nm^3, PCDD/Fs concentration in gas stream during the pyrolysis of raw fly ash is 70.2 ng I-TEQ/Nm^3, which is much higher than the emission standard of PCDD/Fs in flue gas regulated by Taiwan EPA (0.1 ng I-TEQ/Nm^3). The PCDD/Fs in gas stream of a pyrolysis system is also reported by Deng et. al., (2019)[3] possibly due to desorption from fly ash matrix or new formation from precursors and de-novo synthesis. On the other hand, PCDD/Fs concentrations in gas stream during pyrolysis of washed fly ash are lower than the detection limit. Weber et. al., (1999)[4] indicated that chloride content in fly ash strongly affects the formation of PCDD/Fs. Therefore, PCDD/Fs are unlikely to form in the gas stream during pyrolysis of washed fly ash with much lower chloride content.

To understand the origin of PCDD/Fs in gas stream during pyrolysis process, another experiment was conducted for washed fly ash at 3 different temperatures (200°C, 250°C and 300°C). Prior to the experiment, 10 µL of surrogate standard (EPA-M23, Wellington) was injected into the fly ash matrix as tracer. The results presented in Figure 2 indicate that PCDD/Fs in gas stream mostly were formed when the pyrolysis system was operated at 250°C and 300°C. Interestingly, the amount of C_{13} tracer in surrogate solution can only be detected in fly ash matrix and no tracers are detected in the gas stream as reported in Table 3. The results indicate that PCDD/Fs detected in gas stream are mostly from de-novo synthesis or precursor's pathway, and PCDD/Fs are unlikely to desorb from fly ash matrix into gas stream under pyrolysis condition.

Finally, to further increase the removal efficiency of pyrolysis process, 2 g of Pd/Al_2O_3 was mixed with 5 g of washed fly ash. The results are reported in Table 2 and indicate that PCDD/Fs removal efficiencies are 96.7% and 89.1% for the pyrolysis with and without Pd/Al_2O_3, respectively. Chang et. al. (2018)[5] indicated that Pd is one of the most active catalysts for hydrodechlorination process, so the addition of Pd into fly ash matrix may enhance the destruction effectively of PCDD/Fs via hydrodechlorination.

Table 2. PCDD/Fs level in fly ash and gas stream before and after pyrolysis experiment from 200 to 350°C for 1 hour

Congeners	Before pyrolysis (ng/g)		After pyrolysis				After pyrolysis + Pd/Al_2O_3	
			Fly ash (ng/g)		Gas stream (ng/sample)		Fly ash (ng/g)	Gas stream (ng/sample)
	Raw FA	Washed FA	Raw FA	Washed FA	Raw FA	Washed FA	Washed FA	Washed FA
2378DD	0.07	0.13	0.13	0.15	0.85	N.D.	0.25	N.D.
12378DD	0.16	0.25	0.26	0.38	0.97	N.D.	0.29	N.D.
123478DD	0.11	0.16	0.19	0.12	0.92	N.D.	0.07	N.D.
123678DD	0.45	0.83	0.33	0.29	1.09	N.D.	0.15	N.D.
123789DD	0.30	0.45	0.39	0.33	2.09	N.D.	0.21	N.D.
1234678DD	3.94	7.00	1.21	1.75	0.86	N.D.	0.34	N.D.
OCDD	15.0	28.7	0.00	1.77	0.90	N.D.	0.29	N.D.
2378DF	0.41	0.92	0.18	0.24	0.85	N.D.	0.12	N.D.
12378DF	0.49	1.18	0.24	0.28	0.91	N.D.	0.10	N.D.
23478DF	0.57	0.97	0.22	0.21	0.00	N.D.	0.05	N.D.
123478DF	0.67	1.54	0.19	0.21	0.06	N.D.	0.04	N.D.
123678DF	0.75	1.77	0.18	0.26	0.64	N.D.	0.06	N.D.
234678DF	1.19	2.69	0.29	0.23	2.12	N.D.	0.04	N.D.
123789DF	0.23	0.49	0.05	0.04	2.77	N.D.	0.01	N.D.
1234678DF	3.42	7.72	0.52	0.46	3.75	N.D.	0.08	N.D.
1234789DF	0.54	1.28	0.10	0.07	89.1	N.D.	0.01	N.D.
OCDF	4.46	9.62	0.36	0.37	1687	N.D.	0.04	N.D.
Total mass concentration	32.7	65.7	4.83	7.16	1795	N.D.	2.15	N.D.
Total I-TEQ concentration[a]	0.96	1.89	0.57	0.65	5.06	N.D.	0.5	N.D.

[a] *The unit of fly ash samples is ng I-TEQ/g while that of gas stream samples is ng I-TEQ/sample.*

To compare the PCDD/Fs levels in fly ash before pyrolysis with PCDD/Fs levels in fly ash and XAD-2 after pyrolysis, all values are normized to 1 ng I-TEQ to evaluate how much PCDD/Fs is finally released per 1 ng I-

TEQ input. As a result, pyrolysis of raw fly ash, washed fly ash and washed + Pd/Al_2O_3 release 9.09 ng I-TEQ, 0.34 ng I-TEQ and 0.26 ng I-TEQ, respectively.

Table 3. Recovery of surrogate standard (tracers) solution in fly ash and gas samples

Recovery (%)	200°C		250°C		300°C	
	FA	Gas	FA	Gas	FA	Gas
$^{37}Cl_4$-2378DD	54.7	N.D.	62.5	N.D.	55.8	N.D.
^{13}C-23478DF	58.6	N.D.	70.2	N.D.	61.6	N.D.
^{13}C-123478DF	82.7	N.D.	82.2	N.D.	65.9	N.D.
^{13}C-123478DD	84.0	N.D.	70.0	N.D.	49.6	N.D.
^{13}C-1234789DF	66.5	N.D.	63.9	N.D.	32.2	N.D.

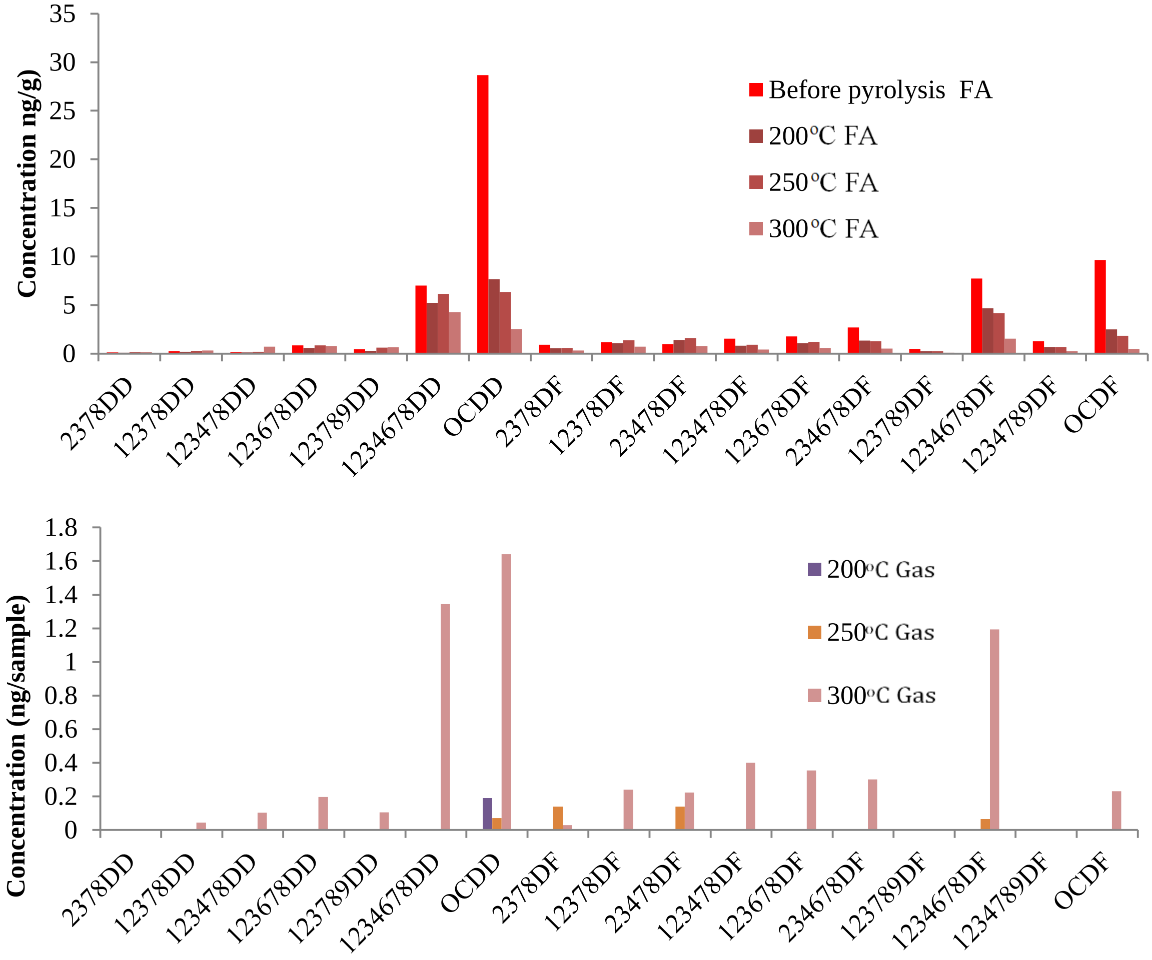

Figure 2. PCDD/Fs levels in washed fly ash (top) and gas stream (bottom) pyrolyzed at different temperatures

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