Removal of Dioxins from Sediment by Oxygen-Free Pyrolysis

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Introduction

There is a growing volume of data reporting contaminated aquatic sediment with dioxins. Currently, there are several methods to remediation sediment, such as mechanical, physical, biological, chemical and thermal processes. Thermal technologies, such as incineration, pyrolysis, those that use heat as a way to volatilize or destroy the organic contaminants, are a preferred method of waste management [1].

Although present in the oxygen atmosphere, the PCDD/Fs content decreased as the heating temperature increased [2], however, de novo synthesis of PCDD/Fs was also found in the oxygen atmosphere for MSW fly ash by incineration treatment [3,4,5]. Therefore, the development of new and improved environmental technologies for sediment to reduce dioxins emission is urgently required. In recent years, pyrolysis processes are technologies that have developed to industrial scale, and have been discussed as alternatives to the existing waste combustion technology. However, the competitiveness of these technologies has yet to be proven [6]. Despite a great deal of research and investigation into the occurrence and effects of dioxins in incineration and pyrolysis processes of MSW, less information is available regarding dioxins formation and conversion during sediment treatment by pyrolysis processes. In particular, no reference currently exists to study the dioxins removal from sediment by anaerobic thermal decomposition (in an oxygen-free environment pyrolysis). Therefore, it is necessary to investigate the dioxins fates during thermal treatment by oxygen free pyrolysis.

In this paper, we focused on the pyrolysis of sediment containing dioxins in an inert atmosphere. The objective was to attain detailed a description of the dioxins concentration in raw sediment and solid residues after pyrolysis.

Materials and Methods

A special horizontal lab-scale pyrolyzer was designed and successfully applied to conduct oxygen free pyrolysis. The pyrolyzer is shown schematically in Fig 1. Experiments were conducted in a quartz tube flow reactor (i.d.=15cm, length= 50cm). We injected nitrogen gas (1000mlN_2/min) into the quartz tube to maintain the non-oxidative conditions during all the pyrolysis process. The gases generated by the pyrolysis reaction were then introduced to an ice-bath. Subsequently, the gas was dust with a water vessels and an activated carbon column. The temperature was increased gradually at a rate of 10°C /min until a final temperature (800°C) was reached. Retention time was 30min, 60min and 90min, respectively. The sediment was obtained from Tagonoura harbor, Japan.

We determined concentration of dioxins based on the modified standard method of Ministry of the Environment in Japan [7.] All the compounds standards solution was obtained from Wellington Laboratories (Ontario, Canada). Analysis of PCDD/Fs and PCBs were performed using an HRGC/HRMS (HRGC: TRACE GC 2000; HRMS: FINNIGAN MAT 95XL) of ThermoQuest co., USA. Ranges of detection limits (DLs) for PCDD/F and PCB congeners were 0.1pg·g^{-1} and 0.2pg·g^{-1}, respectively.

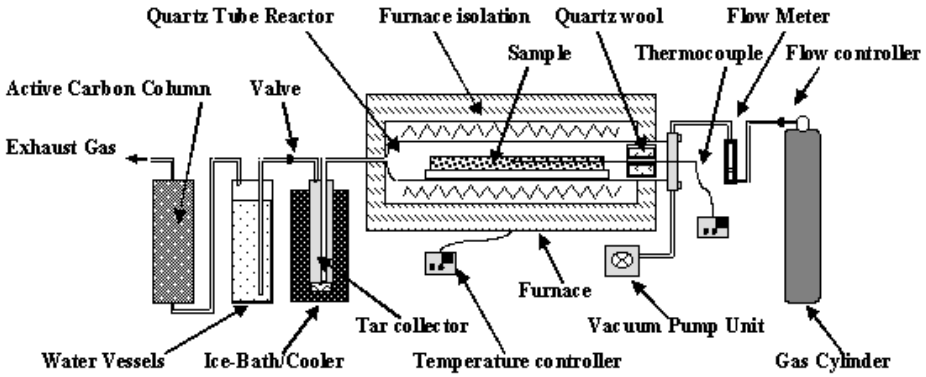

Fig.1. Experimental apparatus

Results and Discussion

The destruction efficiency of oxygen free pyrolysis for the decomposition of PCDD/PCDFs, PCBs was compared in flow experiments over the retention time range 30-90 min at 800°C. Table 1 indicates the toxic equivalent of dioxins in sediment before and after pyrolysis. For the amount of PCDFs, the oxygen free pyrolysis decomposed these molecules in the examined temperature and retention 30-90min with an efficiency of 100%. The concentration of PCDFs in the all solid residues decreased from 4.805 pg-TEQ·g^{-1} to 0 pg-TEQ·g^{-1}. The removal rate of PCDDs also reached 100% in retention times of 30 and 90 min, respectively. More than 99.9990% of PCDDs were decomposed when the retention time was 60 min, and only trace amounts of OCDD (0.0005pg-TEQ·g^{-1}) were detected on the solid products. For the PCBs, the highest destruction efficiency even at retention of 30 min was higher than 99.9994%. Although all PCBs have not been decomposed; the lowest concentrations of PCBs with 0.000085 pg-TEQ·g^{-1} was obtained. Nevertheless, the PCBs concentration increased when the retention

Table 1

Concentrations of PCDD/Fs (pg-TEQ·g-1, dw) and PCBs (pg-TEQ·g-1, dw) in sediment before and after oxygen free pyrolysis from Takonoura harbor, Japan.

Compounds	Raw sediment	Solid residues after pyrolysis at 800°C		
		Retention time (min)		
		30	60	90
PCDFs				
1,2,7,8-TeCDF	0	-	0	0
2,3,7,8-TeCDF	1.1	0	0	0
1,2,3,7,8-PeCDF	0.09	0	0	0
2,3,4,7,8-PeCDF	1.65	0	0	0
1,2,3,4,7,8-HxCDF	0.59	0	0	0
1,2,3,6,7,8-HxCDF	0.39	0	0	0
1,2,3,7,8,9-HxCDF	0	0	0	0
2,3,4,6,7,8-HxCDF	0.5	0	0	0
1,2,3,4,6,7,8-HpCDF	0.41	0	0	0
1,2,3,4,7,8,9-HpCDF	0.061	0	0	0
OCDF	0.014	0	0	0
PCDDs				
1,3,6,8-TeCDD	0	-	0	0
1,3,7,9-TeCDD	0	-	0	0
2,3,7,8-TeCDD	30	0	0	0
1,2,3,7,8-PeCDD	3.1	0	0	0
1,2,3,4,7,8-HxCDD	0.87	0	0	0
1,2,3,6,7,8-HxCDD	3.8	0	0	0
1,2,3,7,8,9-HxCDD	1.9	0	0	0
1,2,3,4,6,7,8-HpCDD	12	0	0	0
OCDD	0.77	0	0.0005	0
PCBs				
3,4,4,5-TeCB(#81)	0.016	0	0	0
3,3,4,4-TeCB(#77)	0.37	0	0.00024	0.0022
3,3,4,4,5-PeCB(#126)	12	0	0	0
3,3,4,4,5,5-HxCB(#169)	0.047	0	0	0
2,3,4,4,5-PeCB(#123)	0.023	0.000085	0	0
2,3,4,4,5-PeCB(#118)	0.63	0	0.00026	0.00421
2,3,3,4,4-PeCB(#105)	0.16	0	0	0.00021
2,3,4,4,5-PeCB(#114)	0.085	0	0	0
2,3,4,4,5,5-HxCB(#167)	0.0056	0	0	0.00012
2,3,3,4,4,5-HxCB(#156)	0.55	0	0	0
2,3,3,4,4,5-HxCB(#157)	0.13	0	0	0
2,3,3,4,4,5,5-HpCB(#189)	0.022	0	0	0
Total PCDFs	4.805	0	0	0
Total PCDDs	52.44	0	0.0005	0
Total PCBs	14.0386	0.000085	0.0005	0.006622
Total Dioxins (PCDFs+PCDDs+PCBs)	71	0.000085	0.001	0.0066
Removal rate of PCDFs / %		100	100	100
Removal rate of PCDDs / %		100	99.9990	100
Removal rate of PCBs / %		99.9994	99.9964	99.9528
Removal rate of total dioxins / %		99.9999	99.9986	99.9907

time was extended from 30 to 90 min with 0.000085 pg-TEQ·g^{-1}, 0.0005 pg-TEQ·g^{-1} and 0.0066 pg-TEQ·g^{-1}, respectively. This result indicated that trace amount PCBs can possible be formed after retention 30 min at 800°C in oxygen free pyrolysis process. It might be due to the PCBs molecules not including oxygen so that the formation of PCBs do not required O_2. For the total dioxins, the decomposition rate of retention 30 min, 60 min and 90 min at were 99.9999%, 99.9986% and 99.9907%, respectively. Almost all the total dioxins detected from the solid residues were PCBs.

The low dioxins concentration in the investigated pyrolysis runs results, in our opinion, mainly for two reasons. One is that it is most likely that the complex organic materialcan be degraded by thermal treatment in an inert atmosphere, causing organic material to change into three phases(liquid, gas and carbon) [8]. High heat processes involve chemical and physical changes resulting in total destruction of the waste. The other may prevented the formation of dioxins under this oxygen free condition. To the mechanisms of formation dioxins, previous studies indicated that oxygen played a crucial role for the two mechanisms of de nove synthesis and precursor reaction of PCDD/Fs in the incineration [5,9].

· From the energy and economy view of point, we believe that retention time of 30 min at 800 °C should be selected to decompose dioxins from sediment by oxygen free pyrolysis. The highest removal efficiency of dioxins reached 99.9999%.

· Oxygen free pyrolysis technology may be undertaken to either prevent formation of PCDD/Fs, or to minimize the release of these compounds into the environment. And the cleaner solid residues are obtained and can be recycled as energy sources in other industrial processes.

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