THE FORMATION OF ORGANIC CHLORINATED COMPOUNDS DURING PVC COMBUSTION AT VARIABLE RESIDENCE TIME OF COMBUSTION AIR FLOW

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Introduction

The organic chlorinated compounds such as polychlorinated dibenzo-*p*-dioxins(PCDDs), polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs) are of environmental concern because of the high toxicity. Chlorine sources are necessary in the combustible to form chlorinated compounds during combustion. Plastics such as polyvinylchloride (PVC) contains chlorine atoms release their chlorine and may be a major source of chlorine during combustion[1].

Extensive studies have been in progress about the formation mechanism and relationship of organic chlorinated compounds like PCDD/Fs and PCBs in the combustion process. However, previous researches have been mostly concentrated on conditions of the post-combustion zone in incineration plants. It could be divided into the field study on the conventional incineration plant related with the formation of PCDD/Fs in the post-combustion zone and the experimental and theoretical studies with laboratory scale experiment about the PCDD/Fs formation mechanism using some materials like flyash[2]. Also most studies have been focused on the temperature window from 200 ℃ through 600 ℃ feasible for the formation of PCDD/Fs[1]. Some researches have been conducted in conditions of high temperature over 800 ℃ at combustion zone outlet using pilot or conventional scale incinerator[3,4].

This paper proposes an approach to research the formation and relationship of organic chlorinated compounds at specific condition close to complete combustion such as high temperature and sufficient residence time during PVC combustion, using simple laboratory scale tubular furnace. For complete combustion, it is required to supply the sufficient combustion air and the "3Ts" are regarded as most important factor. The "3Ts" are high combustion *temperature*(over 800 ℃), sufficient residence *time* of the combustion gas(minimum 2 seconds), and adequate *turbulence* for mixing of the combustion gas with air. In this experiment, it was used downstream tubular furnace for making some turbulence and adjusted to high temperature condition of 900 ℃ that is used at real incineration plant and investigated the effect of air condition by changing air flow rate.

Materials and Methods

The combustion apparatus was consisted of a quartz tube of 40 mm inlet diameter and 900mm length within a 500 mm height tubular furnace (Fig. 1). PVC applied in this experiment was free of additives and used as powders from Aldrich. Temperature was raised up to 900 ℃ at the vessel position and a platinum sample vessel containing the powdered PVC 0.5g was introduced into the furnace. High purity air over 99.999 % was applied downstream at different flow rates (0.5, 2, and 4 l/min). The combustion experiments lasted 15 minutes with a total trapping of incineration products. Thermal decomposition of PVC occurred in tens of seconds after insertion and flue gas was passed through sampling device. The sampling device used in this experiments was consisted of a silica glass microfibre filter followed by XAD-Ⅱ resin and toluene for backup solvent. The concentrations of O_2, CO_2, CO, and NO_2 were measured simultaneously.

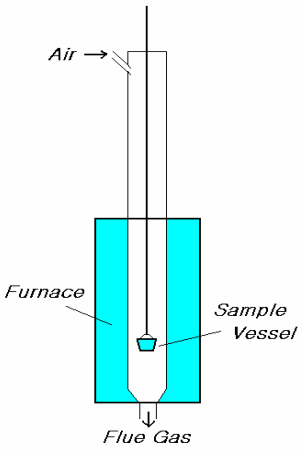


Fig.1. Combustion apparatus

The sample extraction and clean-up procedure were mostly carried out in accordance with Korean Standard Method of Air Pollution. After cooling the furnace to room temperature, filter, adsorbent, and solvent were collected and the filter and adsorbent were soxhlet extracted with toluene for 24 hours. Before sulfuric acid treatment, the sample was replaced into hexane and made up 100 ml For PCDD/Fs and

PCBs analysis, ^{13}C-Labelled compounds of PCBs and PCDD/Fs were added to the sample. The sample clean-up procedure comprised sulfuric acid treatment and a mixed column with differently treated multi-layered silica. Before alumina column, the sample was divided into two parts. One was used for PCDD/Fs analysis, the other was used for PCBs.
The analysis of PCDD/Fs & coplanar PCBs was performed on selected ion monitoring mode with a JEOL JMS-700D high resolution mass spectrometer connected with high resolution gas chromatograph.

Results and Discussion
Detailed measurements of air temperature in the tube revealed that the temperature was maintained about 900 ℃ in 30 cm behind the sample vessel. Therefore, the residence time of 0.5 l/min, 2 l/min, and 4 l/min, after allowance for air expansion, was 11.5 s, 2.8 s, and 1.9 s, respectively.
It is commonly said that the longer residence time of combustion gas, the lower organic pollutants concentration. On the other hand, the combustion air calculated with vinylchloride monomer is demanded approximately 2.33 liter for complete combustion of PVC 0.5 g, theoretically. So, the air might be deficient in case of 0.5 l/min in this experiment and it had been presumed that the formation mechanism of organic chlorinated compounds of 0.5 l/min is different with the others. So, it may be divided into 2 l/min as sufficient air and long residence time condition, 4 l/min as sufficient air and short residence time condition, and 0.5 l/min as deficient air condition. Fig. 2 shows the CO_2 concentration at different flow rates. The combustion of PVC was finished within 2 minutes in case of 2 l/min or 4 l/min, but it was lasted more than 5 minutes at 0.5 l/min. In this paper, the unit of l/min will mark as L for abbreviation.

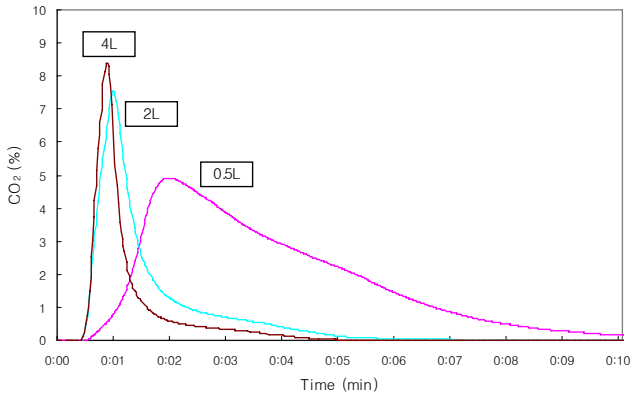
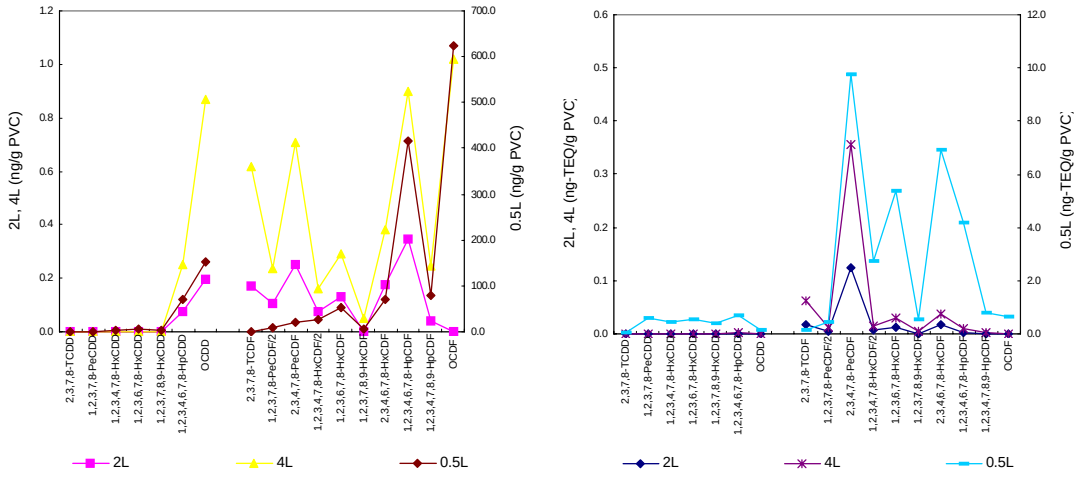


Fig 2. **CO_2 concentration curve of PVC combustion**

PCDD/Fs concentrations
The concentrations of organic chlorinated compounds from PVC combustion were 2 L 〈 4 L 《 0.5 L through overall experiments. The distribution of organic chlorinated compounds from PVC combustion was PCDD/Fs 〉 PCBs in case of 0.5 L, but PCBs 〉 PCDD/Fs at flow rate of 2 L and 4 L. The PCDD/Fs concentration from PVC combustion was 2 L 〈 4 L 《 0.5 L. As the flue gas residence time increased in combustion facility, the concentration of pollutants is generally decreased. But it is thought that the PCDD/Fs were more yielded at the condition of 0.5 L because of air poor condition. Table 1 shows the PCDD/Fs concentration of PVC combustion gas.
While the formation of high chlorinated isomers such as 1,2,3,4,6,7,8-HpCDF, OCDD, OCDF in 17 toxic PCDD/Fs is notable in case of 0.5 L, the portion of low chlorinated isomers in case of 2 L and 4 L is higher (Fig. 3(a)). Regardless of the difference of flow rates, PCDFs were far more than PCDDs, which the ratio of PCDDs was only 12.3~15.5 %. As the TEQ value, 2,3,4,7,8-PeCDF which TEF is 0.5 was the majority of PCDD/Fs in whole experiments, but 1,2,3,6,7,8/2,3,4,6,7,8-HxCDF and 1,2,3,4,6,7,8-HpCDF were also predominant isomers in 0.5 L.

Table 1. PCDD/Fs Concentration

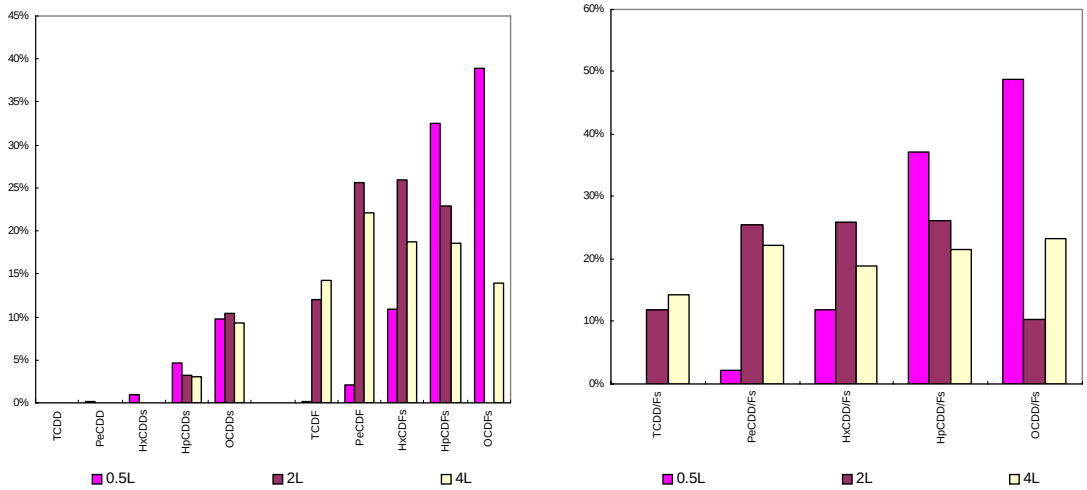
Air flow rate	PCDD/Fs Concentration							
	Total (ng/g PVC)				TEQ (ng-TEQ/g PVC)			
	1	2	3	4	1	2	3	4
0.5 L	1102.356	1007.675	2517.025		27.707	27.892	47.453	
2 L	2.681	0.962	1.800	0.780	0.229	0.123	0.266	0.143
4 L	2.582	4.179	10.425		0.368	0.719	0.512	



(a) Total concentration (b) TEQ concentration

Fig 3. Isomer pattern of PCDD/Fs during PVC Combustion

Fig. 4 shows the relative abundance of PCDD/Fs at different flow rate. As the chlorination degree of PCDD/Fs is increased, the concentration is increased almost linearly in case of 0.5 L. But, the concentrations of PeCDD/F~HpCDD/Fs are almost same in case of 2 L and 4 L.



(a) Congener pattern (b) Chlorination degree

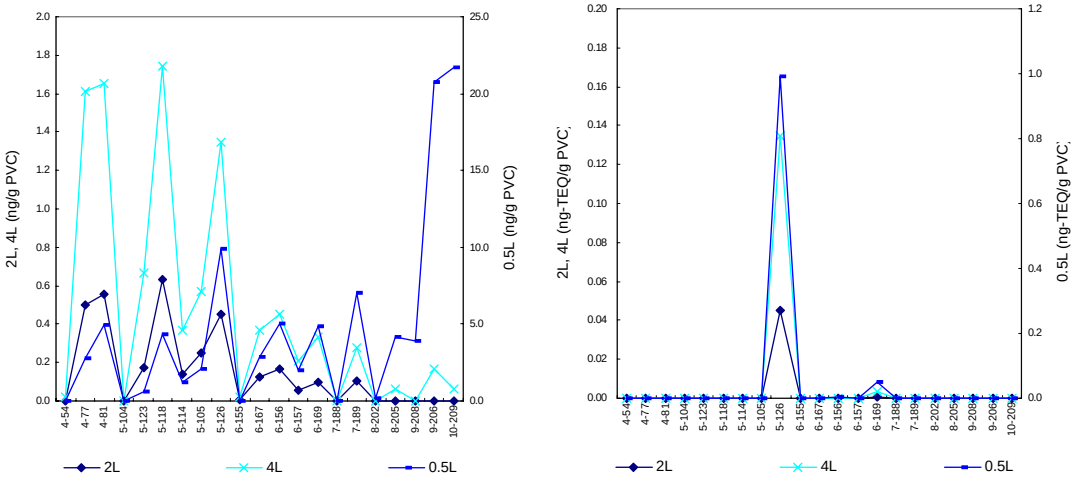
Fig 4. The relative abundance of PCDD/Fs congener during PVC Combustion

PCBs concentrations

It was analyzed 21 isomers with TeCBs through DeCBs in 209 total isomers, where 12 isomers have TEF estimated by WHO in 1997. In case of PCBs, it was shown same tendency with PCDD/Fs for most parts. PCBs concentration at 0.5 L was about ten times higher than 2 L or 4 L. Low chlorinated PCBs such as TeCB and PeCB were most of PCBs at 2 L and 4 L, but NoCB and DeCB were predominant at 0.5 L. The typical characteristics of PCB patterns from municipal waste incineration is a dominance of congeners with 3,3',4,4',5,5'-substitution, particularly for the OcCB and NoCB (Ballschmiter et al.,.1987). Therefore, the result of 0.5 L is similar to isomer pattern of incineration. As the TEQ value, 3,3',4,4',5-PeCB(#126) whose TEF is 0.1 was the major isomer of PCBs (Fig. 5(b)).

Table 2. PCBs Concentration

Air flow	PCBs Concentration							
	Total (ng/g PVC)				TEQ (ng-TEQ/g PVC)			
	1	2	3	4	1	2	3	4
0.5 L	81.322	70.098	143.540		0.894	0.944	1.303	
2 L	3.196	2.794	3.893	3.130	0.049	0.038	0.051	0.047
4 L	7.245	13.110	9.380		0.103	0.186	0.128	



(a) Total concentration (b) TEQ concentration

Fig 5. Isomer pattern of PCBs during PVC Combustion

References:

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