

Study on PCDD/Fs emission from heating of mixed pentachlorophenol and elemental sulfur via precursors formation

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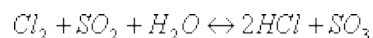
Introduction

Emission of PCDD/Fs from MSW incinerators has caused serious public concerns because of its carcinogenic and hazardous to human health since Olie et al first reported the PCDD/Fs in MSW incinerator fly ash¹. Two main formation mechanisms of PCDD/Fs in the MSW incinerators are reported as: 1) Precursors formation or gas phase formation due to the products of incomplete combustion (PICs), 2) Heterogeneous reaction on fly ash surfaces in post-combustion zone²⁻⁴. It is still uncertain that which one of these two mechanisms plays the main role during PCDD/Fs formation process. A general explanation is: PCDD/Fs in flue gas are mainly formed from PICs when the bad combustion happens and from heterogeneous reaction in cooling gas when good combustion occurs. The technique to control PCDD/Fs emission focuses on so-called "3-Ts" principles, optimal operation of incinerators and adoption of advanced flue gas cleaning system^{5, 6}.

Now incineration has been considered as a primary method for safe disposal and energy recovery from MSW in many Chinese cities. Due to the complex content of Chinese MSW components and low heat value (average about 4200 kJ/kg); it is difficult to maintain stable, complete burning and lower secondary pollution. It is a good idea to co-fire auxiliary coal with MSW in fluidized bed incinerators to maintain stable burning and control air pollutants emission.

It has reported that the co-firing of auxiliary coal with MSW could greatly decrease the PCDD/Fs formation because of the effects of the comparatively higher sulfur content in coal. There are several possible mechanisms to be proposed for PCDD/Fs inhibition by sulfur compounds during co-firing processes of coal and MSW:

(1) The effect of sulphur is to deplete the Cl₂ levels, which is more effective chlorinating agent than HCl, through the gas-phase reaction thereby inhibiting the aromatic substitution reactions⁷.



(2) The role of sulfur dioxide is to reduce the catalytic activity of the fly ash by reacting with the Cu-based Deacon catalyst in the fly ash (e.g., CuCl₂ and CuO). Gullett et al have shown that CuSO₄ is a less active catalyst for the production of Cl₂ through the Deacon process as well as for the biaryl synthesis step of PCDD formation^{8, 9}.

(3) The presence of SO₂ may sulfonates the phenolic PCDD/F precursors, preventing subsequent chlorination and biaryl synthesis, or replacing the oxygen link with S and forming polychlorodibenzo-thiophene (PCDT) and polychlorothianthrenes (PCTA)^{8, 9}.

Pentachlorophenol (PCP) is an important precursor of PCDD/Fs which forms during the process of MSW waste combustion. Since 1950, PCP was widely used as insecticide, aseptic and disinfectant in fields of making pesticides, wood preserves etc. In Japan, the use of PCP resulted in an environmental deposition of decades tons of PCDD/Fs from 1955~1995, equivalent to 250kg WHO-TEQ, became one of the main resources of PCDD/Fs in soil¹⁰. In the past years, ten thousands of tons of sodium pentachlorophenol (PCP-Na) were produced for the prevention of snail fever and oncomelania in the middle and down streams of Yangtze River of China, and Jiang Ke

has found dioxins in some water areas treated by PCP insecticide¹¹. Furthermore, PCP was also found in sludge after sewage disposal¹². Now PCP existed widely in waters, soils, sludge and all kinds of MSW components.

In this paper, experiments on heating of mixed PCP and elemental sulfur are performed to investigate the effects and interactions of sulfur on the PCDD/Fs formation by PCP decomposition.

Methods and Materials

The experiments are performed in a quartz tubular furnace with a PID temperature controller. PCP powder or mixed with elemental sulfur is put in a ceramic boat and covered with some quartz sand which has baked for two hours at 800°C. Then the ceramic boat is pushed into the middle place of the quartz tubular, where the temperature has been heated to desired one. The air is set at 300ml/min and induced into the quartz tubular through a Rota meter. The flue gas was absorbed by XAD-2 resin and toluene. The total reaction time is 30 minutes. In the first stage, the heating of only PCP at 300°C, 400°C, 500°C, 600°C and 700°C are conducted and sampled. Then the heating of mixed PCP and elemental sulfur with S/Cl=1 at same temperatures as above are conducted and sampled. In the third stage, the heating of mixed PCP and elemental sulfur with S/Cl=0.75 and 1.5 at 400 °C are conducted and sampled. In all experiments, S/Cl is described as molar ratio and calculated by mole of mixed element sulfur dividing mole of chlorine in PCP. The amount of mixed element sulfur is weighed according to the set S/Cl molar ratio. The PCDD/F emission factors in this study are defined to the amount of PCDD/Fs emission dividing the mass of PCP, and then the units will be ng/g PCP or ng I-TEQ/g PCP.

The sample pretreatment method employed here was described elsewhere according to USEPA method 8280B¹³. All analyses were performed on a low resolution Thermo Finnigan Voyager mass spectrometer (LRMS) with a trace 2000 high-resolution gas chromatograph (HRGC). Chromatographic separations were carried out on a 60m DB-5 quartz capillary column. The temperature program for GC oven was: initial temperature 100°C, held for 2 minutes; 100~200°C at 25°C/minute; 200~280°C at 3°C/minute; 280°C held for 20 minutes. Carrier gas: Helium (99.999%), 1 ml/min; splitless sample injection. Mass spectrum condition: electron impact ionization 70 eV; electron multiplier voltage 420V; ion source temperature 220°C; interface temperature 250°C; SIM (selected ion monitoring mode). All the isotope standard samples were purchased from Wellington laboratories, Canada.

Results and Discussion

Impact of temperature on PCDD/Fs formation from heating of PCP or mixed elemental sulfur: Temperature is an important factor affecting the formation of PCDD/Fs. In general, the process of precursors forming PCDD/Fs during waste incineration can be divided into two relatively apparent temperature zones⁴: high temperature gas-phase formation (500 °C~800°C), low temperature heterogeneous phase formation (<500 °C). David et al. suggested that the temperature interval of 280°C~450°C was the activity region of PCDD/Fs formation during flue gas cooling⁴.

Figure 1 and 2 show the experiment results of heating of PCP or mixed elemental sulfur at 300°C~700°C. The highest activity temperature zone for PCP (S/Cl=0) forming PCDD/Fs is 500°C~600°C, while at two sides of this temperature zone the emission factors are comparatively lower. The peak of total PCDD/Fs emission factors is at 500 °C, but the peak of I-TEQ PCDD/Fs emission factors is pushed to 600 °C. It seems that the toxicity of PCP forming PCDD/Fs is lagged or advanced by about 100 °C. The results for experiments of S/Cl=1 indicate that the highest activity temperature zone of PCDD/Fs formation is reduced to 400 °C~500°C; the addition of sulfur decreased the highest formation of PCDD/Fs at temperature less than 500°C; the formation of PCDD/Fs reduced greatly when temperature is higher than 500 °C. At S/Cl=1, the peak of total PCDD/Fs emission factors is at 400 °C but the peak of I-TEQ PCDD/Fs emission factors is at 500°C. That is to say, for the case of S/Cl=1, the toxicity of PCP forming PCDD/Fs is also lagged or advanced by about 100 °C. This result corresponds with that of S/Cl=0. This is so-called the phenomenon of toxicity lags or advances of PCP forming PCDD/Fs, which has not been reported in other literature.

The temperature monitoring of reactant in the ceramic boat at each experiment reveals that the oxidation reaction of elemental sulfur does not increase the local reaction temperature for PCP. Environment temperature of reactant is the same for two cases of no sulfur added and sulfur added. In Figure 1 and 2, the addition of sulfur inhibits the total PCDD/Fs emission and I-TEQ PCDD/Fs emission greatly when temperature is higher than 500°C, but the addition of sulfur (S/Cl=1) promoted the PCDD/Fs emission when temperature less than 500°C. The results showed that there is a critical temperature (temporarily set as 500 °C) for the inhibition effects of sulfur on PCP decomposing to PCDD/Fs.

at $S/Cl=1$. At higher temperature than $500\text{ }^{\circ}\text{C}$, the inhibition effect can be observed; while at lower than $500\text{ }^{\circ}\text{C}$ no inhibition exists.

Impact of S/Cl molar ratio on PCDD/Fs formation from heating of mixed elemental sulfur and PCP at 400°C :

A number of good operating practices of waste and coal co-firing in incinerator show that the formation of PCDD/Fs is related to S/Cl ratio in fuel. There is no agreement on the critical S/Cl which promotes or inhibits the formation of PCDD/Fs. Lindbauer et al. found that PCDD/Fs emission reduced dramatically when S/Cl is within 15 for waste and coal co-firing¹⁵. However, Raghunathan et al. suggested that the low S/Cl ratio promote the formation of PCDD/Fs, the enough S/Cl ratio inhibit the formation of PCDD/Fs efficiently¹⁶. Lutho et al. showed that 90% of low temperature formation of PCDD/Fs could be inhibited when S/Cl ratio was 10 in their incineration experiments¹⁷.

In this paper, in order to study the inhibition effects of PCP on PCDD/Fs formation at temperature less than the so-called critical temperature 500°C , the heating of mixed sulfur and PCP is carried at 400°C . Figure 3 and 4 show the relationship between S/Cl ratio and PCDD/Fs emission factors. The results indicate that the addition of sulfur promoted the decomposition of PCP and the formation of PCDD/Fs remarkably when S/Cl less than 1.5. The inhibition effects can only be observed at S/Cl ratio at 1.5 or even higher. In previous studies, it was reported that PCDD/Fs formation was promoted when more sulfur was added in fly ash and heated at $300\sim 500^{\circ}\text{C}$ ¹⁸. The results of this paper suggest that S/Cl higher than 1.5 may lead to inhibit the PCDD/Fs formation from PCP decomposition at temperature 400°C .

Conclusions

The so-called toxicity lags or advances for PCDD/Fs formation during the heating experiments of PCP or mixed elemental sulfur are reported in this paper. When elemental sulfur was mixed with PCP and heated at $300\sim 700^{\circ}\text{C}$, it is found that the inhibition effects on PCDD/Fs formation can only be observed over 500°C . In the lower temperature heating of PCP and elemental sulfur at 400°C , it is found that the inhibition effects on PCDD/Fs formation only happens with S/Cl higher than 1.5.

Acknowledgement

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Figure 1: Effect of temperature on total PCDD/Fs emission factors

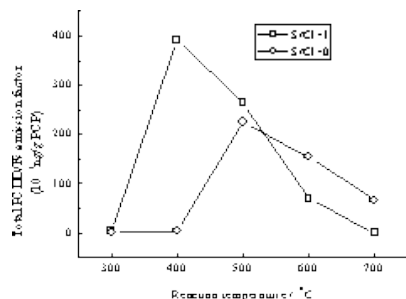


Figure 2: Effect of temperature on TEQ PCDD/Fs emission factors

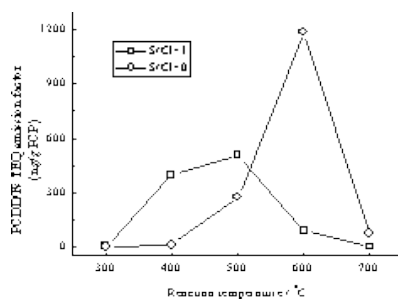


Figure 3: Relationship between S/Cl ratio and total PCDD/Fs emission factor under 400°C

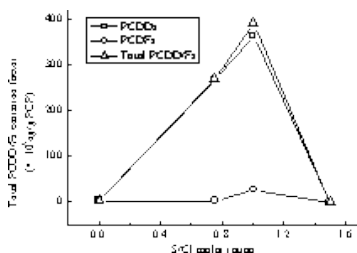


Figure 4: Relationship between S/Cl ratio and total PCDD/Fs emission factor under 400°C

