

EFFECT OF COPPER COMPOUNDS ON PCDD/Fs FORMATION IN MODEL WASTE INCINERATION

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Introduction

Metals in municipal solid waste can promote the formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) during incineration^{1,2}. Stieglitz et al. showed in experiments with model mixtures that copper chloride (CuCl₂) is particularly effective while other divalent metal chlorides such as magnesium, zinc, mercury, cadmium, tin and lead display only limited catalytic activity³. Mattila et al. reported in co-combustion of coal/bark/plastics mixture using a full-scale incinerator that the presence of copper in the fuel mixture leads to increased PCDD/Fs formation⁴. We demonstrated in combustion experiments in a laboratory-scale fluidized-bed reactor that copper chloride in model wastes promotes PCDD/Fs formation via chlorination of organic matters⁵. Isomer distributions of PCDFs also showed that the catalyst takes an important role in the formation mechanisms from carbon in model waste incineration. Copper chloride assists oxidation/oxychlorination and breakdown of carbon to aromatic compounds with catalytic chlorination. Addink et al. showed that copper chloride catalyzes ring closure of the dibenzofuran and dibenzo-*p*-dioxin rings⁶. However, there exist many unclear parts in the catalytic reactions.

The aim of this paper is to study the effects of the form of copper compound as a catalyst on the PCDD/Fs formation in municipal waste incineration. Combustion experiments of model wastes with copper chloride (CuCl₂) and copper oxide (CuO) were conducted in the laboratory-scale fluidized-bed reactor. Comparison of homologue profiles and isomer distributions of PCDD/Fs in both experiments gives us some useful information about the roles of copper in the PCDD/Fs formation during incineration.

Methods and Materials

Figure 1 shows a schematic diagram of an experimental setup, which was used in the previous paper⁵. A primary combustion zone was the fluidized-bed reactor, which had a diameter of 60 mm and a height of 300 mm. Fluidized material was silica sand of 100-140 mm and the bed height was set to 100 mm. A freeboard as a secondary combustion zone was a straight tube of 30 mm diameter and 1450 mm height. All parts of the main combustion section coming in contact with flue gas were made of quartz. As a post-combustion section, three glass tubes, 30 mm diameter and 300 mm height, were used. Air was supplied to the primary and secondary combustion zones from a compressor. Temperatures of the primary and secondary combustion zones and the post-combustion section were controlled individually using external electric heaters. The concentrations of CO, CO₂, and O₂ were measured continuously.

Model wastes were produced to define the waste composition strictly. The base ingredients of the model waste were 45 % unbleached pulp powder, 40 % unbleached flour and 15 % wood powder. Properties and elementary composition of the model waste containing only the base ingredients are shown elsewhere⁴. In addition to the base ingredients, polyvinyl chloride (PVC, degree of

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polymerization $n \cong 1100$, Wako) was mixed as a chlorine source. Copper chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, Wako) and copper oxide (CuO , Wako) were added as a catalyst. All ingredients were ground separately, mixed mechanically, and then pelletized into particles in the range of 1 to 3 mm in diameter. Analyzed Cl and Cu contents are shown in Table 1.

The setup was assembled with new sand for the fluidized material. After each experiment, the quartz surface in contact with flue gas was washed out to avoid the effect of experimental order. The contaminated quartz parts were replaced with new ones because Cu compounds adhered to it by reacting with the quartz surface of the reactor. The experimental conditions are listed in Table 2. The excess air ratio (λ) was set to 2.0 in total. Sampling was carried out for 4 hours or more after the post-combustion section (indicated as point X). Analysis methods are described elsewhere⁵.

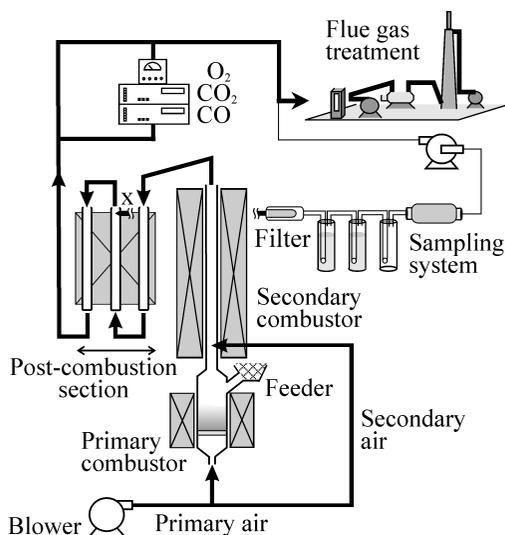


Figure 1. Schematic diagram of experimental setup.

Table 1. Cl and Cu contents in model wastes.

catalyst	Cl content [%]	Cu content [%]
CuCl_2	0.64	0.07
CuO	0.55	0.09

Table 2. Experimental conditions.

temperature	
primary combustion zone	900 °C
secondary combustion zone	900 °C
post-combustion section	350 °C
flow rate	
primary air	0.46 Nm ³ /h ($\lambda = 1.3$)
secondary air	0.26 Nm ³ /h ($\lambda = 0.7$)
fuel feed rate	100 g/h

Results and Discussion

Figure 2 shows the homologue profiles in the experiments of the wastes with CuCl_2 and CuO . Averaged CO concentration of flue gas was 84.4ppm with CuCl_2 and 54.7ppm with CuO . In both experiments, the congener distribution was shifted toward the highly chlorinated species. PCDFs were formed about 6 times as much as PCDDs. The addition of CuCl_2 in the waste increases the amount of PCDD/Fs formed and shifts the homologue profile toward the highly chlorinated species⁵. Figure 2

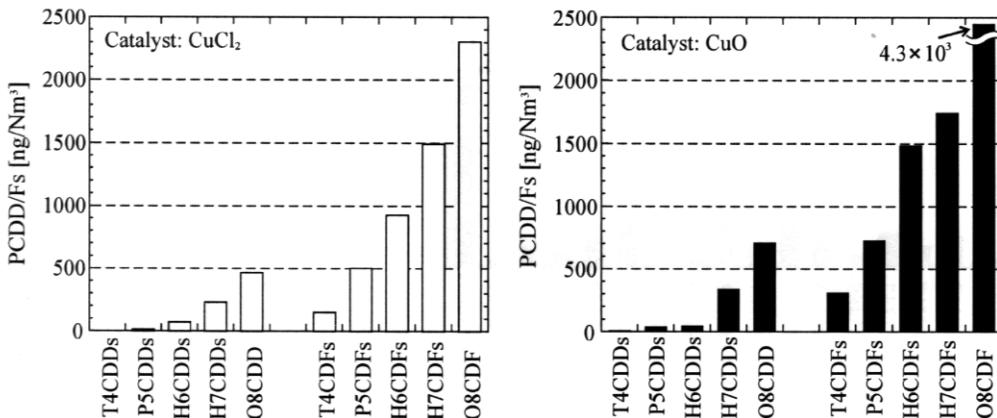


Figure 2. Homologue profiles of PCDD/Fs in the experiments of the model wastes with copper chloride and copper oxide.

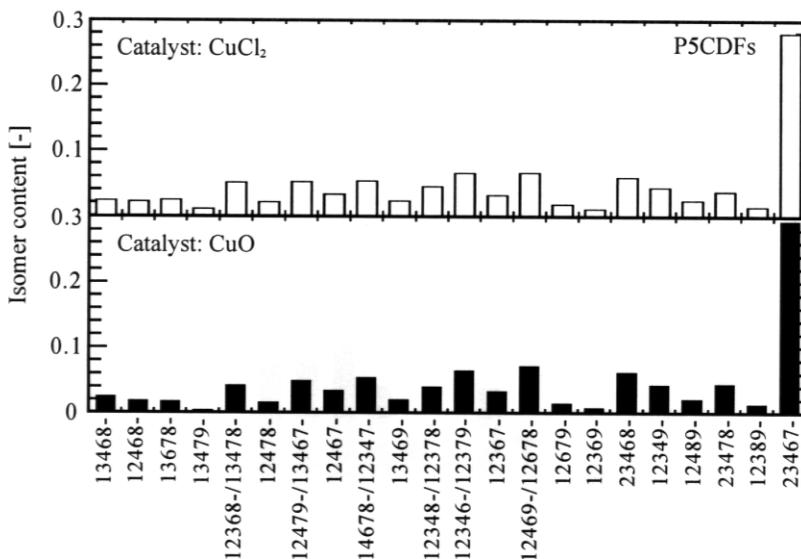


Figure 3. Isomer distributions of P5CDFs in the experiments of the model wastes with copper chloride and copper oxide.

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indicates that CuO in the waste has the same effects on the PCDD/Fs formation as CuCl₂. CuO contributes to the PCDD/Fs formation as a chlorination catalyst of organic matters. This could mean that CuCl₂ in the waste is effective as a catalyst not in its form but via reactions with other compounds such as oxygen and chlorine.

Another important role of the catalyst is in the PCDD/Fs formation mechanisms as mentioned above. It is observed as peculiar isomer distribution patterns that don't appear in the experiment without the catalyst. In combustion experiments with copper chloride, there appear the distribution patterns with only a few isomers mainly formed⁵. Especially, P5CDFs have a characteristic isomer pattern that 2,3,4,6,7-P5CDF is an overwhelming majority. In this study, isomer patterns are examined in the experiment with CuO to clarify the effects of the catalyst on the PCDD/Fs formation mechanisms.

References

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