CONGENER PATTERNS OF PCDD/F IN MUNICIPAL SOLID WASTE INCINERATION BASED ON CHEMICAL EQUILIBRIUM ANALYSIS

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Introduction

In this paper, congener patterns of PCDD/F generated during municipal solid waste incineration are discussed based on thermo-chemical equilibrium analysis and the experimental results obtained at a laboratory-scale fluidized-bed incinerator [1)]. Thermo-chemical properties such as enthalpy, entropy and Gibb's free energies of PCDD/F were calculated based on *ab initio* quantum chemistry using the B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) basis set. Using the computed thermo-chemical properties of PCDD/F, the congener pattern of PCDD/F was calculated based on multi-phase chemical equilibrium with regard to a multi-element system. Computed results provide a good explanation of the congener pattern of PCDD/F emission obtained in the experiments. The results also suggest that higher chlorinated dioxins are likely to be generated in a post flammable zone. On the other hand, lower chlorinated dioxins become stable in the cooling process.

Thermodynamic data and calculation methods

The thermodynamic behavior of PCDD/F has not as yet been adequately determined. Shaub [2)] estimated the thermodynamic data of PCDD/F using the group additivity method, which was proposed by Benson. Koester calculated the thermodynamic data using the semi-empirical molecular orbital method with MNDO [3)]. Recently, Adriaens [4)] and Saito [5)] estimated the thermodynamic function of PCDD/F in the gas phase using the semi-empirical molecular orbital method with PM3. Okamoto [6)] proposed a formation mechanism of a few isomers of PCDD/F in the gas phase from their precursors using the hybrid-density functional theory method with B3LYP as an *ab initio* study. The values reported in the studies mentioned above, however, differ somewhat from those reported here. In the present study, the thermo-chemical properties were calculated based on *ab initio* quantum chemistry using the B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) basis set and CBS-4M. The results show that the B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) basis set yields more accurate value than CBS-4M.

A multi-phase chemical equilibrium calculation was conducted using the computer code ECAT version 6, based on the free energy minimization method [7)]. Carbon graphite was excluded from the equilibrium composition. Although carbon graphite or soot is stable, its formation is controlled kinetically and proceeds gradually under the carbon rich conditions of the combustion processes. Therefore, equilibrium calculations without graphite yield more realistic compositions.

Results and Discussion

In a previous work [8], it was pointed out that PCDD/Fs are not generated even in fuel rich conditions, as long as the solid waste reacts homogeneously. In other words, the generation of PCDD/F in a municipal solid waste incinerator is a result of the heterogeneity of components in a combustion field and a gas cooling process. Water vapor, chlorine and hydrocarbon volatilize sequentially in the process of incinerating solid waste according to the temperature history. In the gas cooling process, the atomic ratio of carbon, hydrogen and chlorine is at high levels in the extreme neighborhood of carbonaceous compounds and the condensed hydrocarbon in the deposited fly ash, and the ratio of oxygen is low in this localized region. Therefore, the atomic ratio of the reactants is likely to be heterogeneous in the area local to a combustion field and a gas cooling process. PCDD/F formation is discussed in relation to this premise.

Figure 1 (a) ~ (f) show the congener patterns of PCDD/F for various atomic ratios of C:H:Cl in the reactants at temperatures of 570 K and 1000 K under the excess air ratios of l = 0.7 and 0.1. The atomic ratio such as C:H:Cl = 1:1:1 can be realized by the reaction between carbon and HCl. From the figures, it is shown that higher chlorinated PCDD/Fs are likely to be generated if the atomic ratio of Cl in the system becomes high and lower chlorinated PCDD/Fs become stable at lower Cl atomic ratio. It is also shown that the congener patterns are influenced by temperature besides the cases of (a) and (e). By comparing the congener patterns of PCDD/F during incineration of artificial solid waste (ASW) contains 4 % PVC in a laboratory-scale fluidized-bed incinerator measured at the outlet of the secondary combustor (T = 1000 K) and at the cooling section (T = 570 K), as shown in Figure 2, with Fig. 1 (b), good agreements are obtained about the temperature dependence on congener patterns, especially for PCDFs. Concentrations of PCDF are much higher than those of PCDD for a both cases of experiment and computations. This suggests that higher chlorinated dioxins are likely to generate in a post flammable zone and lower chlorinated dioxins become stable in the cooling process. Figure 3 shows the congener patterns of PCDD/F at the incineration of Base-, PVC4%-, and PVC 4 %+Cu 2 %-ASW measured at the outlet of the cooling section [1]. The results show that the higher Cl contents promote the formation of higher chlorinated PCDD/Fs. It is also noted that Cu contents in the ASWs strongly promote the higher chlorinated PCDD/Fs. This suggests that Cu makes the atomic ratio of Cl higher around the extreme neighborhood of carbonaceous compound and promote the chlorination reaction. It is well known that Cu act as a catalyst in the PCDD/Fs formation. This result is well coincide with that obtained at the thermo-chemical analysis as mentioned above.

Acknowledgments

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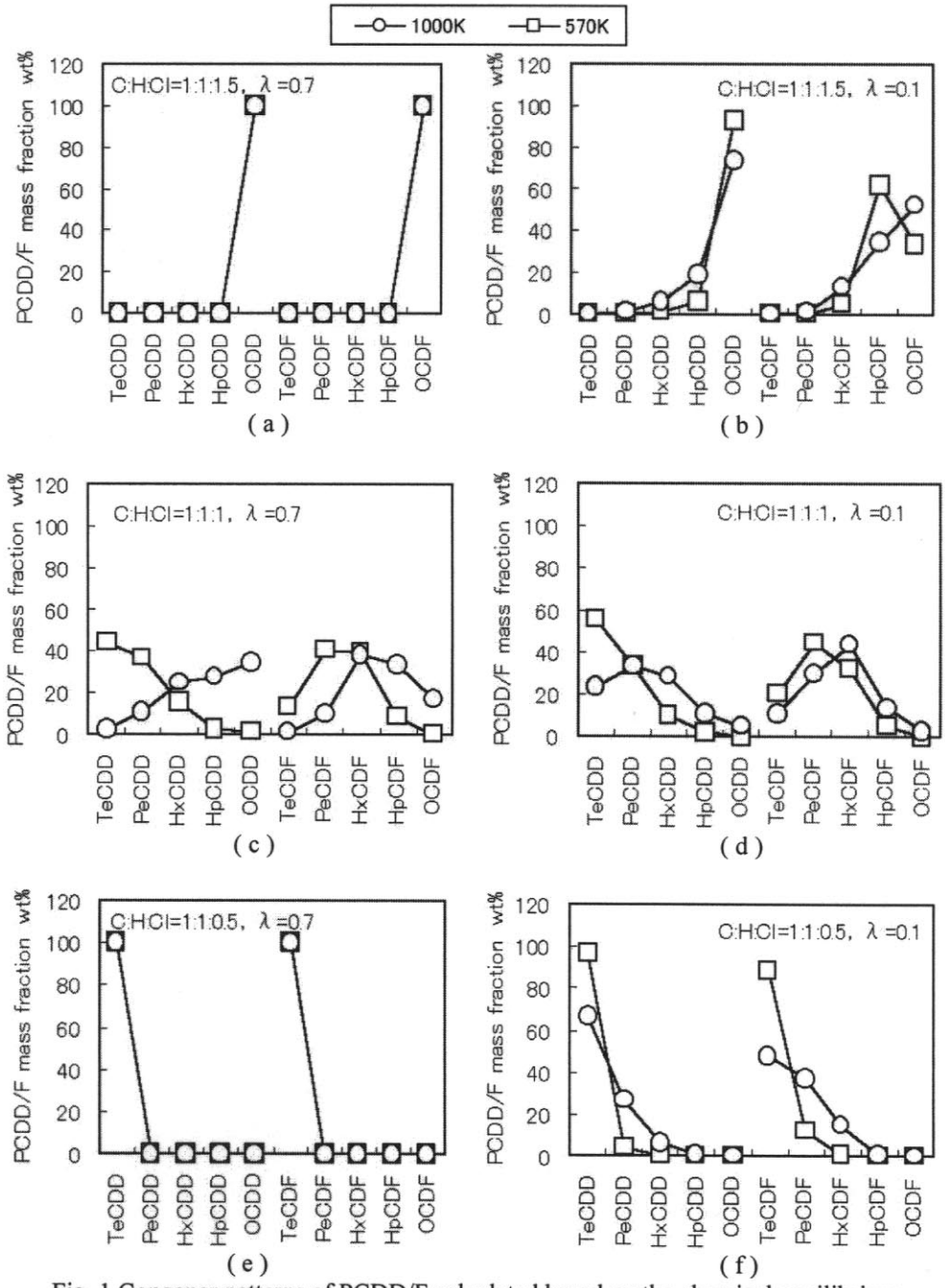

Fig. 1 Congener patterns of PCDD/F calculated based on the chemical equilibrium

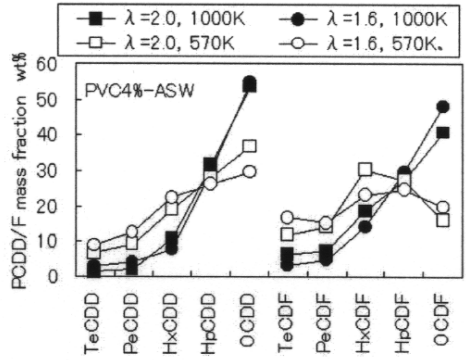

Fig. 2 Congener patterns of PCDD/F at 1000 K and 570 K during artificial solid waste combustion in a laboratory-scale fluidized-bed incinerator

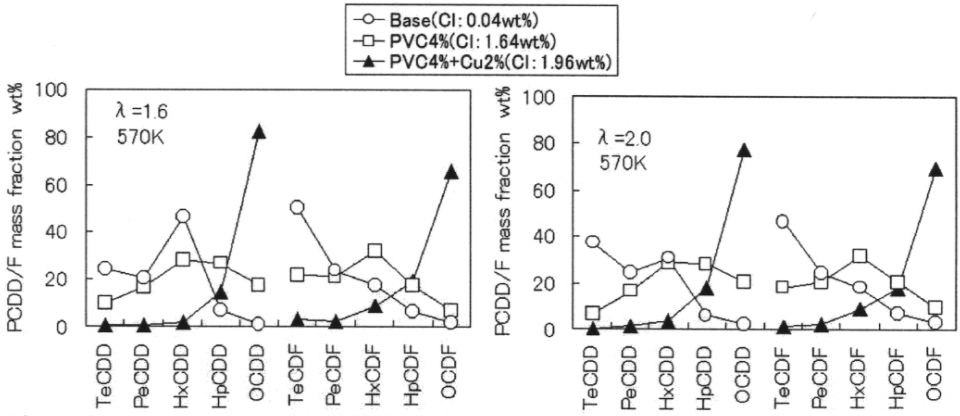

Fig. 3 Congener patterns of PCDD/F at 570 K during artificial solid waste combustion in a laboratory-scale fluidized-bed incinerator

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