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Suppression of Formation of Dioxins in Combustion Gas of Municipal Waste Incinerators by Spray Water Injection

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Dioxins in the combustion gas of municipal solid waste incinerators (MSWIs) are resynthesized when the combustion gas passes from the outlet exaust gas boiler to the outlet gas duct. The objective of the study was to estimate if the suppression of the formation of dioxins depends on the inlet gas temperature and diameter and/or temperature of droplet spray water using an actual incinerator operation data. The dioxin formation and/or the quenching temperature is revealed using the Altwicker theory equation with the information of inlet gas temperature and droplet spray water. The evaporation rate of a spray water droplet also can be estimated using the Mizutani theory. The highest dioxin formation was found at 350°C; thereafter, it decreased quickly. When an area of 500 μm for droplet-formed dioxins is defined as 100%, the values of formed dioxins for 400, 300, 200 and 100 μm droplet areas are estimated as 71, 41, 25 and 18%, respectively. It is revealed that the smaller size of droplet spray water and lower inlet gas temperature enable the decrease in dioxin formation. The decreased dioxin formation and/or the lower quenching temperature is revealed using the Altwicker theory equation with the information of inlet gas temperature and droplet spray water size.

1. Introduction

Dioxin is a common name for a group of compounds classified as polychlorinated dibenzodioxins (PCDDs). PCDDs, which are members of a family of halogenated organic compounds, have been shown to bioaccumulate in humans and wildlife owing to their lipophilic properties and are known teratogens, mutagens, and suspected human carcinogens. Dioxins are produced at small concentrations when organic material is burned in the presence of chlorine, regardless of whether the chlorine is present as chloride ions or as organochlorine, so they are widely produced in various contexts. According to the most recent US EPA data, the major sources of dioxin are coal-fired utilities, metal smelting, diesel trucks, the land application of sewage sludge, the burning of treated wood, and trash burn barrels. These sources together account for nearly 80% of all dioxin emissions.

Dioxins in the combustion gas of municipal solid waste incinerators (MSWIs) are resynthesized when the combustion gas passes from the outlet exhaust gas boiler to

the outlet gas duct. In general, to suppress dioxins in MSWIs, combustion gas is kept at a high temperature, higher than 800°C. In the case of excess air combustion, hydroxyl radical HO• are the major radical species. Hydroxyl radical must be attacked or decomposed to produce dioxins.[1] We have investigated 10 MWSI plants in Nagasaki Prefecture for 6 months in 1998. As a result, we found that dioxins at a concentration of 1 TEQng/Nm^3 in the inlet gas duct of the exhaust gas boiler increased to 6.6 TEQng/Nm^3 in the outlet gas duct, causing the resynthesis of dioxins for about 2 s.[2] As a countermeasure, by using a gas temperature that is lower than the required synthesis temperature and carrying out incineration within the resynthesis time of dioxins, dioxin production could be suppressed.[2] If the spray water droplet diameter (dsp) is 50 μm, the evaporation rate can be estimated using Mizutani's evaporation theory.[3] It is estimated that the evaporation or quenching time is about 0.03–0.05 s when the gas temperature is decreased from 400 to 200°C.[2] Although Hiraoka[4] has pointed out that the dioxin synthesis time is from 0.01 to 0.001 s, the dioxin synthesis time has not yet been confirmed by actual laboratory tests. Since a confirmation of the suppression of dioxin formation will be useful, we have carried out a review of the previous reports concerning dioxin formation. Altwicker *et al.*[5] studied the dioxin formation rate on the basis of an on Arrhenius parameter. Stanmore[6] studied the effect of cooling rate on the suppression of dioxins on the basis of the Langmuir molecular adsorption theory. About 94% of the formed dioxins are formed on the fly ash surface in the heterogeneous gas phase.[7] The objective of the study was to estimate if the suppression of the formation of dioxins depends on the diameter and/or temperature of droplet spray water using the Altwicker and Mizutani theories and actual incinerator operation data.

2. Materials and Methods

2.1 *Formula of dioxin formation and decomposition in incinerator combustion gas*

Regarding dioxin formation and its rate, the applied Arrhenius parameter was introduced by Shub and Tsang[1,8] in 1985. The precursor on fly ash is reacted with a precursor in the combustion gas in a duct (Eley Readel reaction). Then, dioxins are resyntheized on the fly ash. After that, some dioxins are desorbed from the fly ash surface (Fig. 1). Dickson and coworkers[9,10] have studied the conversion of pentachlorophenol on fly ash at various temperatures for resident times of 6 and 60 min and achieved conversion rates of as high as 4%; they also pointed out that fly ash is a catalyzer. Also, their data suggest that decomposition should be added to the original mechanism proposed by Shaub and Tsang. Estimates of the magnitude of preexponential factors and the active energies have been based on their literature

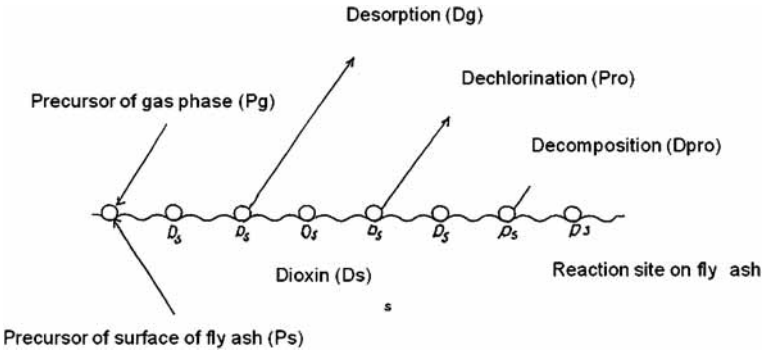

Fig. 1. Scheme of dioxin formation and its degration pathway.

comparisons. At the reaction stage of dioxin formation, K_r (the corresponding rate constant of dioxin formation) in the uneven gas phase including fly ash is linked by the relation using frequency factor (A), activation energy (E), gas temperature (T) and gas constant (R) as follows.

$$K_r = A\mathrm{Exp}(-E/RT) \quad (1)$$

Dioxin formation (D_s) is described as the sum of the number of precursors on the surface of the fly ash (P_s) and in the gas phase (P_g).

$$P_s + P_g \rightarrow D_s \quad (2)$$

After the rate of dioxin formation was discussed by Shaub and Tsang[1,8] and Dickson and coworkers,[9,10] Altwicker *et al.*[5] proposed to modify their rates of dioxin formation because they had shown a four-step rate equation for the formation of dioxins (Fig. 1). In addition, Milligan and Altwicker[11] indicated that the precursor reaction follows a classical adsorption/reaction (dechlorination and decomposition)/desorption pathway. The corresponding rate constants of dioxin degradation pathway indicate K_{des} (desorption), K_{dechl} (dechlorination), and K_{deco} (decomposition).

With the four-step rate equation theory for the formation of dioxins and eq. (1), each stage of dioxin formation can be described as follows:

Reaction: $P_s + P_g \rightarrow D_s$

$$K_r = 5.09E9\sqrt{T}\ \mathrm{Exp}(-20800/RT) \quad (3)$$

Desorption: $D_s \rightarrow D_g$

$$K_{des} = 10^{13}\mathrm{Exp}(-53400/RT) \quad (4)$$

Dechlorination: $D_s \rightarrow Pro$

$$K_{dechl} = 10^{5}\mathrm{Exp}(-15000/RT) \quad (5)$$

Decomposition: $D_s \rightarrow DPro$

$$K_{deco} = 10^{13}\mathrm{Exp}(-37500/RT) \quad (6)$$

P stands for the precursor concentration (ng/m^3), D stands for the dioxin concentration (ng/m^3) (s = surface of fly ash, g = gas phase), K stands for the corresponding rate constants of dioxin formation (1/s), r stands for the reaction of dioxin formation, des stands for the desorption of dioxin, dechl stands for the dechlorination of dioxin, deco stands for the decomposition of dioxin, *Pro* are the products from dechlorination (ng dioxin/m^3), *DPro* are the products from the decomposition (ng dioxin/m^3), R stands for the gas constant (cal/Kelvin/mol), and T stands for the gas temperature (Kelvin).

We tried to substitute the rate constants (3)–(6) into the rate equation to estimate total dioxin formation. The surface coverage (θ) was defined as the number of reaction sites of dioxin formation which locates the surface area on fly ash. Moreover, the formation of dioxin in the uneven gas phase does not take place because there is little formation in the uneven gas phase when compared with the surface of the fly ash. Hence, dioxin formation can be described as $K_r\theta P_g$.

$$D_s = K_r\theta P_g \quad (7)$$

From the information of both the degree of dioxin formation (7) and variation of time (dt), the rate of dioxin formation ($(D_s)_1$) is derived from eq. (8).

$$d(D_s)/dt = K_r\theta P_g \quad (8)$$

The reaction product of dioxin formation ($(D_s)_1$) diminishes by desorption (or evaporation) ($(D_s)_2$), dechlorination ($(D_s)_3$) and decomposition ($(D_s)_4$). $(D_s)_2$, $(D_s)_3$ and $(D_s)_4$ are derived from each of the corresponding rate constants of the dioxin degradation pathway such as K_{des} (desorption), K_{dechl} (dechlorination) and K_{deco} (decomposition). Therefore, the expression for the estimation of the total dioxin formation using the above-described equations (3)–(6) is as follows.

$$d(D_s)/dt = K_r\theta P_g \quad (8)$$

The estimated result is expressed as $(D_s)_1$.

$$d(D_g)/dt = d(D_s)/dt = K_{des}(D_s)_1 \quad (9)$$

The estimated result is expressed $(D_s)_2$.

$$d(D_s)/dt = K_{dechl}(D_s)_1 \quad (10)$$

The estimated result is expressed $(D_s)_3$.

$$d(D_s)/dt = K_{decom}(D_s)_1 \quad (11)$$

The estimated result is expressed $(D_s)_4$.

Finally, the total amount of dioxin formed ($(D_s)_t$) is expressed as follows:

$$(D_s)_t = (D_s)_1–(D_s)_2–(D_s)_3–(D_s)_4 \quad (12)$$

2.2 *Formula for the suppression of dioxin formation by spray water*

Using the dioxin formation rate and droplet evaporation rate, we tried to construct a model for determining the formation rate and suppression rate of dioxins by spray water quenching. On the basis of Mizutani's evaporation theory,[3] the evaporation time of spray droplet and quenching time of combustion gas and fly ash were estimated as follows.

First of all, water temperature T_l which is stated evaporation and its required time (t) are as follows.

$$T_l = T_g–(T_g–T_{l0})\mathrm{Exp}\frac{-6\lambda Nut}{C_{pl}\rho_l d^2} \quad (13)$$

T_g stands for initial gas temperature (°C), T_{l0} stands for initial water temperature (°C), λ stands for gas thermal conductivity (kcal/mh°C), Nu stands for Nusselt number, C_{pl} stands for water droplet specific heat (kcal/kg), ρ stands for water density (kg/m^3), d stands for water droplet diameter (m), and t stands for time (s). Parameters such as λ, Nu, and C_{pl}, ρ_l indicate the value at average temperature of inlet and outlet incinerator.

Secondly, it is assumed that as the water droplet temperature becomes 100°C, its evaporation begins. The square of droplet diameter at evaporation is altered according to the amount of evaporation that can be estimated as the evaporation rate constant C_e (m^2/h) in the combustion gas.

$$t = (d_0^2 - d^2)/C_e \quad (14)$$

d_0 stands for droplet diameter at $t = 0$.

$$C_e = \left[\frac{4\lambda_g Nu}{C_{pv}\rho_l}\right] \ln\left[\left(1 + \frac{4\lambda_{gs} C_{pv'}}{\lambda_{g'} L}\right)(T_g - T_l)\right] \quad (15)$$

$C_{pv'}$ stands for average specific heat of droplet (kcal/kg°C), $\lambda_{g'}$ stands for thermal conductivity of gas and vapour mixture at boundary of droplet (kcal/mh°C), λ_{gs} stands for thermal conductivity of gas on droplet (kcal/mh°C), L stands for water latent heat (kcal/kg°C), and T_l stands for water temperature (°C).

According to these calculation formulas, a quenching time can be estimated for gas temperature from 400°C to 200°C. Also, it is assumed that the fly ash cooling time is equivalent to the gas cooling time.

2.3 *Information of model and given parameters for simulation*

The processing ability of model MSWI is 150 t/d (6169 kg-msw/h) with a bag filter attached, and this model is located in Nagasaki City, Japan. Estimation and simulation are carried out from the incinerator outlet to the cooling tower outlet.

Fixed values for simulation: municipal solid waste (MSW): 6.169 (kg-msw/h), MSW element analysis, carbon (C): 19.3, hydrogen (H): 2.9, nitrogen (N): 0.4, oxygen (O): 15.5, sulfur (S): 0.02, chlorine (Cl): 0.2, water (H_2O): 53.48, ash: 8.2, total 100%. The effective height is 10 m, section area: 2 m^2, divided number (n): 100, gas in waste: 4.916 (kg-fuel/m^2s), excess air ratio: 2, spray water quantity: 5000 kg/h.

Important values for simulation: dsp (μm) values: 100, 200, 300, 400 and 500; inlet gas temperature (°C): 100, 150, 200, 250, 300, 350, 400 and 500.

3. Results and Discussion

3.1 *Calculation of dioxin formation with Altwicker theory*

1) $(D_s)_1 = K_r \theta P_g = 269.8$ (ng/m^3)(1/s)
   The parameters are calculated using the Altwicker model.[5] K_r stands for 27.2 (1/s) in eq. (3) using R (1.987 cal/Kelvin/mol) and T (200+273 Kelvin). θ stands for the surface coverage (0.0004).
   P_g stands for the dioxin quantity (2.48×10^4 ng dioxin/m^3). Because the average gas precursor concentration between the inlet and the outlet is estimated to be 7.56×10^{10} molecules/cm^3, this value becomes 2.48×10^4 ng dioxin/m^3.
2) $(D_s)_2 = K_{des}(D_s)_1 = 0.57\times10^{-9}$ (ng/m^3)(1/s)
   K_{des} stands for 0.21×10^{-11} (1/s) in eq. (4).
3) $(D_s)_3 = K_{dechl}(D_s)_1 = 0.03\times10^{2}$ (ng/m^3)(1/s)
   K_{dechl} stands for 1.17×10^{-2} (1/s) in eq. (5).
4) $(D_s)_4 = K_{decom}(D_s)_1 = 1.26\times10^{-2}$ (ng/m^3)(1/s)
   K_{decom} stands for 0.47×10^{-4} (1/s) in eq. (6).
5) $(D_s)_t = (D_s)_1 - (D_s)_2 - (D_s)_3 - (D_s)_4 = 266.8$ (ng/m^3)(1/s)

3.2 *Calculation of evaporation time of spray droplet and evaporation rate constant with Mizutani theory*

By using eqs. (12)–(14), 100% evaporation time of spray droplet (0.03 s) and evaporation rate constant C_e (0.00023 m^2/h) were calculated using the following given information: initial gas temperature (400°C), outlet gas temperature (200°C), initial water temperature (20°C), evaporated water temperature (100°C), water droplet diameter (50 μm), spray water quantity (5665 kg/h), and gas flow rate (34500 Nm^3/h).

3.3 *Simulation for the suppression of dioxin formation by spray water*

When an additional information for parameters was given (see Materials and Methods), simulation for the suppression of dioxin formation by spray water using the Altwicker theory was performed. The result of alterations of dioxin formation depending on spray droplet and inlet gas temperature is shown in Fig. 2. The dioxin yield must be estimated for each spray water droplet diameter. The highest dioxin formation was found at 350°C; thereafter, it decreased quickly. When an area of 500 μm for droplet-formed dioxins is defined as 100%, the values of formed dioxins for 400, 300, 200 and 100 μm droplet areas in Fig. 2 are estimated as 71, 41, 25 and 18%, respectively. It is revealed that the smaller size of droplet spray water and lower inlet gas temperature enable the decrease in dioxin formation. From these data, a dioxin suppression factor can be estimated. The dioxin suppression factor may be utilized as a useful tool for developing a program to reduce dioxin production using water spay.

Altwicker[5] studied the dioxin formation rate on the basis of the Arrhenius parameter. It has been reported that 94% of the dioxins created are generated on fly ash surfaces in the heterogeneous gas phase.[7] The decreased dioxin formation and/or the lower quenching temperature is revealed using the Altwicker theory equation with the information of inlet gas temperature and droplet spray water size. If the calculation program for the municipal solid waste element analysis is available, dioxin production can be estimated easily and rapidly.

4. Conclusions

In this study, we have established that dioxin formation quantity and the suppression of dioxins depend on droplet spray water. The information in this study will be useful for improving incinerator operation to minimize dioxin production.

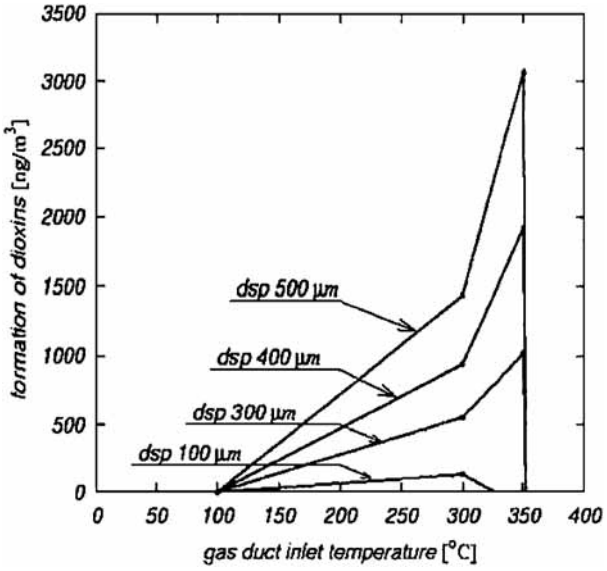

Fig. 2. Alterations of dioxin formation depending on spray water droplet and inlet gas temperature.

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