DIOXIN FORMATION OVER FLY ASH: OXYGEN DEPENDENCE, TEMPERATURE DEPENDENCE AND PHASE DISTRIBUTION

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ABSTRACT

Formation of PCDD/F over fly ash has been studied using fixed bed reactors under de novo conditions. Peak level of PCDD/F has been observed at around 300°C. At 250°C, most of the PCDD/F (>99%) formed are detected in the solid phase. As temperature increases, however, PCDD/F shift to the gas phase stream. At 350°C, only about 6% of the total dioxin are left in solid phase. The equilibrium constant of PCDD/F between those two phases may be represented by equation: $K = 3.5E19\ EXP\ (-26{,}380/T)$

PCDD/F formation has been studied at 300°C with oxygen concentration varying from 0 to 21%. Experimental data may be best fitted by an empirical equation: PCDD/F (ng/g-fly ash) = $455\ [O_2]^{0.5}$

INTRODUCTION

Formation of PCDD/F on fly ash at low temperature post combustion regimes is an important source for the hazardous emissions from Municipal Solid Waste Incinerators. Two major routes for this formation are postulated through laboratory investigations, de novo synthesis from native carbon in fly ash[1)] and formation from chemically similar organic precursors[2,3)]. PCDD/F formation is favored at around 300°C in both cases. Oxygen presence is needed for the de novo synthesis reaction to proceed. PCDD/F production strongly depends upon the oxygen content of the carrier gas.[4,5)] In past studies of the de novo pathway with incinerator fly ashes, a linear increase of PCDD/F yield as reaction time increases was observed;[3)] most of the PCDD/F produced were found in the solid phase.[6)] In this work, we report continuing studies of the de novo synthesis of PCDD/F in terms of oxygen and temperature dependence, phase distribution and reducing gas environmental effects.

EXPERIMENTAL

Two fixed bed reactors have been used in this study. Details of reactor 1 have been discussed elsewhere[7)] hence only a brief description is given here. Basically this is a horizontal tubular reactor 1.2 cm in diameter and 45 cm in length. A glass frit disc is placed in the middle of the reactor to hold fly ash. Mixtures of oxygen and nitrogen are flowed to the reactor through a mass flow controller at flow rates of 20-100 ml/min at reaction temperatures. Reactor 2 consists of a 2 cm diameter and 8 cm long thimble inserted into a temperature controlled 100 cm long vertical tube. Gas phase samples are taken at the top of the reactor by bubbling the outlet stream through a methylene chloride

sampling trap. Before each experiment, fly ash is charged to the thimble and the reactor is brought up to the reaction temperature under nitrogen flow. Reaction gas mixtures (oxygen/nitrogen or oxygen/carbon monoxide/hydrogen/nitrogen) are then flowed into the reactor at flow rate of 0.8 - 1 l/min. After the desired reaction time, the thimble is removed and put into a Soxhlet where it is extracted with toluene for 20 hours. Fly ash extract and gas phase impinger sample are then cleaned up and analyzed separately by GC/MS.

RESULTS

Oxygen dependence of the total PCDD/F formation (sum of those found in gas stream and in solid phase) on an Ontario fly ash is shown in Figure 1. Experimental data were taken at 300°C with both reactors using 1 gram of fly ash. Gas flow rates were 80 ml/min for reactor 1 and 0.8-1 l/min for reactor 2. Reaction time varied from 5 minutes to 1 hour. All the data are adjusted to 1 hour yield based on a linear PCDD/Fs production rate observed with 10% oxygen at 300°C for the same fly ash. As may be seen from this figure, total PCDD/Fs produced using those two reactors with different gas flow rates are in excellent agreement, indicating reactions are in kinetic controlled regime. As indicated in Figure 1, two points were taken with a reducing gas (CO: 36%, H_2: 17%). Interestingly, the same level and congener pattern of PCDD/F were produced as in a nitrogen/oxygen mixture, and CO does not appear to be a major reagent over this fly ash.

A best fit line is given by:

$$\text{PCDD/F (ng/g-fly ash)} = 455\ [O_2]^{0.5} \qquad (I)$$

where PCDD/F is the total of gas and solid phase produced by 1 gram of fly ash. $[O_2]$ is gas stream oxygen concentration in percent.

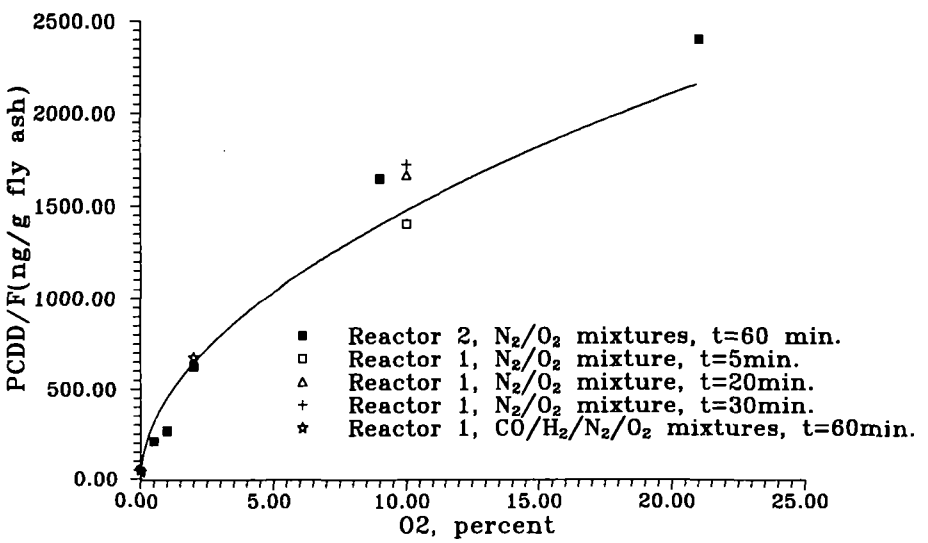

Figure 1. PCDD/Fs synthesis on 1g Ontario fly ash. The dependence of PCDD/Fs on Oxygen concentrations

Based on this result, oxygen concentration in an incinerator should be as low as possible in order to reduce dioxin production potential. It may also help if a stream of inert dilution gas such as nitrogen is introduced after combustion chamber to reduce oxygen concentration before it reaches post combustion regimes where PCDD/F formation rate from fly ash are the highest.

Another interesting phenomena is the phase distribution shift with changes in temperature. Table 1 shows the results obtained with reactor 2 for 250 to 350°C. At 250°C almost all the PCDD/F are found in solid phase, only less then 1% of the total PCDD/F are in the gas phase. As the temperature increases, gas phase PCDD/F rapidly increase, as does the total PCDD/F, up to 300°C. When the temperature increases further, while gas phase PCDD/F concentrations continuously increase, the total PCDD/Fs level starts to drop. At 350°C, most of the PCDD/Fs (94%) are detected in the gas phase and the total PCDD/Fs are less than those obtained at 300°C. Obviously, both desorption and destruction rates increase as the temperature rises.

Table 1 Dependence of PCDD/F formation on temperature over 1g Ontario fly ash. $[O_2]$ = 10%, Flow rate = 0.8 -1 l/min, Reaction time = 1 hour.

Run #	T °C	Gas PCDD	Gas PCDF	Solid PCDD	Solid PCDF	Total ng/g	Gas PCDD/F, %
A0517	250	ND	7	660	320	987	0.7
A0502	285	15	27	420	630	1092	4
A0120	300	231	382	480	559	1652	37
A0510	350	440	980	29	55	1515	94

Apparent equilibrium constant K between gas phase and solid phase PCDD/F may be estimated as:

$$\text{PCDD/F(s)} \underset{E_a}{\overset{E_d}{\rightleftarrows}} \text{PCDD/F(g)}$$

$$\text{PCDD/F(g)/PCDD/F(s)} = K = K_0 \exp -(E_d - E_a)/RT \qquad \text{(II)}$$

Plot logK vs 1000/T in Figure 2 gives $K_0 = 3.5 \times 10^{19}$ and $(E_d - E_a) = 52$ kcal/mol

At lower gas flow rate in reactor 1, no phase shift has been observed up to 300°C. This could have resulted from the lower gas flow rate. These results will be compared to the 4 step model developed previously.[8)]

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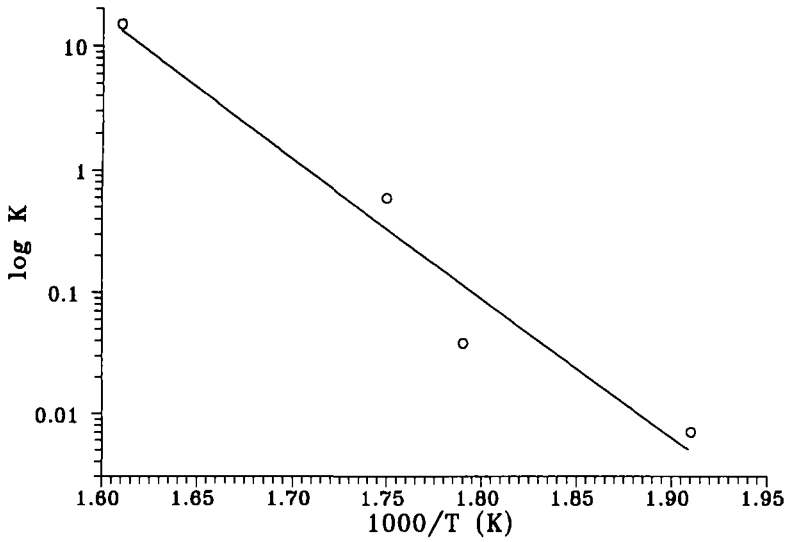

Figure 2 PCDD/F Equilibrium constant vs temperature. The slope gives the difference of desorption and adsorption activation energy.

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