ENGINEERING INTERPRETATION OF SOME KINETIC DATA OF PCDD/F FORMATION

H.HUANG and A.BUEKENS
Free University of Brussels (VUB), Department of Chemical Engineering and Industrial Chemistry, Pleinlaan 2, 1050 Brussel, Belgium

INTRODUCTION

Preventive engineering controls of dioxin formation and emission from municipal solid waste incineration require a better understanding of the mechanisms of dioxin formation. In recent years several laboratory experiments have been conducted to simulate dioxin formation in flow reactors. These experiments have revealed that PCDD/Fs can be formed through two indenpendent pathways, namely, *de novo* synthesis and precursor formation. In *de novo* synthesis, the carbon originates from the solid phase matrix; Carbon, oxygen, hydrogen and chlorine are incorporated through some organic reactions to form the polynuclear aromatic structures of dioxins. In precursor formation, the carbon comes from precursors such as chlorobenzenes and chlorophenols that are present in flue gas stream; these precursors are adsorbed onto solid phase materials, oxygenated and coupled to form dioxins. The two pathways of dioxin formation have been shown to be able to operate simultaneously and independently[1]. Kinetic data relating PCDD/F formation rate to temperatures, carbon concentration and time scale, etc. have been obtained in some cases[2].

However, when trying to apply the results of laboratory studies to incinerator design and operation, several important questions were raised:

—   can laboratory experiments explain the dioxin emission levels measured in industrial scale incinerators?
—   which pathway of PCDD/F formation is more important or are both of them important depending on operating conditions?
—   what are the implications to engineering controls of dioxin emission from municipal solid waste incineration?

This paper examines these problems through some quantitative evaluations of the kinetic data obtained so far.

de Novo SYNTHESIS

Relevant experiments are listed in table 1. Fixed bed reactors were generally adopted. Air or O_2, N_2, HCl and H_2O mixtures were flown through a fixed bed of fly-ash. Gas

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phase PCDD/Fs produced were captured and analysed together with solid phase PCDD/Fs. The various units reporting PCDD/F formation in the literature have been converted into μg/g-solid·min (total PCDD/Fs) to allow for a comparison. From table 1, it can be seen that maximum PCDD/F formations occur at around 300°C and maximum formation rates vary one order of magnitude from 0.034 to 0.321 μg/g·min due to variations in analytical procedure and testing material.

Table 1. *de Novo* Synthesis of PCDD/Fs

Gas phase material	Solid phase material	Temp.[a] °C	Sampling Time (min)	Total PCDD/F formation rate[b] (μg/g·min)	Ref.
O_2 and N_2	Fly-ash	300	30	0.034	[2]
Air	Fly-ash	300	120	0.059	[3]
^{13}C-P_5CP and air	Silica gel, charcoal, $CuCl_2$[c]	300	10-60	0.321 (^{12}C-PCDD/F)	[1]
N_2, O_2 and HCl	Fly-ash (organics removed) and carbon	373	60	0.128	[4]
Air and water vapour	Mg-Al-Silicate, charcoal, KCl and Cu(II)	300	120	0.054	[5]

a. Temperatures at which maximum PCDD/F formations were observed.
b. Total PCDD/F formation rate based on weight of solid phase material (g) and sampling period (min).
c. When without $CuCl_2$, ^{12}C-PCDD/Fs were not detected.

PRECURSOR FORMATION

The experimental rates of PCDD/F formation through precursor pathway differ greatly from 7.2×10^{-6} to 8.67 μg/g·min as shown in table 2. This could have been caused mainly by the different precursor concentrations adopted in experiments. In the first four experiments listed in table 2, chlorocompound precursor solutions were either placed on top of the fly-ash bed or be carried into the reactor by gas from precursor solution reservoirs. It appears that in these experiments, precursor concentrations were much higher than in incinerator postfurnace conditions where only trace quantities of chlorobenzenes/phenols are present in flue gas as the products of incomplete combustion. In Altwicker and Milligan's experiment[2], the precursor concentration was around 3.75×10^5 μg/NM^3. In some incinerator measurements[10], precursor concentrations were typically below 10 μg/NM^3. According to modelling calculation[0], dioxin formation can be assumed to be proportional to precursor concentration. Assuming a first order kinetics, the actual PCDD/F formation rate can be estimated as:

$$k_{actual} = k_{experimental} \cdot [Precursor]_{actual} / [Precursor]_{experimental}$$

$$=1.6 \times 10 / 3.75 \times 10^5$$
$$= 4.3 \times 10^5 \ \mu g/g \cdot min.$$

Thus when comparing to actual incinerator conditions, the data of the first four experiments listed in table 2 should be reduced to 4.3×10^5, 5.6×10^6, 6.7×10^5 and $2.3 \times 10^4 \ \mu g/g \cdot min$ respectively, which are roughly in agreement with the data of the last four experiments in table 2 where the precursors were the combustion products of chlorocompounds.

Table 2. Precursor Formation of PCDD/Fs

Gas phase material	Solid phase material	Temp.[a] °C	Sampling time (min)	Total PCDD/F formation rate[b] ($\mu g/g \cdot min$)	Ref.
2,3,4,6-T_4CP, O_2 and N_2[c]	Fly-ash	325	2-15	1.6	[6]
^{13}C-P_5CP and air[d]	Fly-ash	300	60	0.21	[7]
Chlorophenol, N_2 and O_2[c]	CuO	400	30	2.5	[8]
^{13}C-P_5CP and air[d]	Silica gel, charcoal, CuCl$_2$[e]	300	10-60	8.67 (^{13}C-PCDD/F)	[1]
1,2-D_2CP[f]	Fly-ash	300	30	1.9×10^4	[9]
PCP[f]	Fly-ash	300	60	7.2×10^6	[9]
1,2-D_2CP[f]	Fly-ash	300	180	1.6×10^4	[9]
1,2,4-T_3CP[f]	Fly-ash	300	180	6.0×10^5	[9]

a. Temperatures at which maximum PCDD/F formations were observed.
b. Total PCDD/F formation rate based on weight of solid phase material (g) and sampling period (min).
c. O_2/N_2 mixture was passed through chlorophenol solution reservoirs.
d. Chlorophenol solution was put on top of the solid phase material.
e. Without CuCl$_2$, ^{13}C-PCDD/F formation rate was 0.61 ($\mu g/g.min$).
f. The combustion products of chlorophenols were passed over fly-ash.

COMPARISON OF *de Novo* SYNTHESIS AND PRECURSOR FORMATION

From the above recalculated data, it can be seen that the dioxin formation rate through *de novo* synthesis is in the range of 0.034 to 0.321 $\mu g/g \cdot min$ and through precursor pathway is in the range of 5.6×10^6 to $2.3 \times 10^4 \ \mu g/g \cdot min$. *De novo* synthesis is at least two orders of magnitude larger than precursor formation. The time scale of these laboratory experiments ranged from 2 to 180 minutes. In a shorter time scale, larger initial PCDD/F formation rates are possible both in *de Novo* synthesis and precursor

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formation. But dioxin formation through *de novo* synthesis is still likely to be much more important than precursor pathway.

Precursor formation and *de novo* synthesis may have some common or similar mechanistic steps as both of them have optimal temperatures from 250 to 350°C and are strongly catalysed by Cu(II). But precursor formation can also be catalysed by fly-ash surfaces and other metallic ions.

COMPARISON OF LABORATORY STUDY AND INCINERATOR MEASURMENT

Incinerator measurements are related to PCDD/F formation rate by:

$$D = k \cdot A \cdot t$$

where, D: total PCDD/F formation (μg/NM^3), k: PCDD/F formation rate (μg/g·min), A: fly-ash loading (g/NM^3), t: solid phase residence time in the 250 to 400 °C region (min). As an estimation, neglecting the variations of k with temperature, k can be taken as 0.034 μg/g·min as shown in the first experiment in table 1 where fly-ash was used in the experiment rather than some synthetic materials. Solid phase residence time t is difficult to estimate, as the critical 250 to 400°C region usually lies in the convective part of the boiler or in various air pollution control equipments. The geometries of these equipments are complicated and multiphase, turbulent flow is involved. Alternatively, from known incinerator measurements the required solid phase residence time to reach actual dioxin emission levels can be calculated for comparison.

The calculation requires the knowledge of fly-ash loading and dioxin level (including dioxins in flue gas and fly-ash) before and after the low temperature zone. Some data sets in the literature have been calculated to check the experimental data: Takeshita et.al.[11] reported that in an ESP inlet, gas temperature was 300°C , fly-ash loading was 1.35 g/NM^3 and dioxin level increased by 0.23 μg/NM^3 in the ESP. The average fly-ash residence time required to reach the dioxin level can be calculated as: t = D / kA = 0.23 / 0.034X1.35 = 5 min. Teller[12] reported for a boiler exhaust that total PCDD/Fs were 0.0285 μg/NM^3, fly-ash loading was 4.6 g/NM^3, so that t = 0.0285 / 0.034X4.6 = 10 sec. These calculated residence times are in reasonable ranges. Thus it seems that the experimental PCDD/F formation rate would be able to predict actual PCDD/F emission levels.

SUMMARY

Dioxin formation through precursor pathway is probably very sensitive to precursor concentration. In some laboratory experiments, *de novo* sythesis of PCDD/Fs has been shown to be slower than precursor formation. But when corrected according to actual precursor concentrations in typical incinerator postfurnace condition, *de novo* sythesis has been found to be about two orders of magnitude faster than precursor formation. Thus *de novo* synthesis is probably more important than precursor formation under incinerator postcombustion conditions.

Comparison of experimental PCDD/F formation rate with incinerator measurements appear to indicate that the laboratory studies could explain the observed levels of dioxin emissions from industrial scale incinerators, although more extensive

modelling works are required to verify this. Engineering measures that can reduce fly-ash loading and residence times in postcombustion zone should also be able to reduce dioxin emissions. Such measures may include adjusting underfire air to reduce particle entrainments from combustion chamber, better boiler design to prevent fly-ash deposition and increasing soot-blowing in the 250-400°C region.

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