KINETIC ASPECT OF DE NOVO SYNTHESIS OF PCDD/F IN INCINERATOR FLY ASH

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Introduction

Stieglitz et al.[1,2] found that de novo synthesis is active on incinerator fly ash at time scales of 15, 30, 60 min. Milligan and Altwicker[3] observed de novo synthesis at time scales of 5, 20 and 30 min. Blaha and Hagenmaier[4] tested a model fly ash and discovered that de novo synthesis can take place at a time scale as short as 1 min. Thus de novo synthesis of PCDD/F on various carbon-containing materials and time scales has already been established. In this paper we present a kinetic model for de novo synthesis based on relevant rate processes.

Kinetic Model Development

The following reaction steps are considered:

Rxn. 1: $C + aO_2 \rightarrow bCO + cCO_2 + dAr + e(PCDD/F)_s$
Rxn. 2: $(PCDD/F)_s \rightarrow (PCDD/F)_g$
Rxn. 3: $(PCDD/F)_s \rightarrow$ other products

The subscript s and g indicate solid and gas phase, respectively. Rxn. 1 is a global reaction describing carbon gasification and PCDD/F formation; Rxn. 2 is the desorption of solid-phase PCDD/F to the gas-phase; Rxn. 3 is the degradation of PCDD/F to other products. The differential rate equations for the above set of reactions are:

Eq. 1:
$$-\frac{d[C]}{dt} = k_1[C][O_2]^a$$

Eq. 2:
$$\frac{d[PCDD/F]_s}{dt} = f\,k_1[C][O_2]^a - (k_2 + k_3)[PCDD/F]_s$$

Eq. 3:
$$\frac{d[PCDD/F]_g}{dt} = k_2[PCDD/F]_s$$

where, [C] is the carbon content in incinerator fly ash (g/g); $[O_2]$ is the partial pressure of oxygen (atm); *[PCDD/F]* is the PCDD/F content (μg/g); t is reaction time (min); k_1 is the rate constant of Rxn. 1 (1/min·atm$^{0.5}$), k_2 and k_3 are the rate constant for Rxn. 2 and 3, respectively (1/min). According to the

Arrhenius equation, $k_i = A_i\exp(-E_i/RT)$, where A_i is the pre-exponential factor and E_i is the activation energy; A_i has the same unit as k_i; and E_i has the unit cal/mol. The gas constant R = 1.987 cal/mol·K; T is temperature in K. f is the PCDD/F yield (μg/g) from carbon gasified: $f = 10^{-6}A_4\exp(-E_4/RT)$, and the reaction order a = 0.5 (the parameters f and a are discussed next section). Integration of Eq. 1 gives

Eq. 4: $$[C] = [C]_0 e^{-k_1[O_2]^{0.5}t}$$

where, $[C]_0$ is the initial carbon content (g/g). Substitute Eq. 4 into Eq. 2,

$$\frac{d[PCDD/F]_s}{dt} = f[C]_0 k_1 [O_2]^{0.5} e^{-k_1[O_2]^{0.5}t} - (k_2 + k_3)[PCDD/F]_s$$

The solution of this first-order differential equation is

Eq. 5: $$[PCDD/F]_s = \frac{f[C]_0 k_1 [O_2]^{0.5}}{k_2 + k_3 - k_1[O_2]^{0.5}} [e^{-k_1[O_2]^{0.5}t} - e^{-(k_2+k_3)t}]$$

Substitute Eq. 5 into Eq. 3, and integration leads to

Eq. 6: $$[PCDD/F]_g = \frac{f[C]_0 k_2}{k_2 + k_3 - k_1[O_2]^{0.5}} [1 - e^{-k_1[O_2]^{0.5}t} - \frac{k_1[O_2]^{0.5}}{k_2 + k_3}(1 - e^{-(k_2+k_3)t})]$$

The total amount of PCDD/F is

Eq. 7: $$[PCDD/F]_t = [PCDD/F]_s + [PCDD/F]_g$$

Eqs. 5, 6 and 7 relate the amount of PCDD/F formed to process variables including carbon content $[C]_0$, oxygen $[O_2]$, temperature T (through the rate constants), and reaction time t.

Estimation of Model Parameters

Kinetic parameters for carbon gasification (k_1), PCDD/F yield (f), desorption (k_2), and degradation (k_3) have been estimated. According to refs[5,6], a = 0.5 in Eq. 1. Following ref[2] the parameters of f are estimated in Table 1 (the negative activation energy in this case is a fitting parameter and reflects that f decreases as T is increased). For PCDD/F desorption and degradation, data in papers[7,8] were used. After preliminary estimation of model parameters, experimental data of de novo synthesis were used to check the model, and the parameters were adjusted to obtain a best fit to experimental data. Final model parameters are shown in Table 1. With these parameters, PCDD/F formation levels were calculated from Eqs. 5, 6 and 7, and listed in Table 2 and 3. It can be seen that the model agrees with experimental data within the usual range of uncertainty in de novo synthesis tests.

Table 1. Kinetic parameters for rate equation: $k_i = A_i\exp(-E_i/RT)$.

	A	E (cal/mol)
k_1	5.1×10^{4} l/min·atm$^{0.5}$	17000
k_2	1.05×10^{11} 1/min	35000
k_3	8.5×10^{14} 1/min	44250
f	1.6×10^{7} μg/g	-3500

Table 2. Comparison of PCDD/F formation from laboratory experiment and model calculation.

Oxygen (atm)	Temperature (°C)	Reaction time (min)	Total PCDD/F formation (μg/g)	
			Experiment	Calculation
Series I. Stieglitz et al.[2], $[C]_0$ = 0.045 g/g				
0.21	275	15	1.78	1
		30	1.81	1.91
		60	2.81	3.5
	300	15	1.36	1.55
		30	3.83	2.71
		60	8.12	4.2
	350	15	0.91	1.29
		30	1.67	1.57
		60	4.9	1.89
Series II. Milligan and Altwicker[3], $[C]_0$ = 0.019 g/g				
0.1	275	30	0.3	0.56
	300		0.7	0.82
	325		0.57	0.77
	300	5	0.12	0.1
		20	0.55	0.59
Series III. Altwicker et al.[7], Assumed $[C]_0$ = 0.02 g/g				
0.01	300	60	0.22	0.49
0.04			0.6	0.93
0.09			1.6	1.33
0.21			2.37	1.87
0.1	250		0.98	0.67
	285		1.09	1.28
	300		1.65	1.38
	350		1.51	0.72
Series IV. Addink et al.[9], Assumed $[C]_0$ = 0.02 g/g				
0.1	251	60	0.21	0.69
	275		0.4	1.11
	299		3	1.39
	325		2.94	1.01
	353		1.13	0.7
	400		0.67	0.46
	425		0.29	0.35
	450		0.21	0.26
	500		0.02	0.15
	548		0	0.09

Calculation Results

The differential form of the kinetic model (Eqs. 1, 2 and 3) are numerically integrated with kinetic constants and reaction rates evaluated using local temperatures. To account for ash deposition, an average residence time of fly ash in the relevant regions is assumed, and the actual fly ash amount including fly ash holdup is calculated by: (input fly ash concentration) x (residence time of fly ash) /

Table 3. Amounts of PCDD/F in the gas phase (wt. % of total).

Temperature (°C)	Experiment (Altwicker et al.[7])	Calculation
250	0.7	0.8
285	4	6.3
300	37	14.8
350	94	84.3

Table 4. Calculated PCDD/F formation levels assuming different flue gas/fly ash residence times[a].

Equipment	Temperature[b] (°C)		Residence time		Net PCDD/F formation at the equipment	
	In	Out	flue gas (sec)	fly ash	Gas phase (μg/Nm^3)	Solid phase (μg/g)
Boiler	550	250	5	5 sec	0.009	0.011
				1 min	0.11	0.13
				5 min	0.56	0.66
Electro filter	350	200	5	10 min	0.001	0.42
				30 min	0.004	1.26
Fabric filter	250	150	10	30 min	0	0.12
				60 min	0	0.24

[a]Other input conditions are: fly ash concentration = 10 g/Nm^3; initial carbon content in fly ash = 0.02 g/g; partial pressure of oxygen = 0.1 atm. [b]Decreasing linearly from inlet to outlet temperature.

(residence time of flue gas). [C] and [PCDD/F] now are the actual carbon amount (g/Nm^3) and PCDD/F amount (μg/Nm^3), respectively. The calculation results are summarised in Table 4. In the boiler section if there is no ash deposition (i.e. the residence times of flue gas and fly ash are the same), then the PCDD/F formation level is low. If the residence time of fly ash is increased to several minutes, then the de novo synthesis of PCDD/F is very much increased, and PCDD/F formed at this temperature range have a significant portion present in the gas phase. For electrofilters, the calculated amount of PCDD/F from de novo synthesis is about the same as in the boiler section, although PCDD/F formed in this temperature range are mostly present in the solid phase. For fabric filters, PCDD/F formation from de novo synthesis is predicted to be entirely in the solid phase.

References

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