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Critical Review

Mechanisms of Formation and Destruction of Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans in Heterogeneous Systems

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Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans are toxic compounds formed during natural processes and human activities. The basic questions about PCDD/F formation such as (1) what is the influence of process parameters on the formation process, (2) what reaction mechanisms are involved in formation, and (3) what kinetics describes PCDD/F formation are discussed, and recommendations are given.

Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) are toxic compounds that are formed during some natural processes (*1*) and various human activities (*2*). Their structure is depicted in Figure 1. Anthropogenic sources include the incineration of household waste, a fact which was discovered in 1977 (*3*). Off-gas (flue gas) and residue particles (fly ash), both formed during municipal waste incineration, contain PCDD/F (*4*). The formation of these compounds could occur via homogeneous gas-phase reactions in the combustion chamber. However, Shaub and Tsang showed that PCDD/F formed via such a mechanism is unlikely to survive if temperatures are high enough (>900 °C) (*5*). The PCDD/F concentration in the flue gas leaving the combustion chamber increases while traversing the post-combustion zone (*6, 7*). This observation suggests that the formation takes place in the post-combustion zone, involving lower temperatures and possibly a catalyzed mechanism. In 1985, Shaub and Tsang proposed a heterogeneous and fly ash-catalyzed mechanism of formation (*8*). The catalytic potential of waste incinerator fly ash has been verified in a large number of publications since 1982.

It is useful to make a distinction between collected and uncollected fly ash particles. Fly ash is removed from the flue gas before this leaves the stack. This removal takes place in the air pollution control device in the post-combustion zone. While traversing the post-combustion zone, the gases are cooled down. Collected fly ash, e.g., on an electrostatic precipitator (E-filter) or stuck to the wall, can have a residence time in the post-combustion zone of several hours (*9*), depending on the removal frequency from the E-filter. Uncollected fly ash is not trapped in the air pollution control device and is emitted into the environment with the flue gas. The residence time of these uncollected particles is a few seconds at the most. Obviously on

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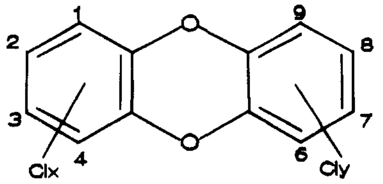
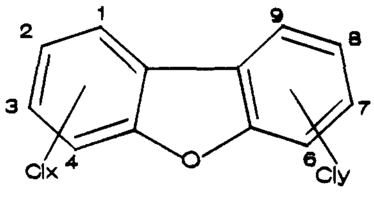


Polychlorinated dibenzo-p-dioxin



Polychlorinated dibenzofuran

FIGURE 1. Structure of polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF).

collected fly ash a much longer time is available for the formation of PCDD/F than on uncollected fly ash. The cooling down of the flue gas from >850 °C in the combustion chamber to ca. 100 °C when leaving the stack provides optimum temperatures for fly ash-catalyzed formation reactions.

Purpose and Structure of Review

Basic questions regarding PCDD/F formation are as follows: (1) What is the influence of process parameters—reactant, surface, chlorine source, temperature, catalyst, reaction time, atmosphere, and water—on the formation process? (2) What reaction mechanisms are involved in formation? (3) What kinetics can be used to describe PCDD/F formation, and can laboratory scale experiments explain the formation rates in real incinerators? What differences exist between formation on collected and uncollected fly ash? We will attempt to answer these questions with the published literature. Table 1 offers a framework for discussion of the parameters listed under question 1. This part is followed by a discussion of questions 1, 2, and 3. Finally, a section with conclusions and recommendations is presented.

Method

Simulation of processes on collected fly ash on a laboratory scale is generally carried out in a flow system, an example of which is given in Figure 2. A general description of the experiment is as follows. Fly ash (or another surface material) is placed in a Pyrex or quartz tube as a fixed, packed bed and heated to the desired temperature in an oven. A calibrated gas stream (simulating flue gas in the post-combustion zone) is passed over for a certain time and in this period the reaction takes place. Reactants are introduced by (i) mixing solid reactants with the matrix physically before the experiment; (ii) mixing the reactant in a solution with the matrix, followed by evaporation of the solvent; (iii) placing the matrix in the oven without reactant and evaporating the reactant onto the matrix at the beginning of the experiment; (iv) passing the gas stream through a reservoir with reactant before entering the reactor; this results in a constant introduction of reactant during the whole experiment.

After the experiment, reaction products are isolated from the matrix, purified, and analyzed by means of GC coupled with mass spectrometry. Reaction products desorbing from the matrix during the experiment can be recovered using a cold trap behind the reactor. Another approach is to monitor the reaction products desorbing from the matrix during the experiment by on-line GC or GC/MS analysis.

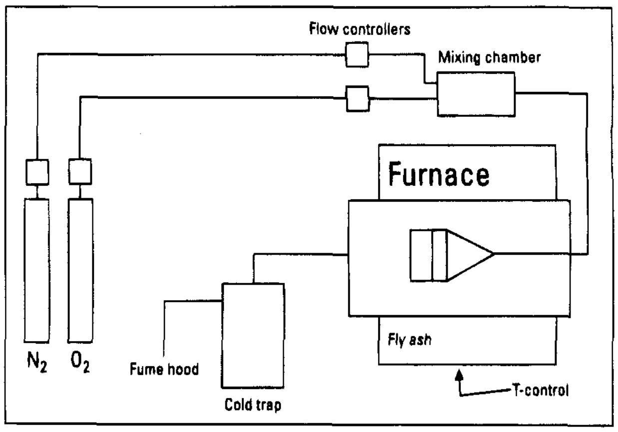


FIGURE 2. Apparatus used for fixed bed experiments with fly ash.

Most of the research carried out in this field has one or more of the following characteristics, which provides the link between laboratory simulation and post-combustion zone conditions: (a) Use of incinerator fly ash as an active surface to stay as close as possible to the fly ash surface generated in incinerators. Model supports used are SiO_2 or Al_2O_3, which have the advantage of a better defined structure. (b) The fly ash is present as a fixed bed, which is simulating the collected fly ash particles, through which a gas stream passes. (c) Temperature ranges studied are in between 200 and 600 °C, which is the relevant temperature for formation in the post-combustion zone (as will be shown below). (d) Mixtures of N_2, O_2, HCl, Cl_2, SO_2, and H_2O among others are used to model the flue gas. (e) Reaction times up to several hours, as the residence time of fly ash particles in the post-combustion zone can be hours.

Influence of Process Parameters

Reactants. Two terms are used for compounds capable of PCDD/F formation: *de novo synthesis* is used for macromolecular carbon structures; *precursors* are used for small organic molecules.

Various carbon species form PCDD/F: activated carbon (*10*), [^{13}C]carbon (*17*), bituminous coal (*55*), charcoal (*31*), residual carbon (i.e., inextractable and naturally present on fly ash) (56), soot (75), and sugar coal (75). No information is presented in the various publications cited on the chemical composition of these carbon species, making a good assessment of the differences between them impossible. One would expect that some characteristics, e.g., the [aliphatic]:[aromatic] ratio or percentage of certain functional groups, have a great influence on the potential to build PCDD/F. Some proof for this hypothesis is found in the fact that graphite (with a low [aliphatic]:[aromatic] ratio and crystalline structure) does not give PCDD/F formation (*75*).

Various classes of precursors capable of PCDD/F formation have been identified: (a) aliphatic compounds: 2,3-dimethyl-1-butene (*37*) and propene (57); (b) monocyclic aromatic compounds without functional groups: benzene (*61*); (c) monocyclic aromatic compounds with functional groups: benzaldehyde (*50*), benzoic acid (*50*), phenol (*23*), and toluene (*50*); (d) chlorinated aromatic compounds: ortho-, meta-, and parachlorophenol (*22*); 2,4,5-, 2,4,6- (*19*), and 3,4,5-trichlorophenol (*45*); 2,3,4,6-tetrachlorophenol (*19*); pentachlorophenol (*19*); 1,2,4,5-tetrachlorobenzene (*83*); (e) anthraquinone derivatives: anthraquinone-2-carboxylic acid (*14*) and 2,6-dihydroxyanthraquinone (*14*). Obviously, a wide range of compounds is capable of PCDD/F formation. Possession of an aromatic ring or Cl and O atoms is no prerequisite. Consequently, the number of different compounds in flue gas which contribute to PCDD/F formation in the post-combustion zone may be very large.

Various specific PCDD/F congeners have been studied. DD and DF (*24*), 1-MCDD (*63*), 1,2,3,4-T_4CDD (*65*), and 2,3,7,8-T_4CDD (*48*) can all be chlorinated using various chlorinating agents. Dechlorination studies have been carried out with 1,2,3,4-T_4CDD (*62*) and OCDD/OCDF (*21*), resulting in lower chlorinated congeners. Br/Cl exchange takes places when heating 2,3,7,8-T_4BDD in the presence of HCl (*51*). These results show that PCDD/Fs are not stable compounds after their formation but will undergo subsequent reactions like chlorination or dechlorination (and probably also decomposition).

Surface. A large number of surface materials have been investigated, apart from fly ash: Al_2O_3 (*10*), $Al_2O_3SiO_2$ (*53*), carbon (*33*), firebrick (*45*), glasswool (*10*), $MgSiO_2$ (*44*), $MgAlSiO_2$ (*75*), SiO_2 (*33*), SiO_2NaOH (*10*), and tenax (*64*).

Formation of PCDD/F from carbon is possible on most of these surfaces, but the presence of a catalyst is essential. These results indicate that those properties of fly ash that are responsible for stimulating PCDD/F formation (a.o. providing a support and presence of catalyst) can be easily simulated on other surfaces (with a catalyst).

Rghei et al. studied the relative rate of chlorination of DD on different surfaces in a HCl/air atmosphere at 150 °C (*64*). Results were 2-MCDD as the major chlorination product with the following relative rates: fly ash 1, SiO_2 0.05, carbon 0.02, and tenax 0.001. Obviously, without an additional catalyst, the model surfaces are much less effective in promoting chlorination reactions than fly ash. However, results found by Schoonenboom et al. (*70*) suggest that the dechlorination of OCDD and OCDF is a fast process on Al_2O_3, when compared with fly ash.

Chlorine Source. Both gaseous and solid compounds appear to be capable of providing the necessary chlorine atoms during the formation of PCDD and PCDF. Gases include HCl (*13*) and Cl_2 (*55*). Salts like KCl (*10*) and NaCl (*55*) act as a chlorine source too. CuCl (*38*), $CuCl_2$ (*27*), and $FeCl_3$ (*61*) can act both as a catalyst and as a chlorine source.

Temperature. Chlorination and dechlorination of PCDD/F on fly ash is possible at low temperatures. DD can be chlorinated already at 50 °C on fly ash in HCl/air; 150 °C is the optimum temperature for this reaction (*63*). A temperature of 120 °C is reported for dechlorination of OCDD on Cu by Hagenmaier et al. (*84*). Stepwise dechlorination of OCDD/OCDF on fly ash in He starts at 250 °C. Rates increase with the temperature. At 450 °C less than 1% of the starting OCDD/F is left (*21*).

The lowest temperature reported for the formation of PCDD/F from activated carbon on fly ash is 200 °C (*12*). Optimum ranges vary: 300 °C for charcoal/fly ash (*75*), 300–330 °C for residual carbon on fly ash (*56*), and 350–375 °C for activated carbon/fly ash (*12, 13*). At 470 °C, a second maximum is observed with residual carbon on fly ash, and detectable amounts of PCDD/F are formed even at 550 °C (*73*).

Formation from phenol on fly ash in the presence of HCl sets in at 325 °C with an optimum at 400 °C, maximum PCDD formation from *o*-chlorophenol is found at 450 °C (*24*). With 2,3-dimethyl-1-butene on fly ash, the optimum temperature for PCDD/F formation lies at 500 °C (*37*); with propene on fly ash, the formation of PCDD/F was observed at 576 °C (*57*).

Catalyst. Both $CuCl_2$ and $FeCl_3$ catalyze formation reactions of PCDD/F from carbon (*75, 79*). CuCl (*38*), $CuCl_2$ (*27*), CuO (*27, 39*), and $CuSO_4$ (*39*) have been identified as catalysts for PCDD formation from phenol. NiO catalyzes PCDD formation from chlorophenols (*40*) as does $Zn(NO_3)_2$ (*43*). $FeCl_3$ catalyzes PCDD/F formation from benzene (*61*). Carbon (matrix and catalyst simultaneously) promotes PCDD formation from pentachlorophenol (*31*). Coupling reactions of chlorophenates, giving rise to PCDD, take place on SiO_2 and SiO_2NaOH without the presence of a catalyst (*47, 60*).

DD/F can be chlorinated by $CuCl_2$ on $SiO_2Al_2O_3$ (*52*). Both OCDD and OCDF can be dechlorinated by Al_2O_3 without a catalyst (*70, 71*).

Reaction Time. Experiments with carbon on fly ash or a model support generally yield PCDD/F for 2–4 h, eventually followed by a decrease of the PCDD/F concentration (*12, 75, 82*). Such a decrease points to depletion of one of the reactants (e.g., carbon) and shows that formation and destruction are simultaneous reactions, the balance depending on the rates of both pathways.

PCDD formation from 2,3,4,6-tetrachlorophenol on fly ash at 300 °C gives a linear relationship between formation and time between 0 and 20 min, afterwards the formation remains linear but at a higher rate (*19*). Using pentachlorophenol on fly ash in air at 300 °C with reaction times of 5–120 min, Ross observed maximum formation of PCDD after 5 min, followed by a strong decrease and dechlorination (*68*).

Chlorination of 1,2,3,4-T_4CDD on fly ash at 150 °C reaches a maximum after 30 min, followed by a decrease of the PCDD formed (*35*). Hagenmaier et al. found that OCDD and OCDF can be fully dechlorinated within 5 min in the presence of Cu at 280 °C, at 120 °C a much longer time is needed (20 h) (*84*). Dechlorination of 1,2,3,4-T_4CDD on fly ash in He at 250–300 °C levels off after 15 min (*62*).

Atmosphere. Oxygen is essential for PCDD/F formation from carbon: when a carbon/fly ash mixture is heated at 348 °C in N_2, no PCDD/F formation takes place. Already with 1% O_2 in N_2 formation starts. At 10% O_2/90% N_2, 11 times more PCDD and three times more PCDF are formed than with 1% O_2 in N_2 (*15*).

Formation of PCDD from trichlorophenols and pentachlorophenol on fly ash is possible in N_2 (*30*). Phenol on $CuCl_2$ forms PCDD in 90%N_2/10%O_2 (*27*) as does pentachlorophenol on fly ash in air (*32*).

Dechlorination reactions to lower chlorinated congeners are observed when heating original fly ash or OCDD/OCDF on fly ash under a He flow (*21*). Collina et al. heated OCDD/fly ash in air, leading to dechlorination too (*28*).

Water. As incinerator flue gas contains H_2O, a number of groups have performed experiments to compare PCDD/F formation with and without water in the gas flow. Results are presented below.

TABLE 1

PCDD/F Formation: Characterization of Parameters Studied

ref	reactant	surface	chlorine source[a]	temp (°C)	catalyst[b]	reaction time	residence time[c] (s)	atmosphere	flow	water[d]
10, 11	activated carbon	various	$CuCl_2$, KCl, HCl	300	$CuCl_2$	120 min	not reported	air, HCl, H_2O	17 mL/min	+
12	activated carbon	fly ash	—	200–400	—	30–360 min	not reported	air, H_2O	17 mL/min	+
13	activated carbon	fly ash	HCl	300–400	—	30–60 min	not reported	N_2, O_2, HCl, H_2O	115–142 mL/min	0–27 mL/min
14	anthraquinone derivs	fly ash	HCl	348	$CuCl_2$	50 min	not reported	N_2, O_2, HCl	119 mL/min	—
15	activated carbon	fly ash	NaCl	348	—	50 min	not reported	N_2, O_2	205–225 mL/min	—
16	activated carbon	fly ash	NaCl	348	—	60 min	not reported	N_2, O_2, H_2O	59 mL/min	+
17	^{13}C-carbon	sieved fly ash	$CuCl_2$, KCl	300	$CuCl_2$	120 min	not reported	air	45–50 mL/min	—
18	various	fly ash	—	300	—	60 min	0.1	air	not reported	—
19	chlorobenzenes, chlorophenols, ^{13}CO, ^{13}C-carbon	sieved fly ash	—	300	—	2–120 min	not reported	N_2, O_2	80 mL/min	—
20	2,3,4,6-tetrachlorophenol	fly ash, glass beads	—	250–400	—	2–15 min	not reported	N_2, O_2	20–100 mL/min	—
21	original fly ash, OCDD, OCDF	fly ash	—	200–470	—	60 min	not reported	He	30 mL/min	—
22	monochlorophenols	fly ash	—	326–375	—	*e*	3.2–5.5	O_2, N_2, H_2O	164–224 mmol/h	0–0.95 mmol/h
23	phenol, chlorobenzene	fly ash	HCl	150–470	—	*e*	0.5–1.1	O_2, N_2, HCl	not reported	—
24	DD, DF, biphenyl, diphenyl ether	fly ash	HCl	150–500	—	*e*	0.5–0.9	O_2, N_2, HCl	not reported	—
25	phenol, DD	fly ash	HCl	150–500	—	*e*	0.4–0.7	N_2, O_2, HCl, H_2O	not reported	$3-7 \times 10^{-5}$ M
26	chlorobenzene, phenol, monochlorophenols	fly ash, Al_2O_3, sand	$CuCl_2$, HCl	150–600	$CuCl_2$, CuO	*e*	0.3–8.0	N_2, O_2, HCl, H_2O	164–214 mmol/h	0.2–0.4 vol %
27	phenol	—	various	300	$CuCl_2$, CuO	30 min	not reported	N_2, O_2, $CuCl_2$	1000 mL/min	—
28	OCDD, OCDF	fly ash	—	200–300	—	15–240 min	not reported	N_2, air, H_2O	not reported	0–150 mg/L of gas
29	original fly ash	sieved fly ash	—	100–200	—	2–48 h	not reported	N_2	100 mL/min	—
30	tri- and pentachlorophenol	fly ash, firebrick	—	300	—	60 min	not reported	N_2	10 mL/min	—
31	charcoal, [$^{13}C_6$]pentachlorophenol	SiO_2	$CuCl_2$	300	$CuCl_2$	10–60 min	not reported	air	3–19 mL/min	—
32	pentachlorophenol	sieved fly ash	—	300	—	60 min	not reported	air	3 mL/min	—
33	charcoal, [$^{13}C_6$]pentachlorophenol	SiO_2	$CuCl_2$	250–350	$CuCl_2$, charcoal	10–60 min	not reported	air	3–19 mL/min	—
34	original fly ash, residual carbon	fly ash	Cl_2	200–300	—	60 min	not reported	Cl_2	10 mL/min	—
35	1,2,3,4-T_4CDD	fly ash	HCl	50–250	—	3–120 min	not reported	air, HCl	20 mL/min	—
36	1,2,3,4-T_4CDD	fly ash	—	30–150	—	10 min	not reported	air, NO_2	not reported	—
37	2,3-dimethyl-1-butene	fly ash	HCl	352–550	—	*e*	2.7–2.9	N_2, O_2, HCl, H_2O	223–289 mmol/h	154 mmol/h
38	phenol	—	CuCl, HCl, Cl_2	350–500	CuCl	60 min	not reported	N_2, O_2, HCl, Cl_2	930 mL/min	—
39	phenol, chlorophenols	—	HCl, Cl_2	300–500	CuO, $CuSO_4$	30 min	not reported	N_2, O_2, HCl, Cl_2, SO_2	not reported	—
40	chlorophenols	—	—	200–500	various	30 min	not reported	N_2, O_2	not reported	—
41	original fly ash	fly ash	HCl	300	—	120 min	not reported	N_2, air, HCl	25 mL/min	—
42	pentachlorophenol	fly ash	—	300	—	60 min	not reported	N_2	10 mL/min	—
43	pentachlorophenol	SiO_2	—	300	$Cu(OH)_2$, $Zn(NO_3)_2$, NaOH	60 min	not reported	N_2	10 mL/min	—
44	original fly ash, charcoal	fly ash, $MgSiO_2$	$CuCl_2$, HCl	300	$CuCl_2$	100–120 min	not reported	N_2, air, HCl, H_2O	100 mL/min	0–30 mg/L of gas
45	phenol and chlorophenols	fly ash, firebrick	—	150–400	—	60 min	not reported	N_2	10 mL/min	—
46	[$^{13}C_6$]pentachlorophenol	fly ash, firebrick	—	150–400	—	not reported	not reported	N_2	not reported	—
47	tri-, tetra-, and pentachlorophenates	SiO_2NaOH	—	280	—	15 min	not reported	N_2	not reported	—
48	[$^{13}C_{12}$]2,3,7,8-T_4CDD	SiO_2	Cl_2	100	—	60 min	not reported	N_2, Cl_2	30–40 mL/min	—

Table 1 (Continued)

ref	reactant	surface	chlorine source[a]	temp (°C)	catalyst[b]	reaction time	residence time[c] (s)	atmosphere	flow	water[d]
49	[$^{13}C_{12}$]1,2,3,4-T_4CDD	SiO_2	$FeCl_3$	265	$FeCl_3$	2 min	not reported	N_2	5 mL/min	–
50	various	fly ash	HCl, trichloroethylene	425	–	90 min	not reported	air, HCl	90–120 mL/min	–
51	2,3,7,8-T_4BDD	Al_2O_3-SiO_2	HCl, $CuCl_2$	200–300	$CuCl_2$	5–15 min	not reported	N_2, HCl	15 mL/min	–
52	DD, DF	$Al_2O_3SiO_2$	HCl, $CuCl_2$	300	$CuCl_2$	30 min	not reported	N_2, O_2, HCl	100 mL/min	–
53	activated carbon	Al_2O_3-SiO_2	HCl, $CuCl_2$	300	$CuCl_2$	120 min	not reported	air, HCl, H_2O	100 mL/min	20 vol %
54	activated carbon, chlorophenols	carbon	HCl, $CuCl_2$	300	$CuCl_2$	60 min	2.8	N_2, O_2, HCl, H_2O	100 mL/min	5 vol %
55	bituminous coal	–	NaCl, HCl, Cl_2	600	–	5–10 min	not reported	air, HCl, Cl_2	50–56 mL/min	–
56	various carbon species	sieved fly ash	–	275–350	–	2–30 min	1	N_2, O_2	20–100 mL/min	–
57	propene	fly ash	HCl	350–548	–	*e*	1.0–1.3	N_2, O_2, HCl, H_2O	201 mmol/h	50 mmol/h
58	[$^{13}C_6$]pentachlorophenol	fly ash	–	300	–	not reported	not reported	air	10 mL/min	–
59	[$^{13}C_6$]pentachlorophenol	various	–	300	–	60 min	not reported	air	12 mL/min	–
60	di-, tri-, tetrachlorophenates	SiO_2NaOH	–	280	–	15–30 min	not reported	N_2	10–40 mL/min	–
61	various	SiO_2	$FeCl_3$	150–400	$FeCl_3$	2–40 min	not reported	He, N_2, H_2O	6–350 mL/min	+
62	1,2,3,4-T_4CDD	fly ash	–	100–300	–	1–15 min	not reported	He, air	not reported	–
63	DD, 1-MCDD	fly ash	HCl, CCl_4	50–400	–	3–10 min	not reported	air, HCl	not reported	–
64	DD	various	HCl	150	–	5 min	not reported	air, HCl	not reported	–
65	1,2,3,4-T_4CDD, OCDD	fly ash	HCl	30–300	–	10 min	not reported	air, NO_2, SO_2, SO_3, HCl, H_2O	not reported	+
66	various	fly ash	–	200–350	–	60 min	not reported	N_2, air	10 mL/min	–
67	[$^{13}C_6$]pentachlorophenol, pentachlorodiphenyl ether	sieved fly ash	HCl	300	–	60 min	not reported	air, HNO_3, H_2SO_4, HCl, NH_4OH, H_2O	3–5 mL/min	0–40 vol %
68	[$^{13}C_6$]pentachlorophenol	sieved fly ash	–	300	–	5–120 min	not reported	air	3–5 mL/min	–
69	graphite	–	Cl_2	350–850	Fe_2O_33	0.5–15 min	not reported	Ar, Cl_2	167 mL/min	–
70	activated carbon, OCDD, OCDF	Al_2O_3	KCl, $CuCl_2$	300	$CuCl_2$, Al_2O_3	30–120 min	not reported	N_2, air, H_2O	50 mL/min	+
71	OCDD, OCDF	Al_2O_3	–	275	Al_2O_3	30 min	not reported	N_2, H_2O	16 mL/min	+
72	activated carbon	Al_2O_3	KCl, $CuCl_2$	200–400	$CuCl_2$	120 min	not reported	air	50 mL/min	–
73	residual carbon	fly ash	–	250–550	–	120 min	not reported	air, H_2O	50 mL/min	120 mg/L of gas
74	original fly ash	fly ash	–	250–350	–	0.5–6 h	not reported	N_2, O_2, CO_2	670 mL/min	–
75	various carbon species	fly ash, Mg-$AlSiO_2$	KCl	250–350	various	2–6 h	not reported	air, H_2O	50 mL/min	0–150 mg/L of gas
76	charcoal	$MgAlSiO_2$	KCl, $CuCl_2$	300	$CuCl_2$	0.25–4 h	not reported	air, H_2O	50 mL/min	150 mg/L of gas
77	activated carbon, charcoal, residual carbon	fly ash	–	300	–	60–120 min	not reported	air, H_2O	50 mL/min	0–150 mg/L of gas
78	original fly ash, charcoal	fly ash	HCl	300	–	120 min	not reported	air, HCl, SO_2, H_2O	50 mL/min	0–100 mg/L of gas
79	original fly ash, charcoal	fly ash, $MgAlSiO_2$	various	300–600	$CuCl_2$, $FeCl_3$, $ZnCl_2$	0.25–4 h	not reported	air, HCl, SO_2, H_2O	50–250 mL/min	0–150 mg/L of gas
80	original fly ash	fly ash	–	275–350	–	0.25–8 h	not reported	air	not reported	–
81	original fly ash	fly ash	–	120–600	–	120 min	not reported	air	670 mL/min	–
82	original fly ash	fly ash	various	200–400	various	2–22 h	not reported	N_2, O_2, HCl, SO_2, H_2O	not reported	0–150 mg/L of gas

[a] – indicates no chlorine added (or only present in reactants or fly ash). [b] (–) indicates no catalyst added (or only present in fly ash). [c] Gas-phase residence time, i.e., {volume of matrix/(gas flow min^{-1})}. [d] When quantified, the amount of water added is given; (+) indicates water added but not quantified; (–) indicates no water added. [e] Continuous sampling, products given in μg/(g of matrix h^{-1}), M^{-1}, or μmol/h.

When using carbon as a reactant, contradictory results have been found. An increase of ΣPCDD/F from carbon/fly ash at 300 °C with water present (compared to experiments without water) is reported by Stieglitz et al. (*77*). The addition of water had no effect on ΣPCDD/F formation using activated carbon on fly ash at 350 °C. However, a shift toward lower chlorinated congeners for PCDD in the presence of water was observed (*13*). A decrease of the total amount of PCDD/F formed in the presence of water is reported by Jay et al. with charcoal/$MgSiO_2$/$CuCl_2$ in air at 300 °C (*44*). With pentachlorophenol on fly ash in air at 300 °C, water stimulates the formation of PCDD, and a shift toward lower chlorinated congeners is observed (*67*). When dechlorinating OCDD and OCDF on Al_2O_3 in N_2 at 275 °C, no influence of water was seen on the rate of dechlorination (*71*).

Reaction Mechanisms

In this section some mechanistic aspects of PCDD/F formation will be discussed.

Mechanism with Carbon. Schwarz studied the oxidation of residual carbon on fly ash at 300 and 450 °C, leading primarily (65–75%) to CO_2, eq 1 (*85*). This suggests that

$$C + O_2 \rightarrow CO_2 \qquad (1)$$

the formation of PCDD/F and other chlorinated organic compounds is only a minor pathway in the oxidative breakdown of carbon on fly ash. Indeed, only 1% of the carbon is converted to chlorinated benzenes and 0.01–0.04% to PCDD/F (*85*).

The following mechanism has been proposed for this reaction, involving Cu and carbon: (i) formation of a copper chloride (halide) complex; (ii) ligand transfer of the halide to a carbon atom contained in a macromolecular structure; (iii) breakdown of the macromolecule into small compounds. In this model, chlorination of the macromolecule occurs before oxidative breakdown into smaller molecules (*85*). Such a mechanism is supported by the observation that PCDD/F formation from carbon on fly ash is possible with NaCl as a chloride source but not with DF with NaCl (*86*). Consequently, NaCl is only capable of chlorinating the macromolecular carbon structure but not PCDD/F after formation, and chlorination has to precede carbon breakdown.

Milligan et al. found that with a higher gasification rate of residual carbon on fly ash, PCDD/F formation increases, linking carbon oxidation with PCDD/F formation. Activated carbon, with a high surface area and good adsorption properties, has a higher gasification rate than carbon species with a low surface area. Mixing with fly ash enhances the gasification rate. The high surface area of the activated carbon obviously provides easy access for the various reactants involved (*56*). More evidence for a relation between carbon gasification and PCDD/F formation is provided by the fact that optimum temperatures for both processes coincide (*85*).

The formation of PCDD/F from carbon raises the question to what extent these structures are present in the carbon. Altwicker et al. (*19*) found the formation of either [$^{12}C_{12}$]- or [$^{13}C_{12}$]PCDD/F when using a mixture of [^{12}C]- and [^{13}C]carbon, i.e., no scrambling occurred. This suggests that DD/F or related structures already exist in carbon and that no free aromatic rings are involved in PCDD/F formation from carbon. Luijk et al. found PCDD formation from carbon/HCl without fly ash, the chlorination pattern of the PCDD formed pointing to chlorophenols as intermediates (*54*). These authors found that the specific chlorination pattern (and hence the route via chlorophenols) disappears when 0.5% $CuCl_2$ is added to the carbon. This explains why such a mechanism is not operative on fly ash, as Cu concentrations are generally too high. However, these results show that more than one mechanism may exist for the formation of PCDD/F during de novo synthesis.

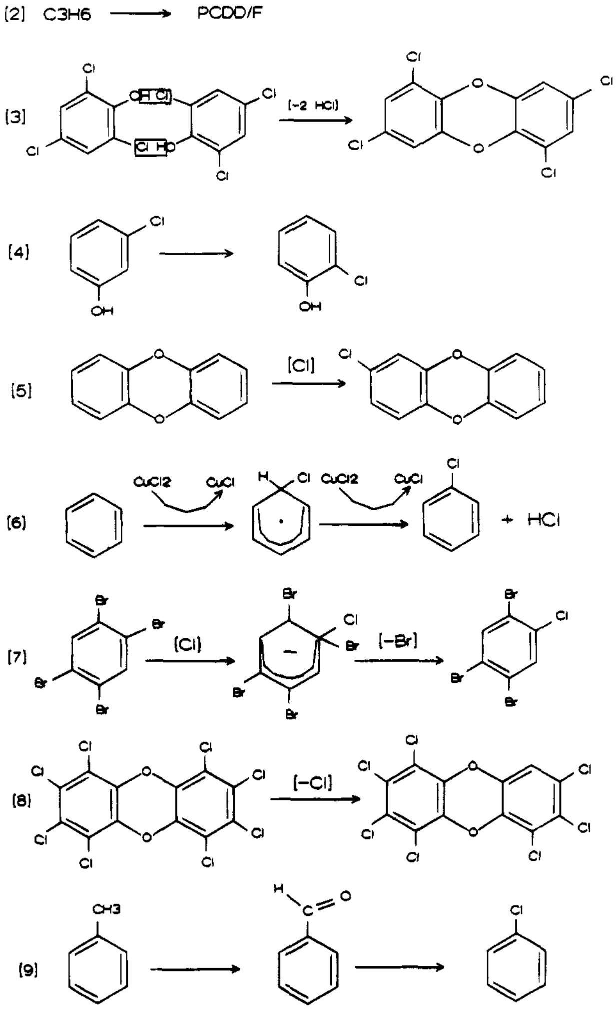


FIGURE 3. Fly ash-catalyzed mechanisms of small organic molecules.

PCDD/F formation from anthraquinone derivatives is stimulated by carboxyl and hydroxy groups, emphasizing the importance of functional groups (*14*). The anthraquinone derivatives can be viewed as carbon model compounds to the extent that carbonyl and carboxyl groups are present in carbon too (*87*). Especially those parts of carbon with quinone-like structures or many functional groups might be very active in PCDD/F formation.

The addition of a radical initiator (dibenzoylperoxide) to residual carbon/fly ash increases the amount of PCDD/F formed with 5–15 times (*85*). Although no detailed mechanism is offered by the author, it is obvious that radical reactions play an important role in the mechanism of de novo synthesis.

Mechanisms Involving Small Organic Molecules. In Figure 3, an overview is given of some reactions leading to PCDD/F and a number of other reaction mechanisms which are operative on fly ash.

Equation 2 shows that propene forms both PCDD and PCDF on fly ash at 576 °C (*57*). The precise route of formation is unknown but will involve C−C bond formation, cyclization, aromatization, oxidation, and chlorination, not necessarily in this order.

Equation 3 shows that chlorophenols condensate easily to PCDD on fly ash; no PCDF is formed. In the example, the chlorination pattern of the phenol is retained in the PCDD (leading to 1,3,6,8-T_4CDD). Isomerization can take place through the Smiles rearrangement (1,3,7,9-T_4CDD) (*54*). Cu(I) has been advanced as the catalyst in a similar reaction: the condensation of a chlorophenol and a chlorophenolate, interacting with both molecules in a nucleophilic aromatic substitution reaction, the Ullmann condensation (*24*).

Equation 4 shows that *m*- and *p*-chlorophenol isomerize easily to *o*-chlorophenol on fly ash. Thus, the presence of an *o*-chlorine atom in the starting phenol is no prerequisite for PCDD formation (*22*).

Chlorination of DD on fly ash with HCl proceeds via an electrophilic aromatic substitution mechanism (eq 5) at temperatures below 425 °C. Above this temperature, the mechanism changes to a homolytic one, resulting in a different chlorination pattern (*24*).

This radical mechanism (eq 6) has been proposed for the formation of chlorobenzenes on a fly ash model surface, $CuCl_2/MgSiO_2$ (*44*).

For the chlorination on fly ash of 1,2,4,5-tetrabromobenzene this addition−elimination mechanism (eq 7) (S_NAr) is proposed, yielding exclusively ipso-substituted products (*88*).

Dechlorination/hydrogenation of OCDD on fly ash is an example of dechlorination reactions taking place on fly ash (eq 8). According to Hagenmaier et al., DD/F are not the final products of dechlorination, but these aromatic structures are further degraded on fly ash (*84*). However, Wania et al. claim that DD is a stable final product of dechlorination during degradation of 1,2,3,4-T_4BDD on Cu powder in sealed tubes. They also observed dimerization of DD (*89*).

Equation 9 shows that toluene is converted to benzaldehyde on fly ash through side-chain oxidation; this reaction is followed by ipso-substitution to chlorobenzene (*50*).

Apart from the condensation of chlorophenols, no detailed mechanisms can be presented for PCDD/F formation from precursors. Formation from, for example, propene probably requires a more complex pathway than from 2,6-dihydroxyanthraquinone, which is already structurally related to PCDD/F. Reactions 6, 7, and 9 do not result in PCDD/F formation, but these mechanisms could be part of more complex formation routes leading to PCDD/F.

Catalysis. Investigation of catalytic processes involved in PCDD/F formation has focused on three different subjects: (i) de novo synthesis from carbon, (ii) ring condensation of aromatic structures and (iii) chlorination/dechlorination.

(i) Both Cu and Fe ions have been identified as catalysts in PCDD/F formation reactions from carbon. Cu ions are 25 times stronger as a catalyst than Fe (*79*). The mechanism of chlorination with Cu has been described above. In this mechanism, the Cu ions are only involved in the chlorination of the macromolecule, not in its oxidative breakdown. If the Cu ion concentration is increased during de novo synthesis, a more than proportional rise of PCDD/F formation is observed (*75*). Recently, $CuCl_2$ has also been advanced as a dechlorination catalyst of PCDD/F already formed (*54*).

(ii) Apart from catalyzing de novo synthesis, Cu ions are capable of assisting ring condensation reactions from, for example, chlorophenols. Cu(I) is thought to catalyze condensation of chlorophenols through the Ullmann condensation (*24*). When comparing the catalytic potential of different Cu species, CuO is better in promoting condensation of chlorophenols than $CuSO_4$ (*39*). Gullett et al. have found that Cu^{2+} is more effective in the condensation of chlorinated phenols than Cu(0) and Cu^+. The catalytic potential of the latter two is nearly equal (*40*).

(iii) Pathways for chlorination are as follows:

(a) Deacon reaction (*90*): involving formation of free chlorine on fly ash according to

$$2HCl + 1/2O_2 \rightarrow H_2O + Cl_2 \qquad (10)$$

This reaction is catalyzed by various Cu species, a.o. Cu, CuCl, $CuCl_2$, CuO, Cu_2O, and $CuSO_4$ (*27, 39*). Fly ash does produce Cl_2: when passing HCl over the fly ash bed, 1.3% is converted to Cl_2 (*91*). A lower conversion was found by Born: 0.1%. However, oxychlorination of ethylene on fly ash yields 30−60 times more chlorinated product than Cl_2 produced through the Deacon reaction (*24*). Therefore, other routes for chlorination have to be operative.

(b) Decomposition of metal chlorides releasing Cl_2: Gullett reports on formation of Cl_2 from a phenol/CuCl mixture (*38*). The addition of HCl increases the yield of Cl_2. In this system, Cl_2 is formed via parallel routes of the Deacon reaction and metal chloride decomposition.

(c) Direct chlorination by metal chlorides: This occurs in the mechanism proposed by Schwarz for the formation of PCDD/F from carbon and is part of reaction (i) (*85*). $FeCl_3$ is thought to be the chlorinating agent on fly ash according to Hoffmann et al. (*92*). In an electrophilic chlorination reaction, the Fe^{3+} is reduced to Fe^{2+}.

Role of Gases. A gas flow is passed over the fly ash bed in most experimental designs to simulate the flue gas passing the collected fly ash particles in the post-combustion zone of an incinerator. The presence of a gas flow is not essential for fly ash-catalyzed reactions, as dechlorination of PCDD/F on fly ash occurs in sealed tubes too (*41*).

Oxygen is essential for the oxidative breakdown of carbon and subsequent PCDD/F formation. It interacts with the Cu ions catalyzing chlorination of the macromolecule and probably also reacts with parts (e.g., organic radicals formed during breakdown) of the macromolecular structure (*85*). Whether it is incorporated into the DD/F structure is not known.

For other PCDD/F formation pathways, e.g., through condensation reactions, the presence of O_2 is not required. In fact, such reactions are possible both in N_2 and O_2 (*27, 45*). Contradictory reports exist on the effect of increased $[O_2]$ on these condensation reactions: both increased or decreased PCDD formation was found from chlorophenols (*66, 33*). O_2 could give a better adsorption to the fly ash surface than N_2 and participate both in condensation or dechlorination/destruction reactions. The final effect of O_2 on PCDD formation from chlorophenols will be the result of these several possibilities.

Oxygen is essential for chlorination through the Deacon reaction (*90*) but not for direct chlorination through a surface-bound metal chloride, e.g., $FeCl_3$ (*61*).

Role of Water. Experiments with and without water have yielded contradictory results regarding its effect on the total amount of PCDD/F formed. Possible effects of water could be as follows:

(a) Presence of an additional hydrogen source. Addition of D_2O to fly ash yields deuterated PCDD/F (*84*). Such an incorporation of H atoms should lead to a lower degree of chlorination of PCDD/F. This has been observed indeed (*13*).

(b) Presence of an additional oxygen source.

(c) Presence of a source of •OH radicals. As described above, radicals probably play an important role in formation reactions.

(d) Competition with possible precursors for adsorption to the fly ash surface.

(e) Water could change the equilibrium in the Deacon reaction and consequently [Cl_2]. Effects b–e have not been investigated yet. Knowledge of these possible effects could shed some more light on the overall influence of H_2O on PCDD/F formation.

Kinetics and Comparison of Laboratory-Scale Experiments and Incineration

De novo synthesis from carbon appears to be a long time scale process (hours) and takes place on collected fly ash particles only. Uncollected fly ash has too short a residence time at optimum temperatures to give a significant contribution in de novo synthesis. With carbon, PCDD/F formation takes place for several hours, afterwards a stable level is reached and eventually a decrease is observed. This suggests that formation and destruction of PCDD/F are competing processes, the overall balance depending on the relative importance of both pathways.

Using laboratory experiments, rate constants have been calculated for PCDD/F formation from carbon. Large differences are reported by various groups: at 300 °C on fly ash, Lasagni et al. found ca. 10^{-3} min^{-1} for all tetra–octa-CDD/F (*93*) and Schwarz found 10^{-5}–10^{-9} min^{-1} for tri–octa-CDD/F (*85*). Rate constants for degradation reactions of PCDD/F on fly ash (300 °C) were calculated by Lasagni et al. (0.2–18 min^{-1} for hexa–oxa-CDD/F (*93*)) and by Schwarz (10^{-2} min^{-1} for tri–octa-CDD/F (*85*)) too. According to these authors, the formation of PCDD/F from carbon can be described by a first-order equation, but it is not clear what is the character of the rate-determining step. Addink et al. found little formation of PCDD/F from carbon on fly ash during 0–2 h, followed by a great rise in formation between 2 and 4 h, suggesting a diffusion-controled reaction in the first part of the experiment (*12*).

To make a good comparison between formation from carbon and from precursors, knowledge of reactivity of both carbon and chlorophenols, preferably within one experiment, is necessary. Large differences were found by various authors: at 300 °C the rate of PCDD formation from 2,4,5-, 2,4,6-, and pentachlorophenol on fly ash is equal to that of PCDD/F formation from carbon (*19*). However, Dickson et al. found that PCDD formation from pentachlorophenol is between 10^2 and 10^5 times faster than PCDD/F formation from carbon (250–350 °C) (*33*).

With such a wide range of rates and rate constants found, only boundaries of PCDD/F formation in incinerators can be calculated. Altwicker developed a model for PCDD formation from chlorophenols in the post-combustion zone based on laboratory rates. The mechanism consists of four steps:

$$P_s + P_g \rightarrow D_s \tag{11}$$

$$D_s \rightarrow D_g \tag{12}$$

$$D_s \rightarrow \text{Pro} \tag{13}$$

$$D_s \rightarrow \text{DPro} \tag{14}$$

where P_s is the adsorbed precursor; P_g is the gas-phase precursor; D_s is the adsorbed dioxin; D_g is the gas-phase dioxin; Pro is the dechlorinated dioxin; DPro is the decomposed dioxin molecule.

A precursor molecule is adsorbed onto the fly ash surface and reacts with a gas-phase precursor molecule to give PCDD, this PCDD molecule either desorbes, dechlorinates, or decomposes. Two kinds of active sites are assumed to exist on fly ash: active and superactive, giving PCDD formation on different times scales. Superactive sites are associated with short time scale kinetics (seconds) and active sites are associated with long time scale kinetics (minutes). E_{act} calculated for these reactions (eqs 11–14) are as follows: eq 11, 14–26 kcal/mol; eq 12, 32 kcal/mol; eq 13, 14 kcal/mol; eq 14, 37.5 kcal/mol (*7, 9, 94*).

With this model, rates of PCDD formation found in the laboratory can explain emission levels found in incinerators. However, the model does not include PCDD/F formation from carbon, whereas rates measured in incinerators include formation from both carbon and precursors. It does not answer the question whether formation from carbon or from precursors is the most important pathway in the post-combustion zone. The model does integrate formation on collected and uncollected particles and shows that PCDD/F formation from precursors can be important on both categories of particles. The occurrence of formation reactions on uncollected fly ash is corroborated by Gullett et al. (*95*), who found PCDD/F formation on particles with a residence time <5 s.

Born et al. found a zero-order dependence in [phenol] for its oxychlorination on fly ash, establishing the heterogeneous nature of the mechanism involved (*24*). The reaction has a fractional order in [O_2] and [HCl].

Altwicker et al. have analyzed PCDD formation on fly ash from 2,3,4,6-tetrachlorophenol in terms of an adsorption–reaction–desorption mechanism. At higher precursor concentrations, PCDD formed escapes destruction–dechlorination by desorption from the fly ash. At these higher concentrations, there is a competition for sorption to the fly ash surface between the reactant and the PCDD formed (*20*).

Conclusions and Recommendations

In this section, we will attempt to integrate the various findings of the research described and to identify future research topics.

Formation of PCDD/F in the post-combustion zone can be separated into four different categories: from carbon on collected fly ash; from precursors on collected fly ash; from carbon on uncollected fly ash; and from precursors on uncollected fly ash. We will use this distinction in the discussion below. This division helps to connect the results of laboratory studies with the chemical processes in an incinerator.

De Novo Synthesis on Collected Fly Ash. The modeling of formation processes on collected fly ash on a laboratory scale has been carried out with both incinerator fly ash and model surfaces (e.g., SiO_2, Al_2O_3). The use of fly ash offers the advantage of staying to the real active surface as close as possible. However, the fly ash often has been collected and stored for many years and may be totally different from freshly generated fly ash in the post-combustion zone. Furthermore, the very complex nature of this surface and the presence of, for example, many different transition metal ions make it unfit for detailed mechanistic studies. In our opinion, the use of fly ash seems justified for studies of a more phenomenological nature (e.g., influence of temperature and time), whereas model surfaces are to be chosen when investigating reaction mechanisms.

The formation of PCDD/F from carbon on collected fly ash is a process, which can continue for several hours. Although the optimum temperature appears to be around 300–350 °C, some formation is still observed at $T > 500$ °C. This finding implies that de novo synthesis of PCDD/F will take place not only on or near the E-filter but also at higher temperatures at the beginning of the post-combustion zone. Fly ash particles may reside on various surfaces (e.g., walls) here and contribute to formation too.

There is more evidence that chlorination of the carbon structure occurs before its oxidative breakdown. Both metal chlorides and gaseous compounds like HCl are likely to act as a chlorine source. With HCl, both direct chlorination or via Cl_2 would seem possible. The contribution from these different chlorination pathways is not clear and deserves further attention. The use of isotopes could shed some light on the possible routes and the relation between them. With this knowledge, one would be capable of determining what is the most important chlorination route during de novo synthesis in the post-combustion zone.

Various catalysts may be involved in the chlorination and perhaps dissociation of the macromolecular structure. Cu and Fe have been advanced as the most important catalysts. Both these elements are present in incinerator fly ash, probably in varying amounts, and could each contribute significantly to formation. With the two most important de novo synthesis catalysts being identified, future research should focus on the influence of parameters like acidity, particle size, and surface area and on the rate and mechanism of catalysis.

The actual process of PCDD/F formation from the carbon structure remains quite unclear. The DD and DF structures could be present in the carbon, stem from related diphenyl ethers, or be formed through condensation reactions. More than one pathway might be operative at the same time. Functional groups exert a certain influence on the potential to build PCDD/F, but the precise role has barely been investigated. The influence of parameters like [aromatic: aliphatic] ratio, chemical composition, and surface area deserves further attention as they could explain the capabilities of different types of carbon to form PCDD/F.

Regarding the kinetics of de novo synthesis, major questions remain unanswered. Rate constants determined show a large degree of variance. This might have several reasons, one of which is simply the fact that authors use fly ash from different incinerators. The different rate constants found probably reflect to some extent the range of de novo synthesis rates in various incinerators. In any case, even the highest rates found cannot explain the levels of PCDD/F found in incinerator emissions. However, freshly generated fly ash might be more reactive in de novo synthesis than the fly ash used in laboratory experiments. A more thorough study of reaction rates from carbon, using model surfaces, is therefore highly recommended. These studies should include the influence of both [Cu] and [C] on formation rates, as these concentrations will vary in incinerators. Rate constants determined are overall values, with no clue as to the nature of the rate-determining step. Possibilities include diffusion or reaction with O_2.

Formation from Precursors on Collected Fly Ash. Formation of PCDD/F on collected fly ash from precursors has been amply studied. However, apart from chlorophenols, which can generate PCDD through direct coupling, no mechanisms can be formulated. Pathways are simply too complicated to allow for easily obtainable mechanistic insight. The wide range of precursors capable of PCDD/F formation suggests that any combination of C, H, O, and Cl could generate these toxic compounds. This may be true, but such an observation does not tell what precursors are more reactive than others in PCDD/F formation. Study of formation rates from chlorobenzenes, chlorophenols, and aliphatic precursors under identical conditions could yield this information. With these facts, it will be possible to determine the most important precursors in incinerator flue gas.

Temperature and time have a different effect on PCDD/F formation from precursors than found with carbon. The optimum temperature window for formation will be different for each precursor and can be well above 500 °C. Consequently, as with carbon, formation can occur at the higher temperature side of the post-combustion zone. Formation reactions from precursors are possible on a much shorter time scale (seconds–minutes) than with carbon. With a continuous supply of reactant adsorbed onto the fly ash from the gas phase, this reaction probably continues for hours.

The role of Cu compounds both in ring condensation and chlorination appears well established. With more unrelated starting material, e.g., propene, the role of the catalyst is less clear. Other transition metal ions beside Cu could catalyze some of the steps leading to PCDD/F.

Kinetics of PCDD formation from chlorophenols, when compared with carbon, show great differences. Again, the use of fly ash model surfaces should be strongly encouraged, as this could yield better reproducible results. The zero-order dependence found for PCDD formation from phenol corroborates the heterogeneous nature of the mechanism. Precursors may compete with PCDD/F for adsorption to the fly ash surface. Knowledge of adsorption and desorption activation energies, degree of fly ash coverage with precursor molecules, and nature of the adsorption (chemical or physical) will help to shed some light on this process.

De Novo Synthesis on Uncollected Fly Ash. As described above, the residence time of a few seconds is probably too low to give a significant amount of carbon oxidation and, hence, PCDD/F formation. However, such a reaction might be possible on fly ash with a slightly longer residence time, say a few minutes, and this topic deserves further investigation.

Formation from Precursors on Uncollected Fly Ash. So far, only a few experiments have been carried out with PCDD/F formation on uncollected fly ash particles. For this purpose, fluidized beds have been used. Such a laboratory design does not generate fresh fly ash, as is done in the post-combustion zone, but offers the opportunity of studying reactions on a short (seconds) time scale. It may in fact be viewed as a simulated flue gas. Some of the basic chemistry involved can be elucidated in this way, e.g., reactivity of chlorobenzenes and chlorophenols on uncollected fly ash. These data may be compared with those predicted for reactions on uncollected fly ash. This will also lead to a better understanding of the reactivity of precursors in the post-combustion zone. Elementary experiments are needed to determine the influence of temperature, residence time, $[O_2]$, and fly ash and precursor concentration.

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