



Kinetics of carbon degradation and PCDD/PCDF formation on MSWI fly ash

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ABSTRACT

The native carbon oxidation and PolyChloroDibenzo-*p*-Dioxins and PolyChloroDibenzoFurans, PCDD/F, formation were simultaneously studied at different temperatures (230–350 °C) and times (0–1440 min) in order to establish a direct correlation between the disappearance of the reagent and the formation of the products. The kinetic runs were conducted in an experimental set up where conditions were chosen to gain information on the role of fly ash deposits in cold zones of municipal solid waste incinerators in PCDD/F formation reaction. The carbon oxidation measured as the decrease of total organic carbon of fly ash was in agreement with the carbon evolved as sum of CO and CO₂. The carbon mass balance indicated an increase in the efficiency of carbon conversion in CO and CO₂ with temperature. The CO and CO₂ formation was the result of two parallel pseudo first order reactions thus giving significant information about the reaction mechanism. PCDD/F formation as a function of temperature showed that the maximum formation was achieved in a narrow range around 280 °C; the time effect at 280 °C was a progressive formation increase at least up to 900 min. The PCDF:PCDD molar ratio increased with temperature and time, and the most abundant homologues were HxCDD, HpCDD, OCDD for PCDD, and HxCDF, HpCDF within PCDF. These experimental results supported the hypothesis that the formation mechanism was the *de novo* synthesis.

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1. Introduction

PolyChloroDibenzo-*p*-Dioxins and PolyChloroDibenzoFurans, PCDD/F, in municipal solid waste incinerators, MSWI, are formed in the so called “cold zones”, after combustion, by heterogeneous reactions between fly ash or soot and flue gases occurring at low temperatures (350–250 °C).

Two main mechanisms have been proposed for the heterogeneous reactions on fly ash surface (see, e.g., the review in Stanmore, 2004): (i) the surface-mediated precursor pathway, e.g. PCDD/F formation from chlorinated benzenes (Altwicker et al., 1994; Procaccini et al., 2003) and/or phenols (Briois et al., 2005) and (ii) *de novo* synthesis, starting from more or less complex non-chlorinated molecules, fly ash native carbon, i.e., unburned unextractable carbon, and soot included, and a chlorine source such as Cl₂, HCl or inorganic chlorides (Stieglitz, 1998). In both cases, fly ash can act as a catalyst; at least in the latter mechanism, oxygen is essential.

Considering *de novo* synthesis, many studies have been carried out on the role of carbonaceous structures on soot (Wikström et al., 2004a,b; Grandesso et al., 2008) or fly ash.

Jay and Stieglitz (1991) showed that carbon type, crystallite size, porosity, active surface area, mineral matter content, oxidant and temperature influence carbon degradation. Carbons having a

microcrystalline structure with higher degenerate graphitic layers, such as activated carbon, are more reactive. Moreover, Milligan and Altwicker (1993) observed that carbon gasification rates were higher for native carbon on fly ash than for activated carbon or amorphous pure carbon, carbon black, alone. When adding activated carbon to fly ash, gasification rates were comparable to those of native carbon, suggesting catalytic activity of fly ash in carbon gasification. Fly ash, in fact, contains significant concentrations of ions of heavy metals or of the transition metal group. The metals act as oxidation catalysts (Gullett et al., 1990; Mul et al., 1997; Fullana et al., 2002; Grandesso et al., 2004; Hatanaka et al., 2004), in particular copper has been identified as the strongest oxidation catalyst (Addink and Altwicker, 1998). However, the effect of iron must not be overlooked since in most fly ashes and other metallurgical process dusts, iron concentration is at least one order of magnitude higher than copper. Iron activity is probably lower than that of copper, but it may play an important role due to its relative abundance (Ryan and Altwicker, 2000).

Kinetic studies were carried out by Stieglitz and co-workers (1993) who monitored the catalytic oxidation of native carbon in fly ash at different temperatures (from 275° to 400 °C) for up to 480 min. The main oxidation product was CO₂ and the reaction could be described by a combination of two first order reactions. They also used differential scanning calorimetry (DSC) to measure the temperature dependence of the oxidation of native carbon, and observed two peaks. They made two hypotheses: (i) in the thermal

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treatment carbon is not only oxidized but also partly converted to a species for which higher temperatures are required for complete oxidation; (ii) the presence of two different reaction pathways, e.g. metal chlorides firstly catalyze the lower temperature carbon gasification, then diminish in the environment and may be supplied to the reaction site only at higher temperatures by diffusion processes.

In a paper on the mechanism of *de novo* synthesis of PCDD/PCDF, Huang and Buekens (1996) report an overview of catalyzed and uncatalyzed mechanisms of carbon gasification in the low-temperature range (200–500 °C) suggesting that, in order to understand the *de novo* synthesis reaction, it is necessary to understand the carbon gasification reaction, especially the O₂ mode of attack on graphitic carbon structures.

Stieglitz (1998) found a correlation between the peak oxidation temperature in DSC and the maximum of PCDD/F formation on MSWI fly ash (300 °C). The importance of intermediate surface oxycomplexes, C(O), as precursors for PCDD/F has been suggested by Wilhelm et al. (1999a,b). They used labeled oxygen to study PCDD/F formation on three different fly ashes. Their work potentially suggested the role of surface oxygen groups on the fly ash carbon in the formation of CO₂. We showed (Collina et al., 2000) that the calculated C(O) formation maximum occurs in the temperature range of PCDD/F formation (250–350 °C) where they are stable for times as long as 24 h.

The literature analysis emphasizes a relationship between carbon oxidation and PCDD/F formation in the cold zones of MSWI but the carbon mass balance before and after this reaction was not reported. Moreover, the details of qualitative and quantitative changes in PCDD/F congener pattern were rarely investigated.

With the aim to establish an experimental correlation between the disappearance of the native carbon reagent and the formation of the products, in this paper we present the results of CO/CO₂ formation and changes in PCDD/F congener pattern as a function of temperature and time. The kinetic runs were conducted in an experimental set up where conditions were chosen to gain information on the role of fly ash deposits in PCDD/F formation at the temperatures typical of MSWI cold zones.

2. Materials and methods

2.1. Reagents

Fly ash samples (raw fly ash, RFA) were collected from the electrostatic precipitator hoppers of an Italian MSWI and kept refrigerated in dark bottles under inert atmosphere. Each sample was homogenized using a ball mill (Retsch, Model S1) operating with three 10 mm-Ø balls and two 20 mm-Ø ones at 80 rpm for 25 min. It was then dried and used for the experiments without further treatment. Physical and chemical characterization of RFA was reported in Fermo et al. (1999, 2000) and Gilardoni et al.

(2004). Major constituents ($\geq 10000 \mu\text{g g}^{-1}$) were Cl, Si, S, Ca, Na, Al, K, Zn, P, Pb, and Mg; minor constituents ($1000\text{--}10000 \mu\text{g g}^{-1}$) included Fe, Ti, Sn, Cu, Ba and Sb (Tables 1 and 2 in Fermo et al. (1999)). More than 75% of the RFA had a particle diameter greater than 150 μm , 15% in the range 150–10 μm and 10% less than 10 μm (Fermo et al., 2000).

2.2. Kinetic runs

The kinetics of PCDD/F formation was studied in a flow-over solids system where RFA samples (10 g) were thermally treated. RFA was used to study CO/CO₂ evolution or PCDD/F formation at different temperatures (in the range 230–350 °C) and time (in the range 30–1440 min).

A closed muffle furnace, internal volume 9 L, was modified by including a stainless steel chamber, volume 5 L. Inlet and output tubings allowed the reaction gas to flow into the reactor. A mixture of oxygen (21 \pm 1 as% v/v) and nitrogen (79 \pm 1 as% v/v) gas was passed in the reaction muffle at 100 mL min⁻¹ flow. The bulk gas flow turnover was 50 min. The flow rates and the composition of the reaction gas were set by mass flow meters (MKS, mod. 2259 C) connected to a control unit (MKS, mod. 647B).

The oven was preheated and the reaction gas was passed through the modified muffle for 60 min. After this conditioning time, 10 g of RFA were placed into the reaction chamber. This operation was done as quickly as possible in order to minimize the variations of the experimental conditions. The temperature in the reaction chamber was measured by a thermocouple; in this way a temperature variability of ± 5 °C at 350 °C was set. The experimental reaction temperatures ranged from 230 to 350 °C. The reaction times varied from 30 to 1440 min.

The exhaust gas stream from the reactor was analyzed by GC for CO₂ and CO. The organic compounds in the exhaust gas were trapped using a sample train with hexane and toluene impingers and a final empty cold trap. The experiment was stopped at each established kinetic time. PCDD/F in RFA sample and sample train were analyzed and the residual TOC content of RFA sample was measured.

Table 2

Estimated values of CO and CO₂ at the maximum of the evolution curves^a.

Temperature (°C)	t_{max} (min)	CO _{max} (mmol)	t_{max} (min)	CO ₂ max (mmol)	CO ₂ max/CO _{max}
230	–	–	64.6	0.0088	–
250	–	–	96.4	0.0213	–
280	78.8	0.0017	90.8	0.0487	28.0
300	72.1	0.0028	74.1	0.0739	26.1
350	54.3	0.0126	56.8	0.1468	11.2

^a The maximum was located by fitting the data around the maximum in Fig. 1 with a parabolic function.

Table 1

Carbon concentration of the sample (TOC_{exp}), reacted carbon (TOC_{react}), CO₂ and CO evolved at the end of each experiment and contribution of CO and CO₂ to the reacted carbon (CRC). TOC⁰ = 3920 \pm 50 ppm.

T (°C)	Reaction time (min)	TOC _{exp} \pm s.d. (ppm)	TOC _{react} ^a (ppm)	CO (mmol/mol C) ^b	CO ₂ (mmol/mol C) ^b	TOC _{CO} (ppm)	TOC _{CO₂} (ppm)	CRC ^d (%)
230	1440	3360 \pm 80	560	0.00 ^c	53.2	0	209	37.3
250	1200	3020 \pm 55	900	0.00 ^c	115.0	0	451	50.1
280	1320	2530 \pm 25	1390	2.92	219.0	11	858	62.6
300	1320	2510 \pm 35	1410	4.89	272.7	19	1069	77.2
350	1320	2530 \pm 25	1390	17.10	332.5	67	1303	98.6

^a TOC_{react} = TOC⁰ – TOC_{exp}.

^b The values refer to the initial carbon in the sample.

^c CO was less than 0.01 mmol/mol C.

^d CRC = 100*(TOC_{CO} + TOC_{CO₂})/TOC_{react}.

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