

PCDD/F formation from 2,4,6- trichlorophenol added model fly ash

Ishrat Mubeen¹, Alfons Buekens^{1,2}, Shengyong Lu^{1*}, Jianhua Yan¹

¹State Key Laboratory for Clean Energy Utilization, Institute for Thermal Power Engineering, Zhejiang University, Hangzhou 310027, China

²Formerly: Chemical Engineering Department, Vrije Universiteit Brussel, Brussels, Belgium

Corresponding author: Shengyong Lu (lushy@zju.edu.cn)

Phone number: +86-139-5713-7049

Fax Number: +86-139-5713-7049

Introduction

Municipal Solid waste incineration (MSWI) fly ash is burdened by heavy metals and polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF); its PCDD/F-load varies with waste composition, combustion conditions, and the pollution control devices used (Weber et al., 2001; Vehlow, 2015). Fly ash contains all ingredients necessary for forming dioxins, including carbon, precursors (chlorophenols CP and chlorobenzenes CBz), chlorides, and metal catalysts. Precursors condense to PCDD and PCDF (PCDD/F) (Altarawneh et al., 2007). De novo synthesis assumes chlorination and subsequent oxidation of carbonaceous structures (Stieglitz and Vogg, 1987; Addink and Olie, 1995; Olie et al., 1998). Chlorinated phenols are known to be important PCDD/F precursors (Ballschmitter, 1988) and 2,4,6-trichlorophenol is among most stable and abundant chlorinated phenols in MSWI fly ashes (Hell et al., 2001). In present study 2,4,6-trichlorophenol was selected to study formation of PCDD/F from model fly ash (MFA) added during de novo tests at different temperatures and reaction times in 10% O₂ and also in pure nitrogen atmosphere.

Materials and methods

Model fly ash (MFA) samples were prepared from silica (SiO₂) as matrix, sodium chloride as source of chloride and activated carbon (AC) as source of carbon. The MFA was mixed with CuCl₂, by grinding these together in a mortar for about 10 min in the following weight proportions: AC (2.5 wt. %), sodium chloride (NaCl; 10 wt. % Cl), 0.2 wt. % copper chloride (CuCl₂) was added and silica (SiO₂) formed the balance. A sample of 2 g of MFA was placed into a vertical quartz tube (53 cm in length and 5 cm in diameter) and fixed by means of glass wool. Then the tube was placed for selected time and temperatures in a preheated electric furnace in a flow of 10% oxygen/90% nitrogen (300 ml/min) to simulate the post-combustion zone of a MSWI, and also in pure nitrogen (see figure 1). 2,4,6- trichlorophenol (TCP) solution in benzene was added at constant rate of 3.18×10^{-5} through a motorized micro syringe pump (HARWARD apparatus, 11plus, Holliston, MA). A blank test was run without sample at similar experimental conditions and after pretreatment sample was analysed for PCDD/F and no compounds were detected in blank test. Every experiment was conducted in duplicate and the average value was further used. US EPA method was used for pretreatment of samples (Zhang et al., 2016).

Analytical methods

The chemical composition of fly ash was analysed by X-ray fluorescence (XRF). The crystalline structure of the fly ash particles was identified by X-ray diffraction analysis (XRD, X'Pert PRO PANalytical B. V.). The microcosmic surface of fly was characterized by SEM (Scanning Electron Microscopy) using scanning electron microscopy (Hitachi SU-70). The BET (Brunauer-Emmett-Teller) surface area and average particle size was measured by Micromeritics Tristar 3020 instrument (results not shown here).

Results and Discussions



Fig. 1. apparatus for de novo tests.

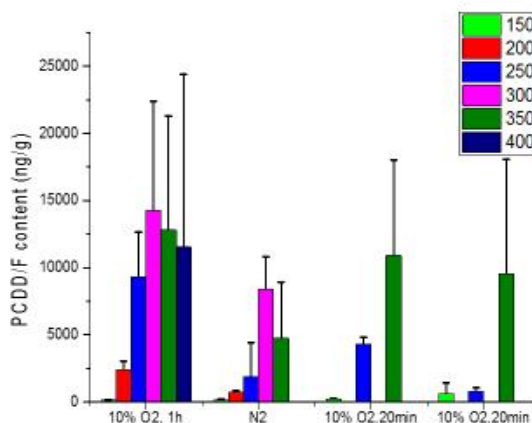


Fig. 2. PCDD/F content (ng/g) at selected temperatures and reaction times.

Fig. 2. represents the PCDD/F-output (in ng/g MFA), as expected, temperature profile of dioxins first increase with temperature, maximum value was observed at 300 °C and after this PCDD/F-output started to decrease in 10% O₂ atmosphere and in pure nitrogen. Addink and Olie (1995) also found the optimum temperature zone of PCDD/Fs formation in the flue gas is 300 to 400°C. In all tested conditions with 0.7 % TCP addition 1,3,6,8-, 1,3,7,9- tetrachlorodibenzo-p-dioxins (T4CDD), 1,2,4,7,9-, 1,2,3,6,8-, 1,2,3,7,9- pentachlorodibenzo-p-dioxins (P5CDD) and 1,2,3,4,6,8- hexachlorodibenzo-p-dioxins (H6CDD) isomers have major distribution among all PCDD isomers (not shown here). These isomers are produced by phenols in MSWI (Ryu et al., 2005). In anoxic conditions, even substantial amount of dioxins have been produced by TCP with high PCDD yield and temperature profile remains same as with 10% O₂ content. De-novo reaction in presence of precursor seems to occur very fast even for a 10 min reaction, and maximum value for PCDD/F was observed at 350 °C and was not much different from a value obtained in 1h reaction time at same temperature

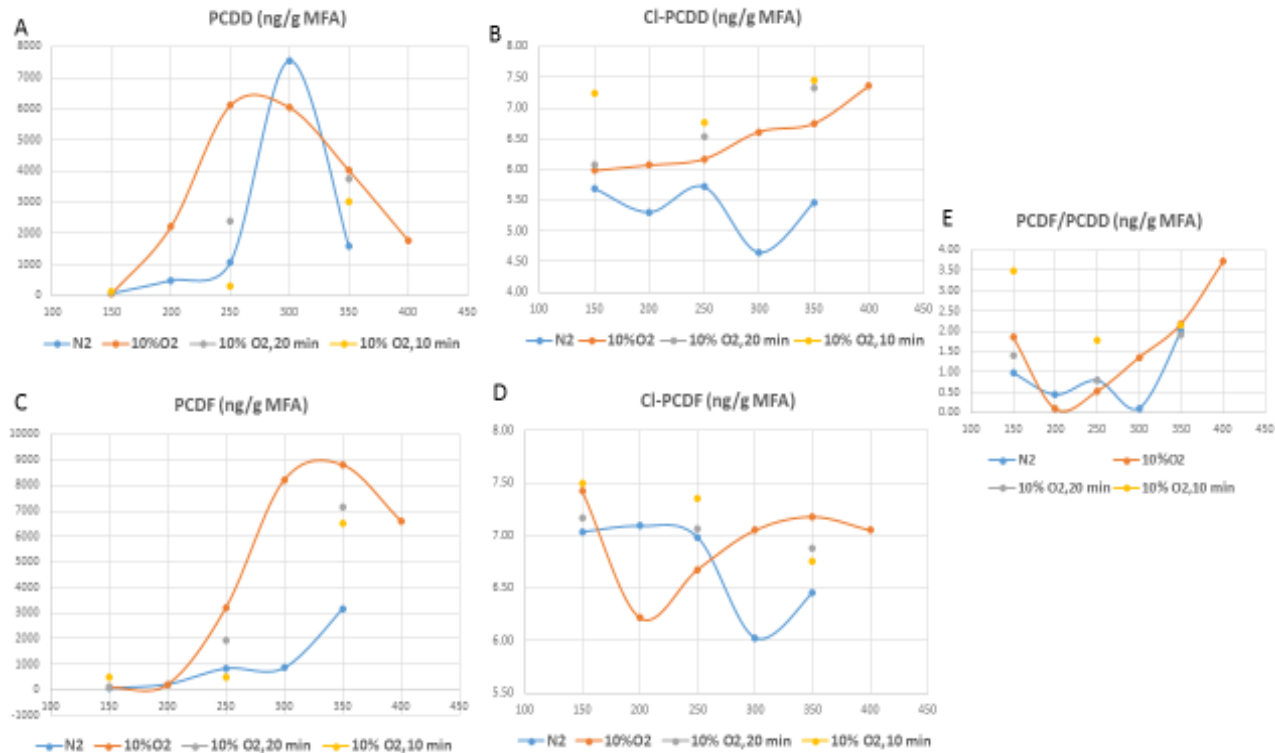


Fig. 3. PCDD, PCDF yield, chlorination level and ratio of PCDF to PCDD (A, B, C, D, E) from 2,4,6-trichlorophenol (TCP) added MFA.

PCDD and PCDF output changes with temperature and reaction time (Fig. 3A and C), Cl-PCDD remains higher than Cl-PCDF (Fig. 3B and D). In all experiments the number of chlorine atoms in PCDD is higher in 10% O₂ for 1h, 20 and 10 min than in N₂. The ratio of PCDF to PCDD has been associated with the respective importance of the de novo and the chlorophenol precursor routes (Huang and Buekens, 1995). Low PCDF/PCDD ratio of some samples suggests their marked preference for the CP-precursor route, whereas, CuCl₂ favours PCDF creation, so with 10% O₂ content, the ratio increased with temperature (Fig. 3E). Fig. 4 shows PCDD/F patterns (PCDD to PCDF = 100%), together with the typical Cu doped MFA pattern. All samples showed T4CDD, P5CDD as dominant homologues among PCDD and O8CDF being the most dominant homologue group in 10% O₂, while in anoxic conditions at 200 and 300 °C T4CDD were most dominant homologues.

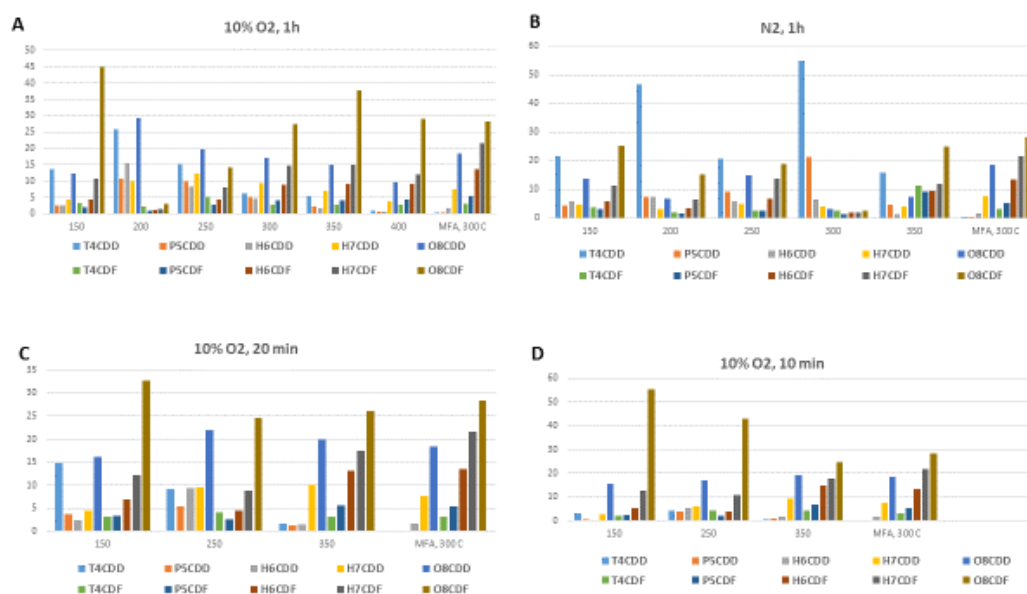


Fig.4. Homologue profiles of PCDD/F (PCDD + PCDF=100 %) at selected temperatures in 10% O₂ and in pure nitrogen.

Acknowledgement: The Project was supported by the National Basic Research Program (973 Program) of China (No. 2011CB201500), the Science and Technology Project of Zhejiang Province (No. 2009C13004), and the Program of Introducing Talents of Discipline to University (B08026) and the Zhejiang University's Pao Yu-Kong International Fund.

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