

Effects of oxygen, sulphur dioxide, sulphuric acid and peroxides on formation of polychlorinated biphenyls (PCBs), dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) on the MWI fly ash.

R. Grabic², S. Marklund^{3*}, V. Pekárek^{1*}, M. Punčochár¹ and J. Ullrich¹

1. Institute of Chemical Process Fundamentals, Czech Academy of Sciences, Rozvojová 135, 16502 Praha 6, Czech Republic
2. Chemical Laboratory of the District Public Health Department, Palackého 121, 73802 Frýdek-Místek, Czech Republic
3. Department of Environmental Chemistry, Umeå University, SE-90187 Umeå, Sweden

Introduction

There exists evidence that catalytic reactions (the so called de novo synthesis) in 200-350⁰C in region on the surface of fly ash particles in postcombustion zone of MWI play an important role in the formation of highly noxious halogene-containing persistent organic compounds (PCBs, PCDDs, PCDFs). However, these reactions strongly depend not only on experimental conditions but also on the presence of compounds which could function as potential precursors for these synthetic reactions. This might be the reason why the results of different authors are not compatible and are sometimes contradictory.

The possibility of PCBs, PCDDs and PCDFs formation by de novo reactions from fly ash, carbon, inorganic chloride and Cu²⁺ salts was described by Stieglitz et al [1-3]. The definite composition of the reaction bed and the fact that the compounds formed were not desorbed under experimental conditions from the fly ash makes possible to study the effects of different compounds on these reactions with good reproducibility.

Material and Methods

Fly ash from fabric filter of MWI CKD-Purotherm (type PL8/100) was soxhlet-extracted with toluene for 24 h, then air dried and sieved to ≤0.25 mm particle size. The main chemical components of the fly ash were: Al 5.96, C 8.24, Ca 4.4, Fe 9.8, Mg 0.38, Si 33.96, Zn 0.2 and water 2.41 all in wt.%. Cr 0.21, Ni 0.36, Cu 0.15 and Pb 0.45 all in mg/g. The mercury density made 1.03 m³/g, calculated porosity equalled to 0.57.

Chemicals. Mixture of N₂+10% O₂, N₂+1% O₂, N₂≥ 99.999 purity and SO₂ (99.9%), were delivered by Linde TÜV, CERT. NaCl, CuCl₂.2H₂O, sulphuric acid and hydrogen peroxide were of Lachema p.a. purity. Activated carbon for chromatography (Merck, 35-50 mesh ASTM), hexachlorobenzene 99% (Aldrich) and 2-ethoxyethanol (puriss. p. a. Fluka) were used as obtained.

Experimental arrangement. The well homogenised mixture of fly ash (0.44 g), NaCl (0.428 mmol), CuCl₂.2H₂O (0.064 mmol) and and carbon (1.998 mmol) were placed at the bottom of U-shaped glass tube. The gases were mixed in a mixing chamber, bubbled through water at laboratory

* The authors to whom correspondence should be sent: pekarek@icpf.cas.cz; smd@chem.umu.se

temperature (for the systems where N_2 -99.999%, H_2O_2 or H_2SO_4 were applied this step was eliminated), preheated at ca $300^{\circ}C$ and introduced into the reaction system which was heated to $340^{\circ}C$ in the temperature controlled reactor. The outlet gases were passed through two washing bottles with 2-ethoxyethanol at ca $0^{\circ}C$. The flow rate of N_2 or mixtures of N_2+O_2 was 10 ml/min, that of SO_2 2 ml/min. The dosing of unheated diluted H_2SO_4 (9.5%), hydrogen peroxide (6%) and of mixture of H_2SO_4 and H_2O_2 , where their concentrations were 9.5 and 6%, respectively, into preheated gases was performed at the inlet of the U-shaped reaction vessel. Before the experiment started the system was thoroughly washed with above gases for 15 min, afterwards it was heated and preheated to 340 and $300^{\circ}C$ and then kept at this temperature another one hour.

Analyses. Samples of fly ash were Soxhlet-extracted with toluene, after HCl pre-treatment. The extracts were concentrated to 10 ml of hexane. The 10% aliquot was analysed. Isotope dilution method according to the EPA 1613 method was used to determine PCDD/Fs (TCDD/Fs to OCDD/F). Internal standard method was applied for PCBs (Tri-CBs to DCB) determination. The samples were concentrated to 100 μ l of nonane (PCDD/Fs) or hexane (PCB fraction). GCQ^(TM) (Finnigan MAT) gas chromatograph coupled with ion trap with external ionisation was used with GCQTM 2.2 software version. MS/MS detection methods were used to achieve corresponding selectivity and sensitivity, using DB-5ms fused silica column (60 m length x 0.25 mm ID x 0.25 μ m film).

Results and Discussion

Effect of oxygen concentration on de novo synthetic reactions is presented in Fig. 1. From our results it is obvious that on decreasing oxygen concentration the formation of hazardous compounds is drastically reduced, in agreement with literature data [4-6]. The PCB formation does not change substantially within the range of 10 to 1% oxygen content. However, the PCDDs and PCDFs concentrations are decreased by about 82 and 35%, resp. Under oxygen-deficient conditions the main process are dehalogenations [7]. About 67% of OCDD is formed at 10% oxygen content. However, at 1% oxygen, the prevailing congeners are OCDD, HpCDDs and HxCDDs (32, 24, and 21% resp.) in agreement with Stieglitz's data [1]. The highest values for TCDDs congeners were found for 1% O_2 system. The congener composition of PCDFs undergoes minor changes as compared to PCDDs, with maximum contents of HpCDFs and HxCDFs congeners. These results confirm the fact that the fly ash can catalyse both decomposition and hydrodechlorination reactions of polychlorinated compounds under oxygen or oxygen-deficient conditions.

Effects of sulphur dioxide and sulphuric acid on de novo synthetic reactions are illustrated in Fig. 2. The contradictory results are published with respect to the SO_2 inhibiting properties for PCBs, PCDDs and PCDFs formation. So called Griffin's postulation that sulphur dioxide in a S/ Cl_2 molar ratio equal to or higher than 0.2 inhibits gas phase formation of PCDDs on the principle of SO_2 reaction with Cl_2 forming SO_3 [8] is given as an explanation of the inhibiting behaviour. In our experiment the inhibiting properties do not seem to be pronounced enough (PCDDs and PCDFs decrease by about 31 and 14%, resp.) as stated in the literature. The isomeric patterns remain unchanged. In the case of H_2SO_4 addition, one half of PCDDs was destroyed and a similar congener profiles were found as with 10% O_2 . The 63% of PCDFs were destroyed, the prevailing congeners being HxCDFs and PeCDFs. There are not enough exact data for understanding the reaction mechanism of this process.

Effect of peroxidic compounds on de novo synthetic reactions is illustrated in Fig. 3. Hydrogen peroxide effectively inhibits PCDDs formation, contrary to PCDFs destruction. The congener

patterns for both compounds show that destruction of the higher halogenated congeners is preferred. The presence of SO₂ influences the destruction of PCBs and PCDDs negligibly. However, surprisingly high values of PCDFs were found in this case. The most efficient destructions were found for the mixture of H₂SO₄ and H₂O₂ where Caro's acid could be formed. In the case of PCDDs, the practically full destruction of TCDDs was found. However, the predominant congeners were OCDD (50%) and HpCDDs (36%).

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Fig. 1

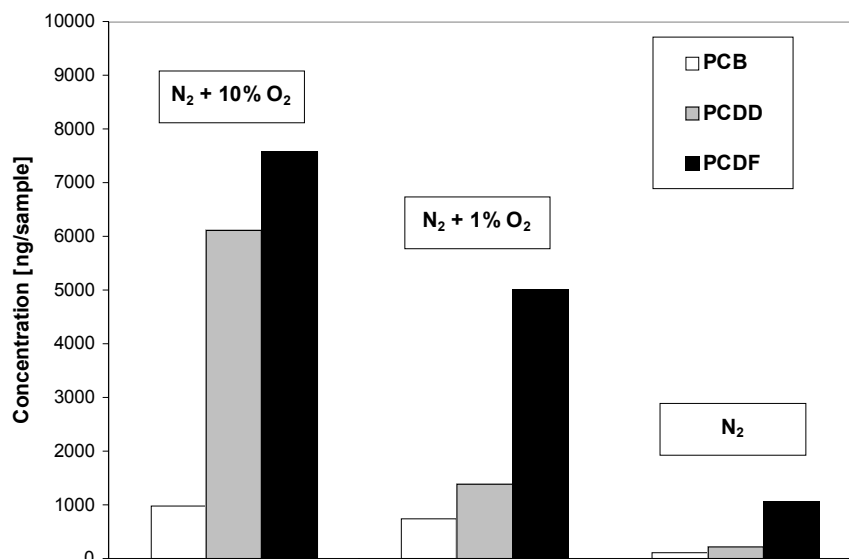


Fig. 2

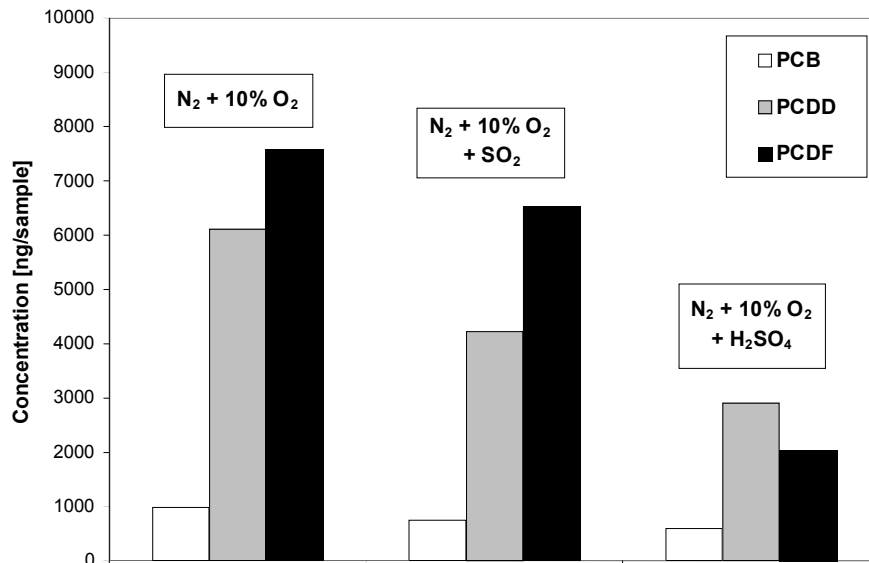


Fig. 3

