

Relevance of PCDD/PCDF Formation for the Evaluation of POPs Destruction Technologies. – PCB destruction by Super Critical Water Oxidation (SCWO)

Roland Weber¹

¹University Tuebingen

Introduction

Persistent Organic Pollutants (POPs) pose a serious threat to public health and the environment^{1,2}. The Stockholm Convention on POPs³ has selected 12 POPs (“The dirty dozen”) to be reduced and/or eliminated within the next two decades. PCBs are one group of POPs of major concern. Although their production has ceased worldwide, PCBs are still present in storages and remain in large quantities in electrical transformers and capacitors, as hydraulic fluids in coal mining or as contaminants in soil and sediment.

The current base line remediation technology for PCBs is incineration. However, temperatures of more than 1100°C are required for their safe destruction, which demand state of the art hazardous waste incineration facilities. These technologies are available only in a few highly industrialized countries. Therefore, during the last two decades several alternative non-combustion technologies have been proposed for PCB/POPs destruction.

Supercritical water oxidation (SCWO) is one technology listed from United Nations Industrial Development Organization (UNIDO) as “Emerging and Innovative Technologies”⁴ and from United Nations Environmental Programme (UNEP) as “Commercialized Technology with Considerable Experience”⁵.

In laboratory experiments and pilot plants it has been shown that PCBs can be destroyed by sub- and super-critical water oxidation^{6,7}. In these studies it was not examined or reported if the formation of PCDFs occurred during the PCB destruction. PCBs exhibit a special challenge because they are PCDF precursors and can be easily oxidized into the more toxic PCDFs. Therefore, during thermal treatment of PCBs, the formation of PCDFs has to be considered, in particular for oxidative destruction technologies. Only Hatakeda et al.⁸ reported the detection of toxicologically non-relevant monochlorinated dibenzofurans as byproducts during

SCWO of 3-monochlorobiphenyl. However, during all thermal treatments of PCBs, the formation of PCDFs, especially the toxic 2,3,7,8-substituted congeners (TEQ), has to be considered as an important parameter and closely evaluated when establishing a treatment method for PCB destruction. It has been shown that the oxidation of PCB to PCDF occurs in the presence of air already at temperature as low as 300°C⁹. Increasing the temperature to 550°C under short term pyrolysis conditions, conversion rates of PCB to PCDF were found to increase up to 25%¹⁰. The present study evaluated the relevance of PCDF formation during SCWO of PCBs and demonstrates the importance of PCDD/PCDF monitoring for the assessment of a PCB/POP destruction technology during pilot and full-scale operations.

Materials and Methods

Chemicals. The PCB mixture used in this study included a Clophen A 30 sample and transformer oil corresponding to Clophen A 60. For the experiments, these PCB mixtures were combined to get a homogeneous homologue distribution of diCB to heptaCB. The mixture also contained measurable amounts of octaCB and nonaCB. Additionally DecaCB was added to enable evaluation of the whole range of PCB homologues in the study.

The PCDFs, generally present in the ppm levels in commercial mixtures^{11,12}, were separated from PCBs on an alumina column before application of the mixtures to avoid their interference with PCDFs that may form during the experiments.

Experimental procedure. A typical experimental procedure was as follows: 11 ml of water were loaded into the reactor and spiked with 100 to 1000 mg PCB mixture. The micro-reactor was filled with oxygen (10 bar) providing an overstoichiometric amount of oxidant. Hastelloy C-276 was selected as a reactor material because it was shown to have favourable anticorrosion characteristics under super critical oxidation conditions.

The sealed autoclave was heated within 5 minutes to the respective temperature and held at this temperature ($\pm 3^\circ\text{C}$) for the chosen reaction time. The reaction was finally quenched by water spray for rapid cooling. The water was extracted with toluene. The reactor was rinsed two times with acetone and two to three times with toluene.

Analysis. Analysis was performed on a HP 6890 gas chromatograph coupled to a HP 5973 mass selective detector or a Micromass Autospec Ultima. The quantification for PCB and PCDD/PCDF was carried out by isotope dilution mass spectrometry with ¹³C-labelled standards. The GC columns used were a SP-2331 column (60 m, 0.25 mm i.d., 0.2 μm film thickness, Supelco, Bellefonte/USA) and

a DB-5 fused silica column (30 m, 0.32 mm i.d., 0.25 μm film thickness, J&W Scientific, Folsom/USA).

Destruction efficiencies of total TEQ (non destroyed PCBs + formed PCDFs) were recalculated to the amount and TEQ of the initial PCB mixture (5.8 $\mu\text{g/g}$).

Results and Discussions

Destruction of PCBs.

The oxidative destruction of PCBs during 15-minute treatments under sub- and supercritical water oxidation conditions is shown in Figure 1. A measurable PCB destruction was detected at 300°C. Under subcritical water conditions at 350°C, the destruction efficiency (DE) was still below 20%. Higher temperatures of supercritical conditions (>374°C) resulted in significant increases of the DE. However the DE at 400°C (87%) and 425 (98.7%) were still insufficient for technical application. Destruction rates greater than 99.99% were finally achieved at 450°C (Figure 1).

PCDD/PCDF formation during PCB destruction.

High concentrations of PCDFs^[1] were formed in all experiments below 450°C (Figure 2). The transformation yields of PCBs to PCDFs under these experimental conditions were in the % range (below 7%) based on the amount of degraded PCBs. The toxic 2,3,7,8-substituted PCDFs were present as major congeners in T₄CDF, P₅CDF and H₆CDF homologue groups. Due to the higher toxic equivalency factors (TEF; calculated according to WHO/ICPS¹⁾) of PCDFs compared to PCBs, the total TEQ of the reaction mixture increased in almost all the experiments compared to the TEQ of the starting PCB-mixture (5.8 $\mu\text{g/g}$) (Figure 3). The increase in TEQ within the 15 minute reaction time was up to 4500% (380°C) (Figure 1B).

The total TEQ decreased only for the experiment at 450°C after 15 minutes residence time (>99.9%). However at 450°C with a residence time of 5 minutes and a PCB destruction efficiency of 99.8%, the total TEQ of the reaction mixture increased by more than 50% (to 8.8 $\mu\text{g/g}$) (Figures 1+3).

Prolonged reaction times resulted in the subsequent degradation of the PCDFs^[2]. This is demonstrated for the oxidative destruction at 400°C by comparison of the

^[1] PCDDs were formed only to a minor extent (<0.01% of degraded PCB).

^[2] The ability of sub- and supercritical water to destroy PCDF and PCDD was also demonstrated by Yamaguchi et al.¹³⁾ and Gräbel and Hagenmaier¹⁴⁾.

15 and 60 minute reaction times (Figure 3) (180.12 and 16.38 $\mu\text{g TEQ/g}$ respectively); however, the total TEQ was increased by ca. 200% after 60 minutes.

Comparison of PCB destruction efficiencies with other studies

The destruction efficiency for PCBs in SCWO in the present study are in agreement with the experiments reported in the literature. For example, Hatakeda et al.⁸⁾ found insufficient PCB degradation rates in SCW with oxygen at 400°C. On the other hand, Anitescu and Tavlarides⁷⁾ found high destruction efficiency in the temperature range between 450 and 550°C within seconds. Lower destruction rates were found in the present experiments when comparing with the results of Anitescu and Tavlarides⁷⁾. One explanation might be the low starting concentration of PCBs in the present study. The low concentration of PCB might prohibit fast progress of degradation via radical chain reactions as could be expected for experiments using higher PCB concentrations. On the other hand the present experiments with low concentrations of PCBs demonstrate that super critical water itself does not have a superior “destruction power” at temperatures below 450°C but probably requires the presence of organics as “combustion fuel”. Therefore, temperatures of more than 450°C and a rigorous monitoring of PCDF have to be applied for a destruction of PCBs (POPs). On the other hand the SCWO process is limited by the type of material used since for most materials unacceptable high corrosion rates are observed in the presence of chlorine already at temperatures around 300°C¹⁵⁾.

Conclusion

High concentrations of PCDFs can be generated during destruction of PCBs under sub- and supercritical water conditions. The increase in total TEQ even when achieving PCB destruction efficiencies of 99.8% (resulting in total TEQ increase of ca. 50%; 450°C, 5 min) or 98.7% (total TEQ increase of ca. 1000%; 425°C, 15 min) demonstrate that destruction efficiencies of PCB/POPs destruction technologies have to be based on total TEQ (toxicological considerations) and not only on destruction efficiencies of total PCBs/POPs. This implicates that PCDD/PCDF monitoring is mandatory in the assessment of a PCB/POPs destruction technology and also essential for the supervision of pilot and full-scale destruction process operation.

The present study further reveals that a technology listed in the highest rank of non-combustion technologies from UNEP and UNIDO has the potential to form high concentrations of PCDFs even at conditions of possible application (the temperature of practical application can not be considerable higher than 450°C due

to material limitations). This shows the necessity of a more rigorous assessment of non-combustion technologies with respect to their PCDD/PCDF formation potential¹⁶⁾ and their actual applicability for PCB/POPs destruction.

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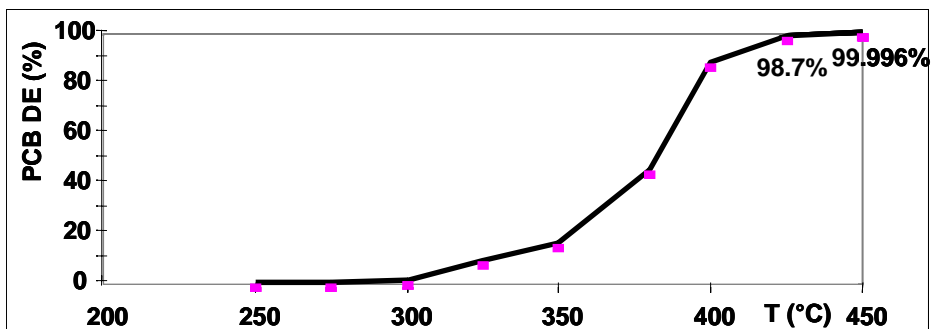


Figure 1: Destruction of PCBs in sub- and supercritical water oxidation experiment (15 min).

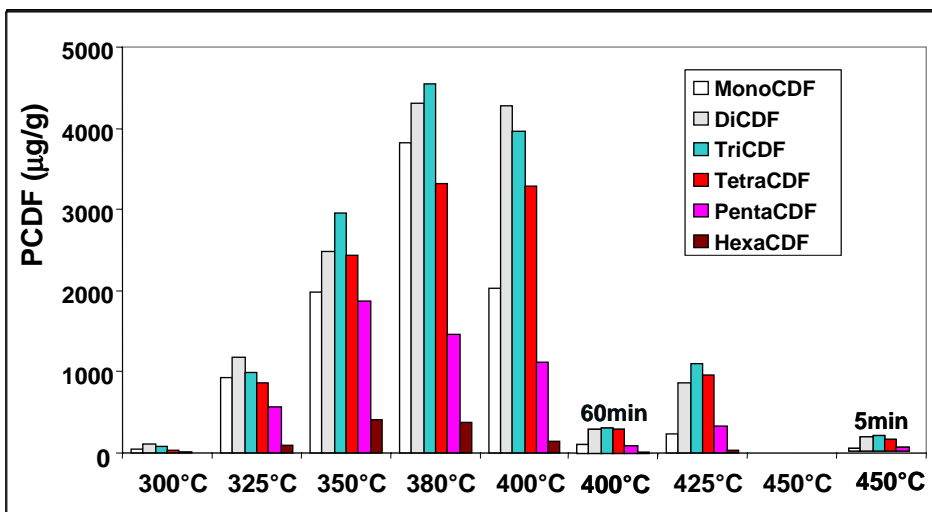


Figure 2: PCDF formed during destruction of PCBs in sub- and supercritical water oxidation in dependence of temperature (15 min).

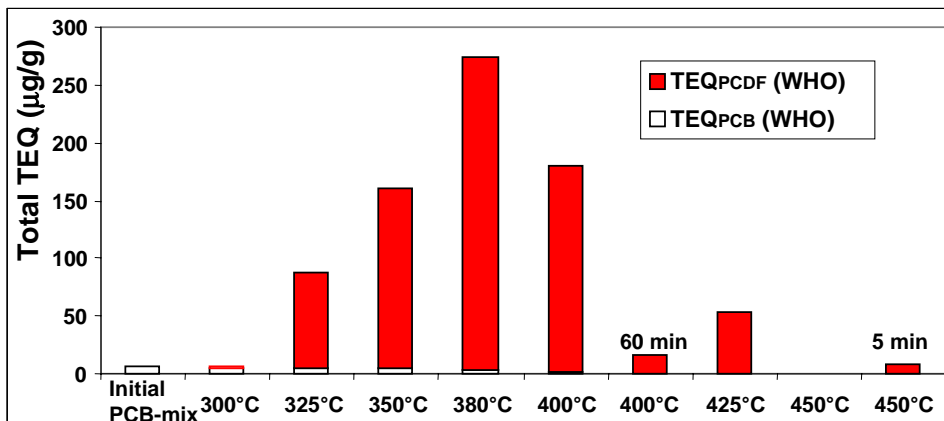


Figure 3: TEQ conc. during destruction of PCBs in SCWO (15 min).