

DESTRUCTION OF PCB IN SUB-CRITICAL WATER - EVALUATION OF THE RELEVANCE OF PCDF FORMATION

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Introduction

The release of polychlorinated biphenyls (PCB) pose a serious threat to public health and the environment. Although their production has ceased world-wide, PCBs are still present in storages and remain in large quantities in electrical transformers and capacitors or as hydraulic fluids in coal mining.

The base line remediation technology for PCB is incineration. However, temperatures of more than 1200°C are required for their safe destruction which demand expensive hazardous waste incineration facilities.

Therefore, during the last two decades several alternative PCB destruction technologies have been proposed including for example based catalysed decomposition (BCD) process¹, destruction in a catalytic reactor² or UV irradiation³.

Supercritical water oxidation has recently been studied as an advantageous oxidation process for the treatment of hazardous waste and developed to commercial scale. In laboratory experiments and pilot plants it has been shown that PCB can be destroyed in sub- and super-critical water^{4,5}.

In these studies it was not examined or reported if formation of PCDF occurs during the PCB destruction. However, during thermal treatment of PCB, the formation of PCDF has to be considered. It has been shown that the oxidation of PCB to PCDF occurs in the presence of air already at temperature as low as 300°C⁶. Increasing the temperature to 550°C under short term pyrolysis conditions conversion rates of PCB to PCDF were found to increase up to 25%⁷.

In this study we investigated the possibility of decontamination of PCB contaminated transformer oils by sub-critical water treatment in the temperature range of 200 to 350°C and evaluate the relevance of PCDF formation during this PCB destruction.

Materials and Methods

The PCB mixture used was Clophen A60 utilised as transformer oil. The commercial PCB mixtures and PCB used in transformer oils themselves contain PCDF at the ppm level. Before the experimental series, these originally present PCDF were separated from the PCB mixture by an alumina column to avoid interference with possibly formed PCDF. After this separation procedure, the PCB mixture used for the experiments was found to be PCDF free.

The PCB content of contaminated transformer oil in Japan lay generally below 100 ppm. We therefore chose a PCB concentration of 100 ppm dissolved in heavy oil or tetradecane for the experiments.

A typical experimental procedure was as follows: measured amounts of 0.1 m sodium hydroxide solution and the PCB contaminated oil were loaded into a Microautoclave. 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 ($\pm 1^\circ\text{C}$) for the chosen reaction time. The reaction was finally quenched by water spray for rapid cooling.

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 ^{13}C -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).

Results and Discussions

Destruction of PCB. A measurable onset of PCB destruction occurred at 250°C . After 1h treatment, still about 90% of PCB were recovered (Figure 1). Increasing the temperature to 275°C more than 80% and at 300°C more than 92% of the initial PCB concentration were destroyed within 1 hour. At 350°C the destruction degree after 1 hour residence time reached more than 99.9% (Figure 1). Therefore the sub-critical water treatment has a high potential to destroy PCB even when dissolved in a hydrophobic media.

PCDF formation during PCB destruction. During all test runs PCDF (but no PCDD) were formed (Figure 2). Sufficient residence time and temperature ($>300^\circ\text{C}$) resulted in the formation of only small amounts of lower chlorinated PCDF and no 2,3,7,8-substituted isomers were detected (Figure 2+3). Under less severe conditions (low temperature or short residence time), T_4CDF , P_5CDF and H_6CDF were formed (Figure 2) including the toxic 2,3,7,8-substituted PCDF as prominent isomers. This shows that PCDF that are formed as intermediate products during the sub-critical water treatment can be destroyed together with the PCB. A destruction of PCDF and PCDD in sub-critical water was also reported by Gräbel and Hagenmaier⁸.

The toxicity of the starting PCB mixture (50 000 ng) was 0.53 ng TEQ*. Applying low temperature and short residence time, the TEQ increased considerably due to the formation of PCDF. The major contributor to total TEQ was found to be predominantly 2,3,7,8- T_4CDF during longer residence times and 2,3,4,7,8- P_5CDF during short residence times. At a destruction degree of around 50% of original PCB concentrations (275°C , 15 min), the TEQ has increased by 25 times (13.2 ng) (Figure 1+3). As can be derived from the second experiment at 275°C (1h) the PCDF formed in the early stage of the treatment (15 min) are subsequently dechlorinated and the toxicity decreased notably (Figure 2 + 3).

At 350°C after 1h treatment, no tetra or higher chlorinated PCDF and therefore no 2,3,7,8-substituted PCDF were detected (Figure 2). With respect to PCBs, only M_1CB to T_3CB were detected which have no assigned TEF factors. Therefore the decrease in TEQ (100%) was even higher than the 99.9% destruction degree calculated for total PCB concentration.

* The TEQs are calculated using the international toxic equivalent factors according to WHO/ICPS⁵

Mechanistic aspects of PCB destruction. During the sub-critical water treatment we observed a homologue shift towards lower chlorinated PCB. Mono- and di-chlorinated PCB, not detected in the starting PCB mixture, were formed. A homologue shift was also observed for the PCDF in dependence of temperature and residence time (Figure 2). Additionally we detected hydroxylated PCBs in the product mixture which were not present in the starting mixture. Therefore the destruction mechanism include both a hydroxylation of the PCB and a dechlorination/hydrogenation.

Under the condition investigated (0.1m sodium hydroxide solution), the hydroxylation is mainly responsible for the destruction of PCB. However, the hydroxylation results in an oxygen insertion in the PCB and partly lead to the observed formation of PCDF. On the other hand the dechlorination velocity above 300°C seems sufficient to overcome the formation of 2,3,7,8-substituted PCDF congeners. By balancing both destruction mechanisms, a safe decontamination of PCB in sub-critical water seems possible.

Conclusion

PCB can be destroyed with high destruction efficiency by sub-critical water treatment. Under the applied conditions, a destruction degree of >99.9% was reached at 350°C within 1 hour. Therefore it seems feasible to destroy PCB in contaminated transformer oils in sub-critical water to levels below the 0.5 ppm regulation limit.

PCDF are formed during this PCB degradation and cause an increase in total TEQ at PCB destruction rates of less than 90%. For conditions that are suitable for technical applications (PCB destruction degrees of more than 99.9%), the intermediately formed PCDF are destroyed together with the PCB and the decrease of TEQ is even higher than the destruction degree calculated for total PCB concentration due to a dechlorination/hydrogenation.

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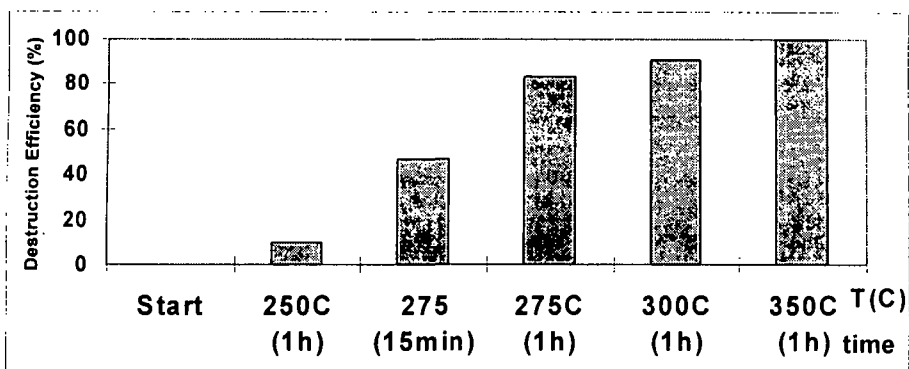


Figure 1: Destruction efficiency of PCB in sub-critical water (0.1M NaOH)

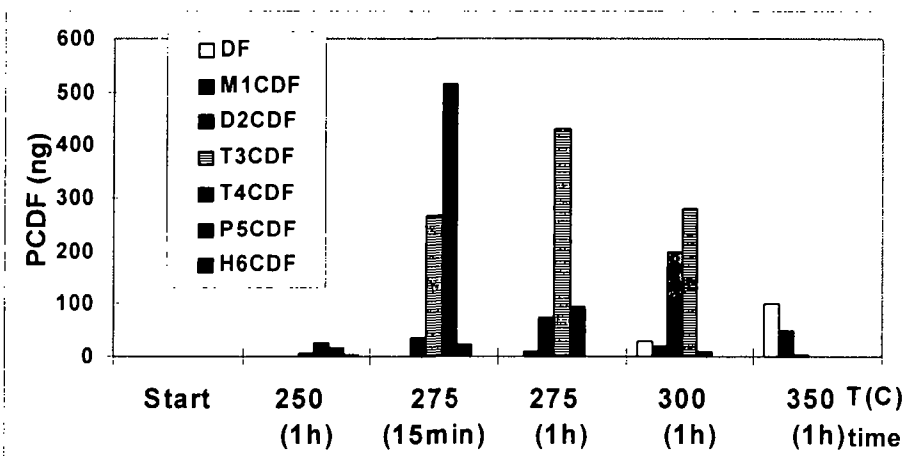


Figure 2: Homologue distribution of PCDF formed during sub-critical water treatment (0.1M NaOH) of PCB (50 000 ng)

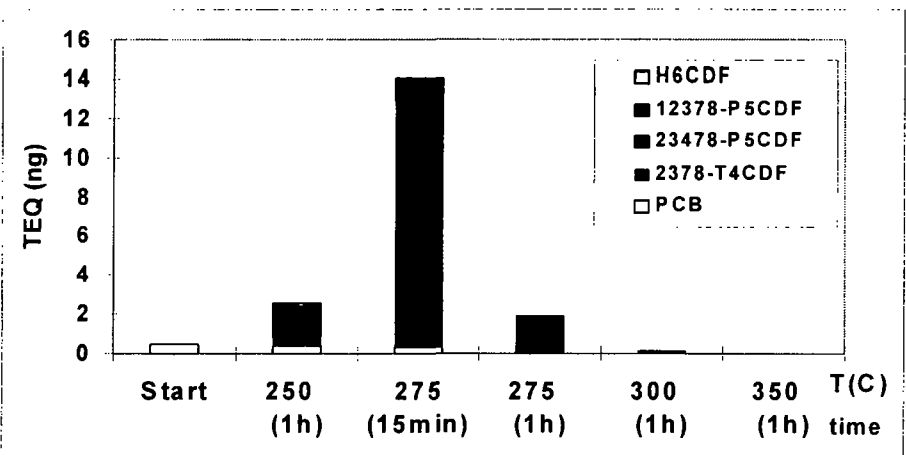


Figure 3: TEQ of reaction mixture before (50 000ng PCB) and after treatments.