# FORMATION AND DESTRUCTION OF PCDD/Fs BY HYDROTHERMAL CARBONIZATION (HTC)

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## Introduction

Hydrothermal carbonisation (HTC) is a thermo-chemical process for biomass conversion[1]. The process reflects the natural process of coal generation. At temperatures around 200 °C and pressures of about 20 bar, solid and wet biomass is dehydrated within hours and transformed in bio-coal with a heating value similar to brown coal [2,3] . The process was first described by Friedrich Bergius at the beginning of the last century when he studied naturally occurring coal formation[4]. By analyzing the dioxins/furans (PCDD/Fs) content of sewage sludge before and after hydrothermal carbonization (HTC) treatment in an industrial plant operating at temperatures around 205 °C, a slight increase in the PCDD/Fs content on the basis of toxic-equivalents (WHO-TEQ) was observed[5] . By varying the experimental conditions of hydrothermal carbonization an unusual high ratio between 1,2,3,7,8,9-HxCDD and 1,2,3,6,7,8-HxCDD and the absence of almost all chlorinated dibenzofurans were also detected [6]. A similar pattern was observed in 1996 in ball clay samples from the Mississippi embayment[7,8,9] . Later in clay samples form Germany, Spain and Japan a similar pattern was also detected[10,11,12] . One "side effect" of this transformation is the partial lateral de-chlorination of higher chlorinated PCDDs which increases the toxicity on a TEQ basis. Since the de-chlorination process is temperature dependent, we wanted to test how the HTC reaction evolves at higher temperatures.

## Materials and methods

Sludge, or clay matrix samples, were put in a hermetically sealed stainless steel reaction vessel and heated for 15 hours (overnight) in an oven to the temperature set for the experiment. After cooling at ambient temperature, the vessels were opened and the resulting material was first filtered and then dried in an oven.

Sewage sludge from a municipal waste water treatment plant, after anaerobic digestion, with a dry mass content of about 20 %, was analyzed for PCDD/Fs before and after the HTC treatment at various temperatures. After the treatment, the sewage sludge was transformed into a black, lignite like slurry.

To create a sample with a matrix elemental constitution similar to clay, we mixed together basic alumina oxide (Alumina B – Super 1 from MP Biomedicals, Germany), silica gel (MP Silica 63-200, active 60A from MP Biomedicals, Germany), dry green cut (hay) and de-ionized water. The green cut and the water are necessary to obtain HTC conditions once the sample is heated up. This clay matrix was then mixed with fly ash from a municipal solid waste incinerator and analyzed for PCDD/Fs content before and after HCT treatment.

In order to get information on the homogeneity of the samples, two samples of the sewage sludge and two samples of the obtained coal sludge were analyzed for PCDD/F content.

Sample extraction, clean-up and quantification of tetra- to octa-chlorinated PCDD/Fs were performed according to US EPA 1613 method[13] . This involves isotope dilution using high resolution gas chromatography coupled with high resolution mass spectrometry (HRGC/HRMS) using an Agilent 6890 N gas chromatograph and a Thermofinnigan MAT 95 XP mass spectrometer at 10 000 resolving power (10 % valley definition). Gas chromatographic separation was performed on a DB 5 ms column, 60 m x 0.25 mm i.d. x 0.25 µm film thickness (Agilent).

## Results and discussion

In Fig. 1 the results of the HTC experiments at different temperatures are noted. HTC mainly causes a de-chlorination of higher chlorinated PCDD/Fs in the lateral position (Tirler and Basso, 2013), but peri de-chlorination, to a lesser extent, also happens and, in this case, 2,3,7,8 -substituted, lower chlorinated PCDDs with a relatively high toxicity are the result. The increase of the total toxicity after HTC is mainly caused by this de-chlorination in the peri position (loss of chlorine in one or more of the 1,4,6,9 -positions). If we look on how HTC transforms the PCDD/Fs content based on toxicity using WHO 2005 TEFs, we see that sewage sludge increases considerable, by factor of about 25, after HTC treatment at 255 °C. If we increase the temperature to 275 °C, we observe a lower toxicity than at 255 °C. Surprisingly, a further increase of the HTC temperature to 310 °C leads to nearly complete destruction of all PCDD/Fs of the sewage sludge sample. It seems that HTC

can cause a remarkable increase in toxicity at lower HTC temperatures, but at higher temperatures, the de-chlorination process proceeds in a way which nearly destroys all tetra-, to octa-chloro substituted DD/Fs. The result is a complete de-toxification, regarding PCDD/Fs. If we apply HTC to fly ash, clay matrix, and green cut mixture, we see no increase at a temperature of 255 °C, but an decrease in toxicity. At a temperature of 275 °C, we observe a slight increase in toxicity in the case of this fly ash, clay matrix and green cut mixture. The de-chlorination process seems to proceed much faster in sewage sludge. One of the possible causes could be the relative higher titanium content of sewage sludge, compared to that of fly ash, clay matrix and green cut mixture [14] . Anyway at a HTC temperature of 310 °C, we observed a nearly complete removal of all PCDD/Fs in the case of the fly ash, clay matrix, green cut mixture. Table 1 shows the abatement rates for PCDD/Fs and PCBs we found after HTC at 310 °C when fly ash, clay matrix and green cut mixture was spiked also with PCBs. In this case our sample contained dioxins and PCBs before HTC.

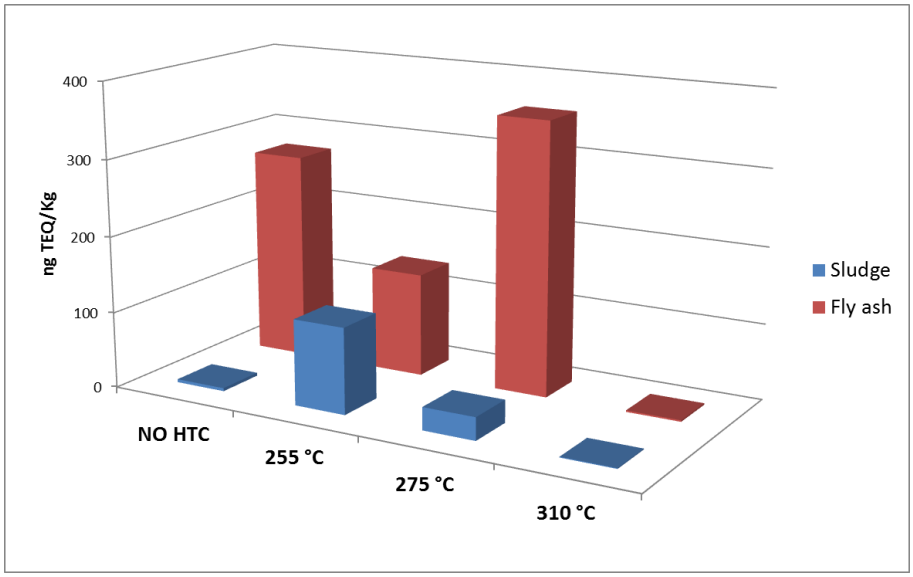

Fig. 1: Results of HTC at different temperatures

| | Fly ash + clay matrix + green cut | After HTC | Abatement in % |
|---|---|---|---|
| Dioxin in pg TEQ/g (WHO 2005) | 256 | 1,9 | >99 |
| PCB pg TEQ/g (WHO 2005) | 40 | <0,2 | >99 |

Table 1: Abatement efficiency of HTC for PCDD/F and PCBs at 310° C.

In order to have a closer look at how HTC works, instead of using material known to be contaminated with PCDD/Fs, such as fly ash from a municipal waste incinerator or sewage sludge samples from a municipal waste water treatment plant, we tested by spiking the clay matrix only with octachloro-dibenzo-p-dioxin (OCDD).
In this case tetra,- penta,- hexa, and hepta CDDs can only be formed by de-chlorination of OCDD, and so we can exclude all other possible formation reactions of these compounds by possible unknown processes related to hypothetical "precursor" molecules. These experiments were performed with and without green cut.
Without green cut means without bio-mass and, in this case, we have only hydro-thermal conditions. In simple words, no bio-mass means no carbonization reaction. In Fig. 2, we see that the carbonization reaction at 235 °C proceeds if only OCDD is present in the material exposed to HTC treatment. OCDD is partially transformed into HxCDDs and, within these group of compounds, we note the dominant 1,2,3,7,8,9- HxCDD congenere, usually observed in natural clay minerals. In Fig. 3 we report the results of HTC experiments when only OCDD, with and without green cut (bio-mass), on a percentile scale. The effect of the bio-mass is clearly visible. Without bio-mass at a temperature of 235 °C, we hardly find any de-chlorination: de-chlorination is inhibited. OCDD remains intact, and practically 100 % of all PCDDs relates to OCDD. Adding bio-mass (green cut) enables to start the HTC reaction and OCDD is de-chlorinated. In Fig. 3 we see that HxDDs are formed and 1,2,3,4,6,7,8 - HpCDD is even higher than OCDD.

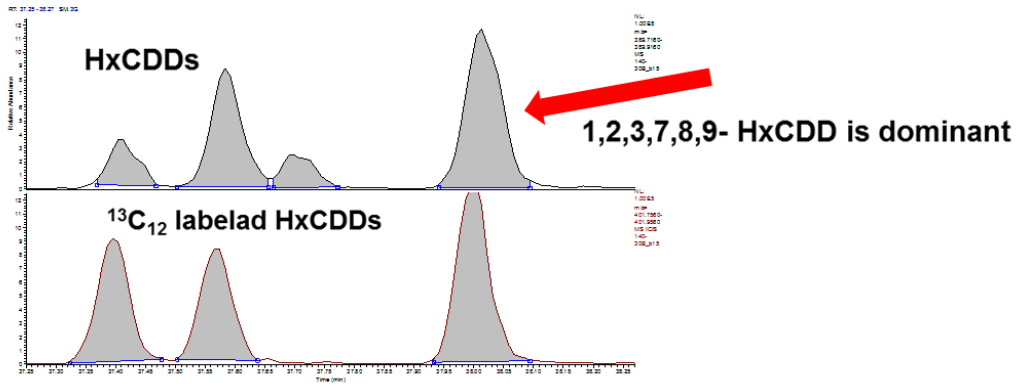


Fig: 2 Chromatogram of HXDDs of fly ash + clay matrix + green cut spiked with OCDD, after HTC at 235°C

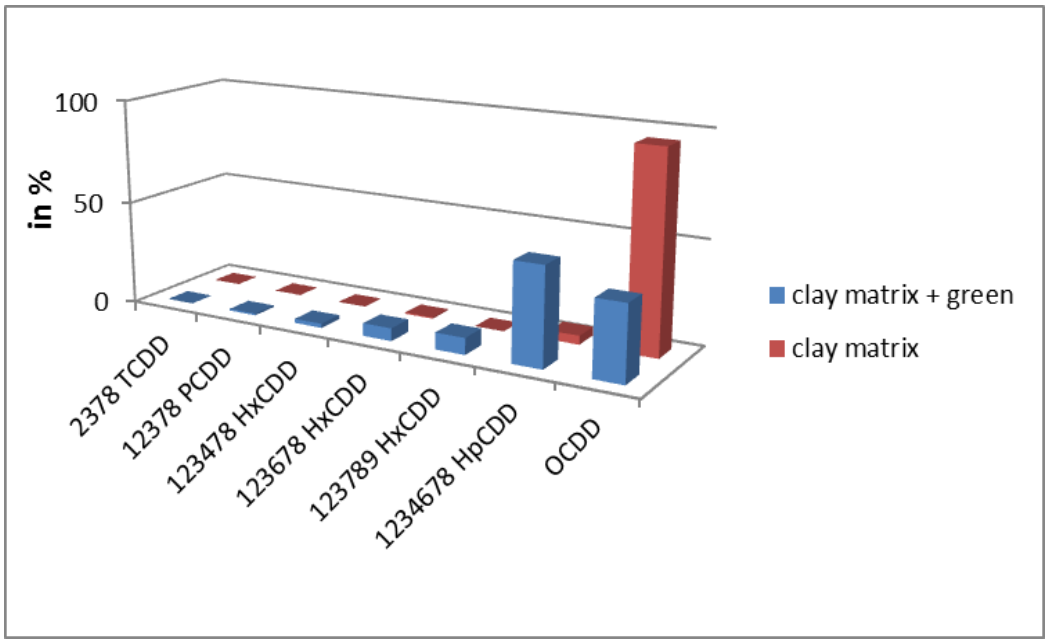


Fig: 3: Percentile distribution of different 2,3,7,8- substituted PCDDs after HTC of fly ash + clay matrix + green cut spiked with OCDD at 235 °C

HTC transforms biomass into a brown coal like slurry, resembling the natural (geological) process of coal formation. By this process, already present PCDD/Fs (eg. from a natural source) undergo a transformation consisting in predominantly lateral (2,3,7,8-positions) de-chlorination[15,16] .
However peri (1,4,6,9- positions) de-chlorination also happens, leading to a total dioxin toxicity (on WHO 2005 TEQ basis) of one to two orders of magnitude higher (in the case of sewage sludge). OCDD can also, on a long time scale, be transformed by a natural geological process into much more toxic, lower chlorinated 2,3,7,8 substituted PCDDs.
The de-chlorination reaction is temperature dependent. On moderate temperatures, egg. around 255 °C, a considerable increase of the dioxins on a TEQ basis is possible. This increase is the result of the formation of lower-chlorinated DDs (tetra, and penta) from higher chlorinated DDs (HpCDDs and OCDD) by de-chlorination. At higher temperatures these de-chlorination reaction proceeds further to lower chlorinated DDs.

When tetra and penta CDDs are also de-chlorinated, all 2,3,7,8 – chloro-subsituted dibenzo-p- dioxins are destroyed and the result is that we have a complete removal of all toxic PCDDs.
HTC has the potential to increase the toxicity of a material already contaminated with PCDD by the formation of very toxic tetra- and penta- CDD by de-chlorination of higher chlorinated dibenzo-p-dioxins. At higher temperatures HTC converts into a very efficient POP elimination process.

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