Hydro-thermal carbonisation: a new approach in waste treatment?

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Abstract
Just heat and pressure enable the hydrothermal carbonisation (HTC) to remove water from biomass converting it in a coal-water slurry. The process reflects the natural process of coal generation and can be applied to several biomass products including organic bio waste. Using sewage sludge some changes in the PCDD/F congenere distribution were observed after the treatment. The HTC process can therefore be considered as a strong chemical process, which leads in a few hours to chemical modifications normally observed when high temperatures or very reactive chemicals are used. By adapting the process conditions several different materials, ranging from green cut, sewage sludge to contaminated soil can be handled.

Introduction
Hydrothermal carbonisation (HTC) is a thermo-chemical process for conversion of biomass in a coal-water slurry. The process reflects the natural process of coal generation. At a temperature of 180°C to 220°C and pressures around 20 bar, solid and wet biomass is dehydrated within hours and transformed in bio-coal with a heating value similar to brown coal. The process by itself is not new. In 1913 Friedrich Bergius studied the natural occurring coal formation. In 1931 he received the Nobel Prize in chemistry for the development of chemical high pressure methods. Almost a century later, in 2006 Markus Antonietti presented the results of his work "Magic Coal from the steam cooker" the successful application to a wide range of biomass including organic waste [1].
During the process the macromolecular structure of the original biomass will be destroyed resulting in an easy to dry product. Beside the use as substituent fuel in thermo-electrical plants the product can also be used as soil conditioner in regions with low organic content in the soil [2]. The process was applied to several biomass product including also organic bio waste.
Sewage sludge of municipal waste water treatment plants is, beside its use in agriculture, is nowadays frequently burned in incineration plants. But also HTC operates at conditions that allow a secure sanitation. Waste incineration was in the past associated with dioxin emissions. And despite modern plants present very low emission levels the public acceptance is sometime still low. Sewage sludge can by themselves carry persistent organic pollutants and in several countries limits to the agriculture use on the dioxin content where set [3].
In the present study the fate of PCDD/F during HTC of sewage sludge was therefore investigated. The process is slightly exothermic and some of the gas phase was discharged via a back pressure valve. This leads to emissions (mainly steam and CO_2), but the amount is minimal. Compared to the combustion of biomass a 100 to 1000 times' lover volume of gaseous emission are produced. This means also that the energy efficiency of the transformation to bio-coal is very good, since the relative amount of produced CO_2 is low. Nearly all the energy content of the biomass can be preserved.

Materials and methods
At a HTC plant in Naquera (Spain) with a capacity of about 0,4 tons of biomass per hour, samples of either the sewage sludge before the treatment and of the resulting bio coal product were analysed. The plant normally operates in converting waste biomass, like cut of the green along roads. This bushy material is not easy to use as a fuel material, because its hard to dry. On the other site it contains a lot of natural herbicides, it is hard to compost and therefore not suited for amendment in agriculture. After few hours of HTC this biomass is converted in a easy to dry product and can be used as a kind of fertilizer. For our test runs the plant operation was changed to accept sewage sludge with 17% dry matter. After approximately 8 hours at 200 - 207°C and 16 - 18 bar, the produced coal sludge was analyzed. Determination of PCDD/Fs were performed by isotopic dilution on a Thermo MAT 95 XP (HRGC/HRMS) following US EPA method 1613.

Table 1: PCDD/F results before and after HCT: all results in ng /Kg dry matter

	Sewage sludge 1	Sewage sludge 2	Coal slurry 1	Coal slurry 2	I-TEF	WHO-TEF 2005
2,3,7,8 TCDD	0.09	0.02	0.41	0.11	1	1
1,2,3,7,8 PCDD	0.68	1.00	0.30	0.72	0,5	1
1,2,3,4,7,8 HxCDD	0.48	0.65	7.63	8.20	0,1	0,1
1,2,3,6,7,8 HxCDD	3.25	2.44	12.77	13.18	0,1	0,1
1,2,3,7,8,9 HxCDD	1.57	0.65	16.83	10.17	0,1	0,1
1,2,3,4,6,7,8 HpCDD	88	60	300	278	0,01	0,01
OCDD	739	435	1109	1071	0,001	0,0003
2,3,7,8 TCDF	5.43	2.49	3.78	5.16	0,1	0,1
1,2,3,7,8 PCDF	2.92	0.89	2.27	3.02	0,05	0,03
2,3,4,7,8 PCDF	0.83	0.44	5.50	2.89	0,5	0,3
1,2,3,4,7,8 HxCDF	2.38	0.44	2.34	1.09	0,1	0,1
1,2,3,6,7,8 HxCDF	2.27	0.97	3.72	1.86	0,1	0,1
2,3,4,6,7,8 HxCDF	3.64	0.96	2.46	2.24	0,1	0,1
1,2,3,7,8,9 HxCDF	0.04	0.16	0.17	0.13	0,1	0,1
1,2,3,4,6,7,8 HpCDF	9.75	12.03	15.33	21.36	0,01	0,01
1,2,3,4,7,8,9 HpCDF	1.80	2.44	5.81	4.98	0,01	0,01
OCDF	7.67	9.23	2.70	3.74	0,001	0,0003
ng WHO 2005 TEQ/Kg dry matter	**4.2**	**2.9**	**10.9**	**9.4**		
ng I-TEQ/Kg dry matter	4.6	2.9	12.7	10.4		

Results and discussion

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

The resulting total equivalent toxicity varied from 2.9 to 4.2 ng WHO TEQ/Kg dry matter in the case of sludge and from 9.4 to 10.9 ng WHO TEQ/Kg dry matter in the case of the bio-coal product.

It seems that during the process some change in the congenere distribution happens. The product presents slightly higher values in terms of total equivalent toxicity, but are still low when compared to the limit value (100 ng TEQ/Kg dry matter) for restrictions of the use of sewage sludge in agriculture proposed in European countries [3]. Its interesting that some congenere increases significantly, like observed on 1,2,3,4,7,8 HxCDD, 1,2,3,6,7,8 HxCDD,1,2,3,7,8,9 HxCDD and 2,3,4,7,8 PCDF. On the other hand OCDF seems to decrease. In any case some changes during the process can be observed. This is notable, considering PCDD/F as some of the most chemical stable organic compounds and that this change happens in few hours at relatively mild conditions (200°C and 20 bar). The HTC process can therefore be considered as a strong chemical process, which leads in a short time to chemical modifications normally observed when high temperatures or very reactive chemicals are used. Also by simple composting of biomass changes in the congenere distribution can be observed [4,5,6]. But when composting some change happens after several weeks, not after 8 hours.

In our case we observed a slightly increase of the total toxicity, but during the process no control and correction of the pH values were performed. By adding some additive and by operating at different pH values we should have the possibility to influence the reaction mechanism in a way to selectively remove contaminants. It should also be possible to adapt the process to several remediation processes.

References:

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