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Analysis of organic compounds (PCDD/Fs in flue gas; PCDD/Fs, PAHs, PCBs in different ashes) of wood waste fired boilers.

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1. Introduction

In order to study the emission of organic compounds of wood waste (bark) fired boilers from an existing heating plant, analyses of PCDD/Fs in the flue gas as well as analyses of PCDD/Fs, PAHs and PCBs in the bottom ash, cyclone fly-ash and electrostatic precipitator ash of two different boilers (2,5 MW_{th} and 4 MW_{th}) were carried out. The knowledge of these substances is very important, as they are beside the heavy metals a potential risk for the environment. That means, if you are looking for possibilities of utilization, for example as a fertilizer, you have to know the content of organic compounds, too. Futhermore we wanted to compare the emission of organic compounds of bark fired boilers with the emission of a brown coal fired boiler (full load 290 MW_{th}) too. Normally the heat for the district heating comes from this boiler, but if the boiler is out of service (approximately 6000 h/year) the wood waste boilers are in service.

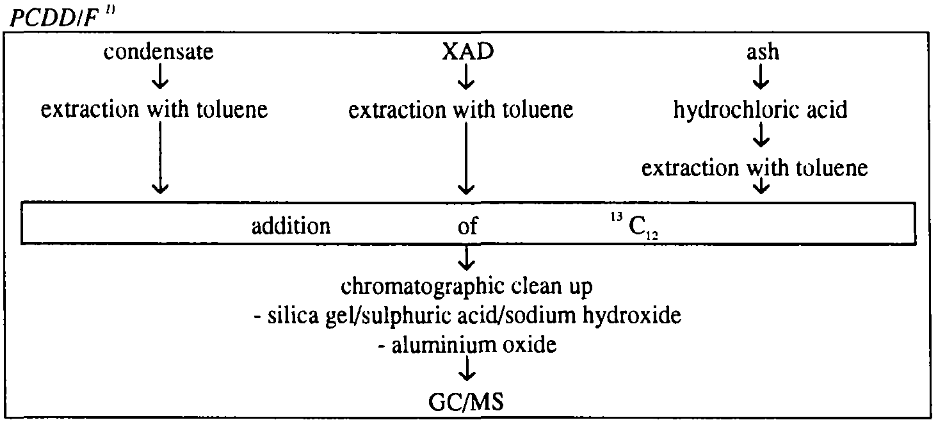
2. Methods

2.1 Sampling

Samples of flue gas, bottom ash, cyclone fly-ash and of the electrostatic precipitator fly-ash were taken under different conditions of the boilers. For sampling of PCDD/Fs and PAHs in the flue gas we used the condensation method.

2.2 Analytical procedure

2.2.1 PCDD/F [1]



For the identification of the PCDD/F peaks we used the following four conditions: massnumber, retention time, M-COCl peak and the probability to find a ^{37}Cl-atom (binominal distribution).

$$P_k = \binom{n}{k} * \left(\frac{1}{4}\right)^k * \left(\frac{3}{4}\right)^{n-k}$$

P_k = Probability of ^{37}Cl-atom
n = Number of Cl-atom in the molecule
k = Number of ^{37}Cl-atoms in the molecule

2.2.2 *PAH*

condensate → liquid/liquid extraction with cyclohexane[2)]
ash → soxhlet extraction with hexane/acetone[3)]
↓
chromatographic clean up[4)]
- sodium sulphate
- silica gel
- pentane/dichlormethane
↓
GC/MS[5)6)]

The number of compounds depends on the sample. For liquid sample (flue gas condensate) we analysed 6 compounds and for solid samples (all kinds of ashes) we analysed 16 compounds.[6)]

2.2.3 *PCB*

ash
↓
soxhlet extraction with hexane/acetone[3)]
↓
addition of decachlorbiphenyl (209)
↓
chromatographic clean up[7)]
- sodium sulfate
- Florisil
- hexane/ethyl ether
↓
GC/ECD[8)]

3. Results

As boiler 1 has only one ash removal system for bottom ash and cylone fly-ash a difference of these ashes was not possible. But the greatest part of ash is the bottom ash with approximately 50 - 70 % of the total amount. The part of the electrostatic precipitator fly-ash is approximately 10 % of the total amount.

Table 1: *Organic compounds in the flue gas*

	Boiler 1 ($2{,}5MW_{th}$)		Boiler 2 ($4MW_{th}$)		Coal fired boiler
	low load	full load	low load	full load	
Σ PCDD/Fs [ng/m³ TEQ][9]	0,084	n.d.	0,012	0,013	n.d.
Σ PAHs [µg/m³ in C]	(-)	12,02	(-)	(-)	(-)

Table 2: *Organic compounds in the bottom ash*

	Boiler 1 *)		Boiler 2	
	low load	full load	low load	full load
Σ PCDD/Fs [pg/g TEQ][9]	n.d.	n.d.	n.d.	n.d.
Σ PAHs [µg/g in C]	(-)	10,01	99,56	2,99
Σ PCBs [ng/g]	(-)	1,07	(-)	19,72

Table 3: *Organic compounds in the cyclone fly-ash*

	Boiler 2	
	low load	full load
Σ PCDD/Fs [pg/g TEQ][9]	n.d.	n.d.
Σ PAHs [µg/g in C]	0,35	1,17
Σ PCBs [ng/g]	(-)	18,71

*) includes the cyclone fly-ash too
n.d. = not detectable
(-) = not determined

Table 4: *Organic compounds in the electrostatic precipitator fly-ash*

	Boiler 1		Boiler 2		Coal fired boiler
	low load	full load	low load	full load	
Σ PCDD/Fs [pg/g TEQ][9]	15,8	18,4	27,1	15,2	n.d.
Σ PAHs [µg/g in C]	(-)	(-)	0,739	439,68	0,038
Σ PCBs [ng/g]	(-)	(-)	(-)	263,03	**5,47**

4. Discussion

Bark fired boilers show more emission of organic compounds than the coal fired boiler. In spite of the low content of chlorine in the bark (~ 0,02 %), the formation of PCDD/Fs is possible. This is, because the content of sulphur in the bark is very low (approximately ten times lower than in the coal)[10]. There is not much difference how the boilers are in service.

Figures 1-2 show the distribution of PCDD/F in the flue gas and in the electrostatic precipitator fly-ash.

Figure 1: *Distribution of PCDD/F in the flue gas of boiler 1*

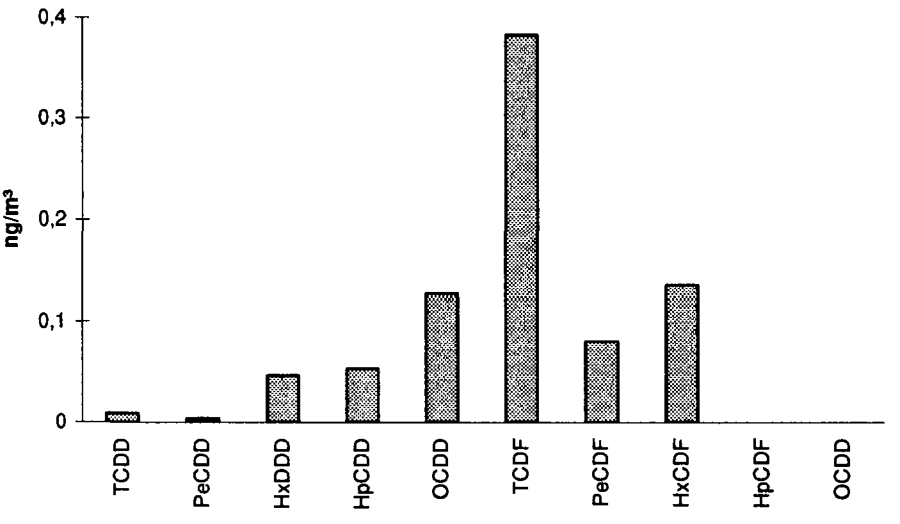
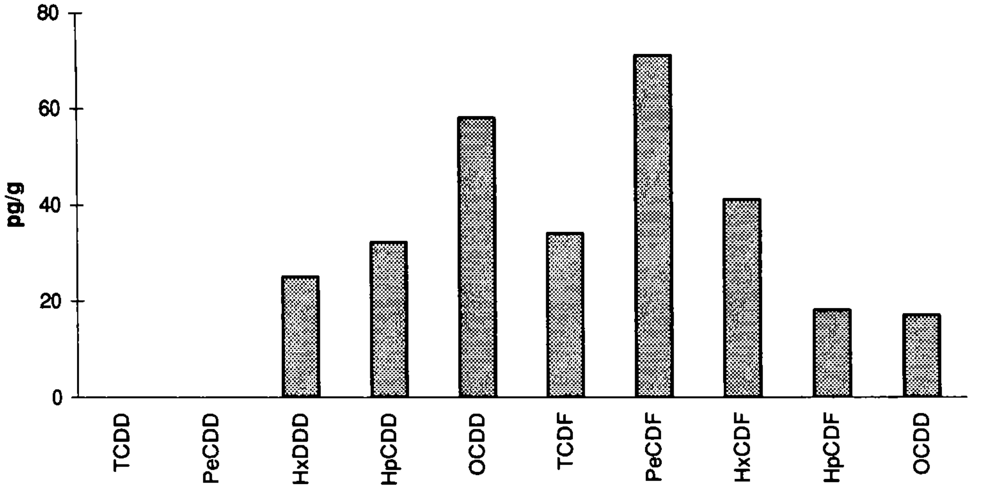


Figure 2: *Distribution of PCDD/F in the electrostatic precipitator fly-ash of boiler 2*



Next we found, that the distribution of the PAHs depends on the boiler load. If the boilers are in low load service the concentration of organic compounds in the bottom ash is much higher than in full load service. Otherwise, if the boilers are in full load service the concentration of organic compounds in the ashes of the flue gas cleaning system of the boilers are much higher. This is because if the boilers are in full service, the speed of the flue gas is higher and more unburned carbon comes into the back part of the boilers. This is a good condition for the formation of organic compounds, such as PAHs[11].

Figure 3: *Distribution of PAHs in the cyclone fly-ash and bottom ash of boiler 2*

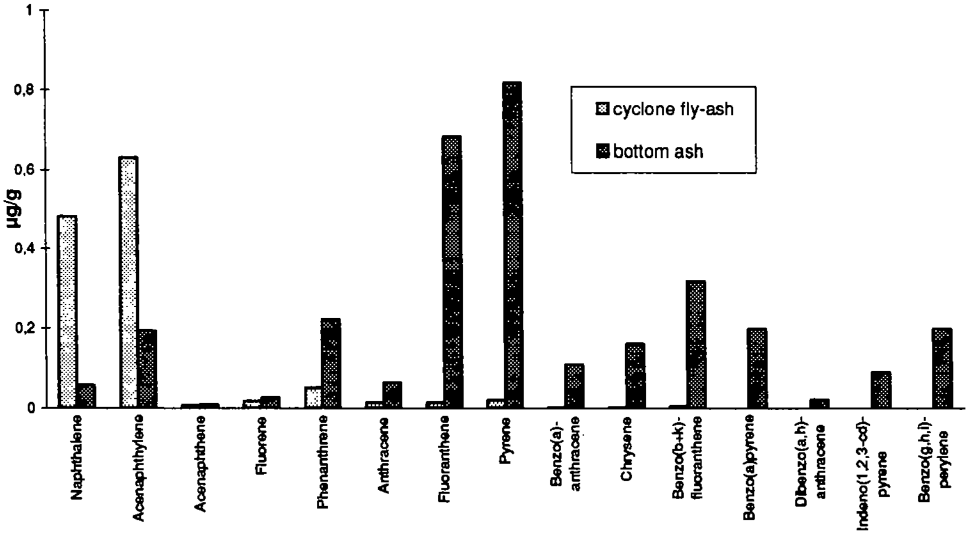
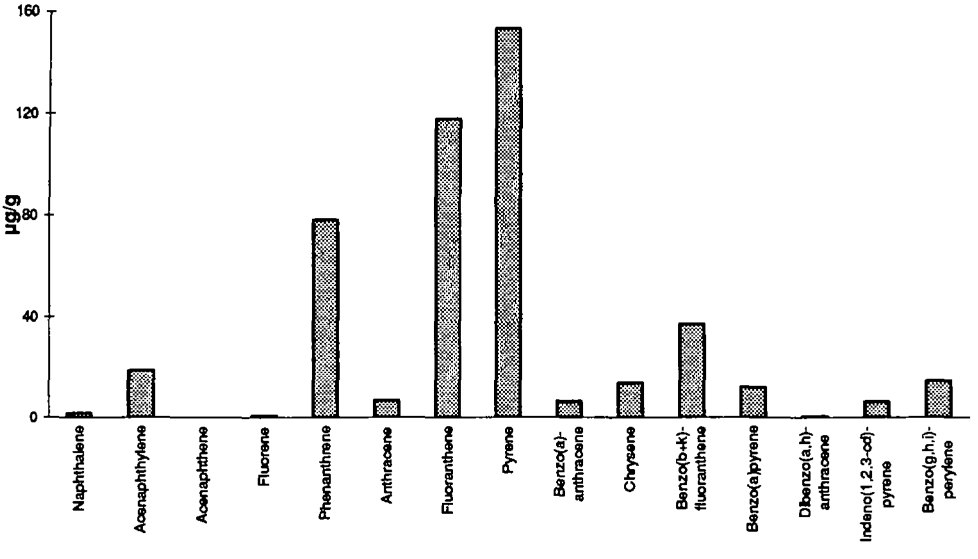


Figure 4: *Distribution of PAHs in the electrostatic precipitator fly-ash of boiler 2*



5. References

[1] Messen von polychlorierten Dibenzodioxinen und -furanen im Rein- und Rohgas von Feuerungsanlagen mit der Verdünnungsmethode, Bestimmung in Filterstaub, Kesselasche und in Schlacke, VDI 3499, Blatt 1

[2] Separatory funnel liquid - liquid extraction, EPA Method 3510, September 1986

[3] Soxhlet extraction, EPA Method 3540, September 1986

[4] Silica gel cleanup, EPA-Method 3630, September 1986

[5] Messen von polycyclischen aromatischen Kohlenwasserstoffen (PAH) an stationären industriellen Anlagen - Verdünnungsmethode (RWTÜV-Verfahren)- Gaschromatographische Bestimmung, VDI 3873 Blatt 1, Mai 1989

[6] Polynuclear aromatic hydrocarbons, EPA-Method 8100, September 1986

[7] Florisil column cleanup, EPA-Method 3620, September 1986

[8] Bestimmung polychlorierter Biphenyle (PCB), Flüssigchromatographische Vortrennung und Bestimmung 6 ausgewählter PCB mittels eines Gaschromatographen mit Elektronen-Einfang-Detektor (ECD) DIN 51527 Teil 1, Mai 1987

[9] Bundesgesetzblatt für die Republik Österreich, Luftreinhalteverordnung für Kesselanlagen 1989, BGBl. Nr. 19, 8. März 1990

[10] Hagenmaier: Untersuchung von Kraftwerksabgasen auf polychlorierte Dibenzodioxine und Dibenzofurane, Abschlußbericht zum VTG - Forschungsprojekt Nr. 90, 1987

[11] Obernberger: Skriptum zur Vorlesung - Thermische Biomassenutzung, Institut für Verfahrenstechnik,Technische Universität Graz, 1996