THE EMISSION OF PCDD/PCDF's, RELATED COMPOUNDS AND HEAVY METALS FROM COMBUSTION OF MSW WITH WOOD CHIPS IN A GASIFIER

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ABSTRACT

In order to study the incineration of crushed municipal waste as fuel in existing district heating plants together with wood chips, and to analyse PCDD/PCDF, PAH and chlorinated benzenes and chlorophenoles as well as heavy metals, tests and sampling was carried out at one district heating plant using gasification technology in energy production. For flue gas cleaning a multicyclone was used.

The results showed that the combustion of a mixture of ca. 85 percent (weight) of slightly presorted and crushed municipal waste and ca. 15 percent (weight) wood chips as fuel can be done with low emissions of PCDD/PCDF, PAH, PCBz and PCP. The addition of waste into the gasifier resulted an expected slight increase in heavy metal emissions compared to wood chips incineration.

KEYWORDS

Waste combustion, Wood Chip combustion, Gasification Technology, Emission measurements, PCDD, PCDF, Chlorobenzenes, Chlorophenoles, PAH, MSW, Heavy Metals, Wood Chips.

THE GASIFICATION PLANT, TEST PERIODS AND SAMPLING

The plant located in the county of Kitee is a 5 MW gasification unit usually fired with wood chips. Flue gas is cleaned with one multicyclone. Schematic figure of the plant is shown in Figure 1. In the gasification system solid fuels are wholly converted into combustible gases, which are then burned in a conventional boiler. The fuel mixtures burned during the experiments are shown in Table 1. Each test period lasted ca. seven

hours of which sampling and measurements took ca. four hours.

Table 1. Fuel mixtures on the test plant., weight basis.

Plant	Experiment number	Main fuel	MSW type	MSW amount (%)
Kitee (gasification unit)	1	wood chips (reference)		0
Kitee	2	municipal waste	crushed	65
Kitee	3	municipal waste	crushed	85

Flue gas analyses were carried out both (plant equipment, additional equipment) continuously and on a sampling basis. Measurement data was collected by a HP 3497 data logging system, and processed by a HP 9845 computer. For HCl-sampling in the flue gases a special sampling train was used. The particulate collection was performed by isokinetic sampling on flat quarz fibre filters. For trace element sampling (Hg, Zn, Cd, Pb) in the flue gases, impenger systems designed for respective metalic elements were used.

Chlorinated compounds and PCDD, PCDF as well as PAHs in the flue gases were sampled with all glass sampling train (Jansson, Bergvall, 1987,/2/). The sampling point is shown in Figure 1. The volume of the samples ranged from 1.5 to 3 Nm^3. The sampling equipment fractionated the material in three parts: particles, condensate and matter adsorbed by XAD-2 resin. In the sampling no internal standard (spiking) was used. The samples were extracted with toluene and/or hexane, evaporated to dryness and diluted in hexane. The hexane phase was extracted with a water solution of K_2CO_3. The water phase was treated with acetic acid anhydride, extracted with hexane and analysed for chlorophenols on a high resulotion gas-chromatograph (HRGC) equipped with an EC-Detector. The original hexane phase was purified with H_2SO_4 and analysed for Polychlorinated biphenyls (PCBs) and chlorinated benzenes (PCBzs). A small aliquotes was injected on a HPLC and anlayzed for Polyaromatic hydrocarbons (PAHs). The hexane phase was further purified on an alumina oxid column and a charcoal column and analysed for PCDDs and PCDFs on a HP-MSD quadrupolic masspectrometer (HRGC-LRMS).

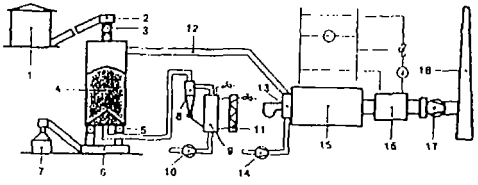

Figure 1. Flowchart of the gasification plant "Kitee"

FUEL PREPARATION AND OBSERVATIONS OF THE BURNING

The municipal solid waste used in the experiments was collected within the city of Jyvaskylä and processed (presorting, crushing) by a local company. Fuel mixtures were prepared by mixing MSW and wood chips from separate fuel silos. Mixture properties are described later. These mixtures were fed to the gasifier using the existing fuel handling equipment.

The fuel mixture vaulted in severly during the experiments. This was caused mainly by the crushed wood (wood waste) chips fraction. The vaulting resulted a lower than expected MSW content in the fuel, ca. 65 %, and inhomogenities in the fuel feed into the gasifier. When chopped wood (wood chips) was used with MSW the vaulting tendency was not so obvious and the amount of MSW in the fuel mix was much higher, ca. 85 %. It seems obvious that a gasifier with good bed temperature control and proper fuel handling equipment is suitable for burning ordinary solid fuel and presorted and crushed MSW.

FUEL PROPERTIES AND MEASURED EMISSIONS OF PCDD/PCDF's, RELATED COMPOUNDS AND HEAVY METALS

The properties of the fuel mixtures used in the experiments are presented in Table 2. In total ca. 60 tonnes of waste fuel was burned in the experiments.

Table 2. Fuel properties used in Kitee

		Wood chips	Waste wood	MSW
Moisture	w-%	25.9	35.6	38.0
DRY SUBSTANCE:				
Effective heating value	MJ/kg	19.6	18.6	18.0
C	w-%	51.6	49.4	46.0
H	w-%	6.2	6.0	6.1
N	w-%	0.3	0.1	0.7
Volatiles	w-%	81.6	80.1	71.5
Hg	mg/kg	0.03	0.03	0.8
Cd	mg/kg	1.4	2.1	1.5
Pb	mg/kg	1.1	5.2	39
Zn	mg/kg	32	52	340
Cl	g/kg	0.3	0.3	12
S	g/kg	0.3	0.6	1.5
Ash content	w-%	0.9	2.9	13.3

The concentrations of chlorinated phenoles in the flue gases are given in Table 3.

Concentrations of PCDD and PCDF identified isomers in flue gas samples in Kitee are shown in Table 4. Concentrations are given in ng/Nm^3 dry gas and as $TCDD_{equ.}$ (according Eadon) reduced to 10 % CO_2.

Table 3. Concentrations of chlorinated phenoles in flue gas samples in Kitee. Concentrations are given in ug/Nm^3 dry gas reduced to 10 % CO_2.

Test	1	2	3
23DCP	ND	0,07	ND
25DCP/24DCP	ND	0,21	0,34
34DCP	ND	ND	ND
35DCP	ND	ND	ND
26DCP	0,07	0,05	0,07
235TCP	ND	0,06	0,04
236TCP	ND	0,03	0,04
245TCP	0,02	0,11	0,12
234TCP	ND	0,05	0,07
246TCP	0,02	0,43	0,65
345TCP	ND	ND	ND
2345TeCP	ND	0,03	0,05
2346TeCP	ND	0,19	0,29
2456TeCP	ND	ND	ND
PCP	0,01	0,05	0,09
Sum Chlorinated Phenoles	0,1	1,3	1,8

ND = not detected

Table 4. Concentrations of PCDD and PCDF in flue gas samples in Kitee. Concentrations are given in ng/Nm^3 dry gas and as $TCDD_{equ.}$ (according Eadon) reduced to 10 % CO_2.

PCDD/PCDF-isomer	test 1	test 2	test 3
2,3,7,8-TeCDD	ND	ND	ND
1,2,3,7,8-PeCDD	ND	0,048	ND
1,2,3,6,7,8-HxCDD	ND	ND	ND
1,2,3,7,8,9-HxCDD	ND	ND	ND
1,2,3,4,7,8-HxCDD	ND	ND	ND
2,3,7,8-TeCDF	ND	0,675	0,964
1,2,3,7,8-PeCDF	ND	0,042	0,057
2,3,4,7,8-PeCDF	ND	0,061	0,086
1,2,3,4,7,8-HeCDF	ND	ND	ND
1,2,3,6,7,8-HeCDF	ND	ND	ND
1,2,3,7,8,9-HeCDF	ND	ND	ND
2,3,4,6,7,8-HeCDF	ND	ND	ND
TCDD-ekv. (Eadon) ng/Nm^3	ND	0,8	1,1

ND = not detected

The detection limits for chlorinated benzenes and chlorinated phenoles as well as PCDD/PCDF compounds are 3 - 30 ng/Nm^3 and 0,01 - 0,20 ng/Nm^3 respectively (depending on the isomer).

The concentrations of different emission compounds are summarized in Table 5. Table shows

metals is low.

Table 5. Concentrations of emission compounds in the flue gases in Kitee. Concentrations are reduced to 10 % CO_2.

	Test 1	Test 2	Test 3
Fuel (mixture) per cent, dry	Wood chips 100	w. waste/MSW 40/60	w. chips/MSW 15/85
Particul. mg/Nm^3	64	318	294
Hg (s+g) ug/Nm^3	62	85	84
Cd (s+g) ug/Nm^3	7	5	7
Pb (s+g) ug/Nm^3	13	27[2)]	27[2)]
Zn (s+g) mg/Nm^3	1	30	32
Fe (s) mg/Nm^3	14		
NO_x ppm	300	350	360
SO_2 ppm	30	100	130
HCl mg/Nm^3	4	200	290
ClPh* ug/Nm^3	0,1	1,3	1,8
ClBz* ug/Nm^3	<0,1	0,9	1,1
PAH* ug/Nm^3	7,2	6,8	2,5
TCDD-equ. ng/Nm^3	NC	0,8	1,1

* Total sum of different analyzed isomers or compounds.

NC = not calculated

RELATIONS BETWEEN EMISSIONS AND SOME OPERATING PARAMETERS

Some relations between emissions operational parameters are summarized below:

- the particulate concentration in the flue gases follows the mixing ratio of waste and the ash content in the fuel mix,
- the concentrations of SO_2 and NO_x in the flue gases increase when MSW is mixed with wood chips. This is because of the sulphur and nitrogen contents of the MSW fuel,
- the concentration of hydrochloric acid in the flue gases follows the mixing ratio of MSW.
- the increase in the mercury emission was lower than expected, the mercury concentration in the MSW-fuel was "normal", however.
- the gasification process was more stable with chopped wood than crushed waste wood fraction.

The vaulting tendency with all the fuels was in experiments the main reason to operational disturbances.

CONCLUSIONS

No PCDD/PCDF compounds were found when wood chips alone were burned.

The addition of MSW into the fuel seems, however, when considering the PAH's in the analysis, decrease the sum concentration in the flue gases.

The concentration of chlorinated phenoles, and especially pentachlorophenole, shows a clear covariation with the amount of MSW added to the main fuel.

The mixing of MSW into the fuel (wood chips, crushed waste wood) will immediately increase the levels of chlorinated benzenes and chlorinated phenoles in the flue gases. This has been shown in Table 2. for chlorinated phenoles.

The heavy metal emissions were relatively low in the experiments. For example, the measured mercury and cadmium emissions were lower than the German TA-LUFT 86' stipulates. The measured emission of zink was high, which is typical for gasification process.

Correlating the observed concentrations of PCDD and PCDF and related compounds as well as heavy metals with operating parameters can be done. There seems to exist a "co-variation" between the gas temperture in the gasification, amount of MSW and observed PCDD/PCDF concentrations. If internal standards (spiking) had been used in the experiments, the analytical accuracy could have been better. Also if more efficient flue gas cleaning had been used, the emission of PCDD/PCDF-compounds could have been lower.

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