HIGH TEMPERATURE GASIFICATION (HTG) PILOT PLANT STUDIES WITH DIFFERENT WASTE MATERIALS: FORMATION OF PCDD/F AND OTHER ORGANIC POLLUTANTS

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ABSTRACT

This paper presents the results of test runs with the High Temperature Gasification (HTG), a newly developed technology of a thermal treatment of hazardous waste of the VOEST-ALPINE Industrieanlagenbau. When measuring the emissions special attention was paid to organic pollutants, such as polychlorinated dibenzo-p-dioxins (PCDD), polychlorinated dibenzofurans (PCDF), polychlorinated biphenyls (PCB), chlorobenzenes (CB), chlorophenols (CP), polycyclic aromatic hydrocarbons (PAH) and others. The results of the tests with various waste show that the HTG pilot plant produces a relatively low emission level as far as organic pollutants are concerned. The concentrations of PCDDs and PCDFs in flue gas reaches from not detectable up to 0,04 ng/Nm³ of 2,3,7,8-TCDD-equivalents (I-TEF), thus remaining remarkably lower than the Austrian limit for municipal waste incinerators of 0,1 ngTE/Nm³ (I-TEF).

KEYWORDS

Thermal treatment of hazardous waste, high temperature gasification, emission of organic pollutants, PCDD, PCDF, PCB, CB, CP, PAH.

INTRODUCTION

Controversial discussions concerning emissions from waste incineration plants, especially PCDD and PCDF emissions, and the fixing of limits has brought about the development of new technologies with the aim to minimize the emissions of pollutants and to achieve more inert residues. The concerned citizens have had a say in the whole procedure of testing the HTG pilot plant for a thermal treatment of hazardous waste, developed by the VOEST-ALPINE Industrieanlagenbau. A special group of experts fixed the program for the test runs and their

analyses. One of the aims of the tests was to get to know more details about the functioning of the HTG about a possible formation of organics and their destruction. There exists an official report on the whole procedure of the citizens' participation [1].

EXPERIMENTAL

High Temperature Gasification pilot plant (HTG)

The HTG is a newly technology based on a combined current and counter-current gasification in the thermal treatment of waste. In this gasification which, contrary to ordinary incineration, works under reduced conditions a combustible gas is produced, which may provide energy. This technology brings about a distinct separation of drying and gasifying in the process from the following burning. Theoretically this might be advantageous as far as the destruction of organic substances in contrast to the usual incineration processes is concerned.

The HTG plant can be roughly subdivided into: waste entry system, gasifier, heat exchanger, gas cleaning system, waste water purification, gas burning. The HTG pilot plant in Linz, Austria, has a capacity of about 5000 t/y.

The gasifier consists of two zones, namely the combustion chamber and the adjacent second chamber. Liquid primary fuels or waste oils and solvents are combusted with preheated air at a temperature of about 1600 °C. At this high temperature the charged solid and pasty waste are gasified and produce a combustible reducing gas. This passes a coke bed in the second chamber of the reactor, which is more or less used up, according to the working conditions and which is furthermore used as a hot gas filter possibly including crack-processes. The HTG-gas with its main components CO (11-24 %), H_2 (8-14 %), CH_4 (0,1-0,5 %), CO_2 (4-9 %) and N_2 (60-70 %), depending on the waste, which is used, leaves the coke bed at a temperature of about 900 °C. At the bottom of the combustion chamber liquid slag develops, which turns into a glassy granulate in a water bath underneath.

The primary HTG-gas still contains dust, HCl and sulfuric compounds (H_2S, COS and CS_2). The gas cleaning system consists of an electric filter and two different scrubbers, one eliminates HCl and the other one H_2S. This cleaned HTG-gas (about 2700 Nm^3/h) is then used as fuel. Part of the gas (about 100 Nm^3/h) is burned in a special combustion chamber designed for tests and analyses.

Test program

The efficiency of this pilot plant concerning organic pollutants was tested by adding organic compounds to the regular waste, mainly chlorinated organics like PCBs, PVC and solvents. Table 1 shows the used materials, the inputs, the percentage of chlorine and the PCB content.

Analysis program

Samples of both, the cleaned HTG-gas and the flue gas, were taken. Then slag, filter sludge (residues from purified waste water) and sulfint sludge (residues from H_2S-scrubbers) were tested

e 1: Materials, input, chlorine and PCB content

	Test run 1 15.11.1988		Test run 2 30.11.1988		Test run 3 31.03.1989			Test run 4 21.04.1989		Test run 5 22.04.1989			Test run 6 24.04.1989		Test run 7 26.04.1989	
	Input kg/h	Cl %	Input kg/h	Cl %	Input kg/h	Cl %	PCB mg/kg	Input kg/h	Cl %	Input kg/h	Cl %	PCB mg/kg	Input kg/h	Cl %	Input kg/h	Cl %
F[1]	294	0,78														
C	6	46,6														
REDDER MAT.[2]			399	1,95												
E SLURRIES					367,5	0,1							200	0,05	154	0,05
CQUER RES.[3]										40						
NS										80						
LVENTS[4]													8,1	49,4	0,5	32,4
STICIDE RES.[5]															154	18,5
B[6]										0,1	42,0					
STE OIL+PCB[7]					154	2,4	149									
STE OIL			130	0,16												
EL OIL	135	<0,01						165	<0,01	177	<0,01		157	<0,01	164	<0,01
tal	435		529		521,5			165		297,1			365,1		472,5	
an		1,17		1,51		0,78	44		<0,01		-0,02	404		1,13		6,08
KE	37	0,01	42	0,01	188	0,01		271	0,01	220	0,01		153	0,01	98	0,01

Processed municipal waste
Remnants from automobile shredding
Lacquer residues
Test run 6: 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene, toluene, styrene (1/1/1/1/1)
Test run 7: 1,2-dichlorobenzene
Residues from pesticide production (Pyridate)
Aroclor 1242
Waste oil enriched with Aroclor 1242 and 1,1,1-trichloroethane

The sampling of the PCDDs and PCDFs, PCBs, CBs and CPs was carried out according to a condensation method, analogous to the LAGA-method [2]. The sampling equipment, completely made of glass, consists of a heated (about 100 °C) filter tube, filled with two types of quartz wool (cross-section of the fibers: 3 and 9 µ), condensation apparatus, two impinger trains filled with ethylene glycole and a XAD-2 adsorption filter.

The sampling of PAHs was carried out with an apparatus, also completely made of glass. A quartz wool filter was used to separate particles, followed by the condensation, the separation of mini-particles through glass fiber filter and after that the adsorption of PU-foam or XAD-2 resin

Extraction and clean up of PCDDs, PCDFs, PCBs, CBs, and CPs: first ^{13}C-2,3,7,8 labelled congeners of PCDDs and PCDFs (tetra- to octachlorinated compounds) were added as internal standards to the samples. The solid samples were extracted with toluene in a Soxhlet-apparatus, the liquid samples also with toluene in a conventional liqid-liquid extraction. For the further extraction KOH (the CPs were separated, HCl was added to the water fraction and then the CPs were extracted with benzene), H_2SO_4 und H_2O were used. The concentrated extracts were cleaned up by passing through a combined silica column (silica/NaOH, silica/H_2SO_4, silica) eluted with hexane. Then PCBs and CBs were separated from PCDDs and PCDFs by using hexane/dichloromethane mixtures of various polarity on a basic aluminia column. A further clean up of the PCDD/PCDF-fraction was carried out with cyclohexane/ethylacetate on a BIO-BEADS SX-3 column.

Extraction and clean up of PAH: The extraction of samples was performed after adding the internal standards (3,6-dimethylphenanthrene, 2,2'-binaphthyle, benzo(b)chrysene) with cyclohexane. Clean up was carried out by a liquid-liquid distribution with cyclohexane/dimethylformamide/water in varied proportions and a chromatographic separation on a silica column with cyclohexane.

The identification and quantification of PCDDs and PCDFs were performed on a HRGC-MS (EI, 70 eV) (Carlo Erba, QMD 1000; Howlett Packard 5995) with selected ion monitoring. The GC was equipped with a fused silica capillary column (SP-2330, 60 m) for the separation of the toxic from the non toxic isomers, a second fused silica capillary column (Ultra-2, 50m) and with helium as carrier gas. The quantification was performed by direct comparison of peak areas of mass fragmentograms for $[M]^+$- and $[M+2]^+$-ions of PCDD/PCDF isomers and the coresponding ions of the ^{13}C-labelled reference standards. The quantification of PCBs, CBs and CPs was done by HRGC-MS (fused silica capillary column: Ultra-2, 50 m; HP-1, 25 m) by comparison to external standards. The recovery of PCBs was determined by an internal standard. The PAHs were identified by HRGC-FID (Dani 3865) and HRGC-MS (fused silica capillary column: DB-5, 30 m), thereby external standards were used for the quantification and internal standards to find out the recovery rate

RESULTS AND CONCLUSIONS

The test run results of the HTG pilot plant are shown in table 2 (gases) and in table 3 (solid residues).

Table 2: Results of analyses of organic pollutants in HTG-gas and in flue gas all results refer to dry gas, flue gas to 11 % O_2

Pollutants Chlorine-Atoms Amount	PCDD[1] PCDF (4-8) ng/Nm³	PCB (3-8) ng/Nm³	CB (2-6) ng/Nm³	CP (2-5) ng/Nm³	PAH[2] µg/Nm³
Test run 1 HTG-gas	0,19	1060	46	128	17,4
Test run 2 HTG-gas	0,20				19,8
Test run 3 Flue gas	nd[3]	59	983	17	1,66
Test run 4 HTG gas	nd	14	131	6	58,3
Test run 5 HTG-gas Flue gas	nd nd	101 57	223 589	10 11	
Test run 6 HTG gas Flue gas	nd nd	32 5	142 309	10 8	
Test run 7 HTG-gas Flue gas	nd 0,02 0,04[4]	1750 74	274 859	12 38	0,87

1 The amounts of PCDD/PCDFs are 2,3,7,8-TCDD-equivalents according to I-TEF
2 The PAHs contain the following compounds: acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, 2-methylanthracene, 1-methylanthracene, 9-methylanthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, triphenylene, benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene, benzo(a)fluoranthene, benzo(e)pyrene, benzo-(a)pyrene, perylen, indeno(1,2,3-cd)pyrene, dibenz(a,c)anthracene, dibenz(a,h)anthracene, benzo(ghi)perylene, anthanthrene, coronene
3 not detectable (< 0,01 ng/Nm³)
4 Parallel analysis of a split sample by ÖKOMETRIC, Bayreuther Inst. f. Umweltforschung

Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD, PCDF)

Measuring the HTG-gas proved that there were detectable PCDD and PCDF concentrations only in the test runs with RDF (processed municipal waste) (0,19 ng/Nm³ TE, I-TEF [3]; 0,39 ng/Nm³ TE, BGA [4]) and remnants from automobile shredding (0,20 ng/Nm³ TE, I-TEF; 0,25 ng/Nm³ TE, BGA). The pattern of the tetrachlorinated PCDDs and PCDFs is very interesting, because of their strong tendency towards volatile compounds in comparison to common incinerators. No traces of 2,3,7,8-TCDD were detectable in either test runs. The non-existence of PCDDs and PCDFs in the HTG-gas in the test runs with toxic waste may be due to changes in the

adjustment of the primary burner after the first runs with RDF and shredder material. There is no indication that the chlorine content of the input materials influences the amount of PCDDs and PCDFs in HTG-gas.

Only in the test run with residues from pesticide production PCDDs and PCDFs were found in the flue gas in a parallel analysis performed by ÖKOMETRIC and FTU (ÖKOMETRIC: 0,04 ng/Nm³ TE, I-TEF and BGA; FTU: 0,02 ng/N³ TE, I-TEF and BGA). This difference can be explained by the fact of deviation of measurements at such low concentrations. 2,3,7,8-TCDD was detected in the samples by both institutes at a level of 0,01 ng/Nm³. It is interesting to note that the simultaneous measuring of the HTG-gas showed no traces of PCDDs and PCDFs. This suggests a de novo synthesis in the combustion chamber (of the HTG-gas) due to an obvious insufficient efficiency of the combustion chamber.

In the solid residues of the test runs only PCDDs and PCDFs were found in the samples of the test with PVC-enriched RDF, all of them with higher chlorinated compounds. Their amount in the slag of the test run with RDF indicates an incomplete destruction of organics.

Polychlorinated biphenyls (PCB)

The PCB amounts in the HTG-gas reaches from 14 ng/Nm³ in the test run with coke up to 1750 ng/Nm³ in the test with residues from pesticide production. The flue gas results show a level from 5 to 74 ng/Nm³. Test runs with added PCBs (liquid and solid waste) resulted in flue gas emissions of 59 resp. 57 ng/Nm³ and are thus within the limits of the other results. PCB-enriched solid input caused an increase of PCBs in the flue gas because of the inefficient combustion chamber. The two other test runs with simultaneous measuring showed a decrease.

The destruction rates for PCBs are

- The PCB-enriched liquid input amounted to 23 g PCBs/h (resp. 44 ppm with an input without coke) and brought about 0,47 mg PCBs/h in flue gas which means a DRE of 99,9980 %
- The PCB-enriched solid input amounted to 120 g PCBs/h (resp. 404 ppm with an input without coke) and brought about 0,43 mg PCBs/h in flue gas which means a DRE of 99,9996 %.

The unexpectedly high amount of PCBs (1750 ng/Nm³) in HTG-gas, when residues from pesticide production were used, does not correspond to the level of the test runs with PCB-additions and requires additional testing.

No PCBs were found in the filter sludge during the test run with PVC-enriched RDF.

Chlorinated benzenes (CB)

The results of the HTG-gas are between 46 and 274 ng/Nm³ and those for the flue gas between 309 and 963 ng/Nm³. These values make evident that all three simultaneous measurings show a very strong increase of CBs in the process of incineration.

The test run with PVC-enriched RDF shows 41,6 µg/kg (ppb) of CBs in the filter sludge which proves an incomplete destruction of organic compounds.

Table 3: Results of analyses of organic pollutants in slag, filter sludge and sulfint sludge
Results refer to dry weight

Pollutants Chlorine Atoms Amount	PCDD[1] PCDF (4-8) ng/kg (ppt)	PCB (3-8) µg/kg (ppb)	CB (2-6) µg/kg (ppb)	CP (2-5) µg/kg (ppb)	PAH mg/kg (ppm)
Test run 1 Slag Filter sludge Sulfint sludge	 0,96 2,18 1,54	 nd	 41,6	 52,6	 70,0
Test run 3 Filter sludge Sulfint sludge	 nd nd				 1500,0
Test run 7 Filter sludge Sulfint sludge	 nd nd				 365,0

1 The amounts of PCDD/PCDF are 2,3,7,8-TCDD-equivalents according to I-TEF

Chlorinated phenols (CP)

The amounts of CPs in HTG-gas reach from 6 to 128 ng/Nm³, those in flue gas from 8 to 38 ng/Nm³. Again there was a de novo synthesis in the combustion chamber, in the same way as with the PCBs here with the CPs, but not so massively.

Besides PCDDs, PCDFs and CBs chlorinated phenols (52,6 µg/kg) were detected in the filter sludge in the test run with PVC-enriched RDF.

Polycyclic aromatic hydrocarbons (PAH)

The amounts for PAHs in HTG-gas are between 17,4 to 58,3 µg/Nm³, the highest are in the test run with coke. Flue gas results are remarkably lower, namely 0,87 to 1,66 µg/Nm³. There is a main amount of the more volatile PAHs in the emissions. 5 to 15 % of the complete emission of PAHs are carcinogenous compounds.

Very high amounts of PAHs were to be found in filter sludge samples (70 to 1500 mg/kg (ppm)). The highest amount (of three test) was found in the filter sludge of test run 3 This high PAH content of the filter sludge requires a further treatment of the material in order to make possible an ecologically correct deposit of such sludge.

Further organic compounds

When working with the PAH samples one group of substances interfered, it could be identified as phthalic acid esters. Results concerning the quantity of this substance group are not

available yet. But we may assume that the quantity is considerably higher than that of PAHs, especially in filter sludges

In conclusion we can say that the HTG pilot plant, as far as organic pollutants are concerned, can be regarded positiv on the whole. Starting with test run 3, when the primary burner had been altered, no PCDDs and PCDFs were detectable in the HTG-gas. The concentrations of PCDDs and PCDFs in the flue gas of the HTG pilot plant reach from non dedectable to 0,04 ng/Nm³ of 2,3,7,8-TCDD-equivalents according to I-TEF. Thus the achieved results are lower than the Austrian limit fixed in the "Luftreinhalteverordnung für Kesselanlagen" 1990 [5] for the pollution of air by municipal waste incinerators (0,1 ng/Nm³ TE, I-TEF) used for an anologic evaluation. Its technical standard can compete with the usual incineration plants for hazardous waste in the fields of PCBs, CBs, CPs and PAHs. the same is true with the destruction rate for PCBs. It is definitely negative that the combustion of the HTG-gas in the insufficient combustion chamber caused de novo synthesis of organic pollutants. Another problem is the producing of soot particles in the primary chamber of the HTG reactor which may also lead to the formation of organic compounds. It turned out that beside the two above described shortcomings the installed gas cleaning system did not meet the ecological demands. For the time the experiences made in the test runs are being used to plan a new HTG plant with another gas cleaning concept.

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