Emissions of polychlorinated aromatic compounds in the combustion of biofuel and compared with emissions from the combustion of paperbased packaging material.

S. Marklund, E. Wikström, G. Löfvenius and C. Rappe
Institute of Environmental Chemistry, University of Umeå, S-901 87 Umeå, Sweden

1. Abstract

The aim of this project was to study the formation of polychlorinated organic compounds in the combustion process when miscellaneous packaging material is burned in order to evaluate the emission of specific toxic compounds such as chlorinated dioxins and dibenzofurans. The packaging materials have also been combusted together with waste pellets with a composition corresponding to municipal solid waste (MSW) in order to determine the contribution of the packaging material to the total emission in the flue gas. Exclusively model waste pellets, used packaging pellets and a pelletized biofuel have been burned with the intention of using these as references in this study.

The results clearly show that the paperbased packaging material is comparable with biofuel. The emission is comparable to the emissions from the combustion of biofuel. No increase in the emission of chlorinated organic compounds could be seen even when the paperbases held extended amounts of aluminum or copper. The results of the biofuel and model waste combustion experiments are in agreement with data from full scale incinerators, consequently the emissions from combustion of the paperbases in the pilot reactor are comparable to emissions in full scale combustors without flue gas cleaning.

2. Introduction

This study has been performed in a small pilot 5kW fluidized bed reactor at the university. The pilot reactor simulates full scale waste incinerators very well [1]. Studied compounds include polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs) and chlorobenzenes (PCBzs). Furthermore, all measured combustion parameters such as temperatures and air flows have been stored for further statistical treatment. Inorganic gases NO_x, SO_x, CO_2, O_2 and CO have been continuously measured using conventional instruments in the flue gas and the most frequent metals in the fly ash have been analyzed.

To obtain comparable results, all emissions were measured without any air pollution control device (APCD). This results in higher emission levels in this study than in a full scale incinerators, since all full scale MSW incinerators have some type of APCD. The biofuel combustors normally have an electrostatic precipitator (ESP) to separate the particular matter in the flue gas (efficiency better than 95%). From full scale measurements we know that the emission of dioxins follows the emission of particular matter in the stack, as most of the dioxins are bound on the particles. A particle filter can consequently be used to reduce the dioxin levels in the flue gas. This will result in emission levels of

dioxins lower than 0.1 ng/m^3 (I-TEF) when the paperbases are combusted in a full scale incinerator equipped with an ESP or other APCD.

3. Experimental design.

In order to study the influence of the different components in the fuels, an experimental plan of full factorial design was used. The components to be studied were bleached versus unbleached paperbase, addition of Al-foil to the paperbase, addition of printing ink with small amount of copper. Eight different types of paperbases were mixed according to the experimental plan: Unbleached or bleached paper with and without aluminum and printing ink as shown in Table 1. All combinations were combusted singly but also together with our model waste pellets mixed in the ratio 1:1 by weight in the feeding chamber just before the feeding into the combustor.

In addition to the experimental plan a separate experiment was performed with packaging material source separated from municipal solid waste and two reference experiments, one with pelletized biofuel and one with model waste pellets only. The contents of the model waste pellets have been specified in previous publications[1]. The biofuel pellets are a mixture of 75% cutter chips and 25% bark. The cutter chips consist of a mixture of softwood (fir) and hardwood tree. This results in total 19 different combustion experiments. During the experiments two flue gas samples and one fly ash sample were collected which in total resulted in 38 flue gas samples and 19 fly ash samples. Presamples, where propane has been used as fuel instead of pellets have been performed regularly in order to control the memory effects in the reactor and in the cooling device.

Table 1. Types of paperbased pellets used in the experimental plan.

Fuel pellets	Unbleached paperbase	Bleached paperbase	Al-foil	Printing ink
A	✓			
B	✓			✓
C	✓		✓	✓
D	✓		✓	
E		✓		
F		✓		✓
G		✓	✓	✓
H		✓	✓	

4. The pilot reactor

The experimental reactor designed for these and similar studies is a small bubbling fluidized bed reactor (i.d. = 0.1 m height 1.9m) with an effect of 5kW. The temperature in the bed and in the freeboard can be controlled by an internal gas burner and also by three electric heaters outside the wall. The distribution of the primary and secondary air can be varied so that the combustion conditions in the reactor can simulate a full scale MSW incinerator. Fig. 1 is a schematic picture of the reactor. The fuel pellets are loaded in the container (1) and feeded to the reactor via a screw feeder (2). The primary air (3) and secondary air (6) are preheated in order to obtain optimal and stable combustion conditions. The freeboard (7) is heated electrically to avoid cold zones in the combustion chamber. The temperatures in the bed and at three levels in the freeboard are measured continuously (8). Following the freeboard a cyclone (10) is connected to the reactor where part of the fly ash and part of the bed material is separated from the flue gas. Propane is introduced into the reactor during the warm-up procedure (4)

and through the inspection glass the bed is seen (5). A fly ash collector is located in the top of the freeboard (9).

The flue gas is cooled in a cooling section consisting of five cooling devices (11-15). Each device, (length 3m) can be individually heated or cooled to simulate different temperature profiles in a full scale MSW incinerator. In this study only three units were connected and the temperature profile should correspond to an MSW incinerator profile. A fan (16) draws the flue gases throughout a activated carbon filter (17) where all remaining organic micropollutants are collected.

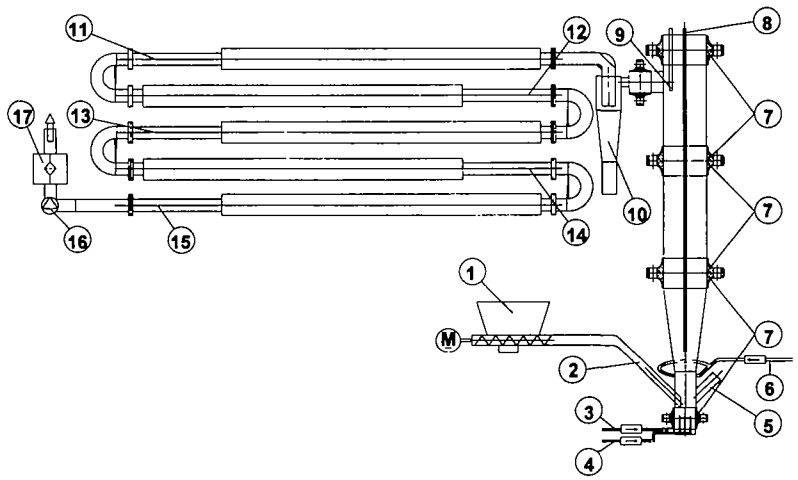

Fig. 1 Schematic drawing of the experimental reactor.

Table 2. Continuously monitored parameters in the experimental reactor.

	Parameter	Unit	Average*	Scattering Lowest	Highest
Flue gas:	CO_2	%	11	8	15
	O_2	%	9,1	6,5	12
	CO	ppm	117	23	408
	SO_x	ppm	39	1,4	82
	NO_x	ppm	117	83	150
Temperature:	Bed	°C	775	646	900
	Freeboard				
	H= 400 mm	°C	747	669	874
	H= 800 mm	°C	727	684	778
	H=1200 mm (exit)	°C	643	592	719
	Cooling unit				
	first device	°C	413	403	429
	second device	°C	314	293	339
	third device (exit)	°C	207	182	224
Flow:	Primarily air flow	m^3/s	fixed	4.9	
Secondary air flow	m^3/s		fixed	3.3	
	Propane	m^3/s	fixed**	0.2	

* Time weight mean value
** Only during the preheating procedure

5. Experimental

The combustion parameters were monitored continuously during the experiment in order to follow the predesigned combustion conditions. Table 2 lists the operating parameters that have been monitoring together with the average, the lowest and the highest value during all experiments. All combustion experiments were performed under equal combustion conditions

Sampling of the organic compounds in the flue gases was performed according to a validated sampling method described in earlier publications [2,3,4].

Chemical analyses

The fuel pellets and the ashes have also been analyzed of the following compounds: C, H, N, S and O using an elementary analyzer. Al_{tot}, V, Cu, Mn, Cr_{tot}, Ni and Pb are analyzed by inductively coupled plasma (ICP) technique. Cd, Co, Hg, Sb and Sn are analyzed with flameless atomic adsorption and Cl_{tot} is analyzed using X-ray spectroscopy.

All sample analyses of organic compounds have been extracted, cleaned-up and analyzed by validating methods as earlier described [5].

6. Results

Dioxins. The results from the combustion experiments shown in Tables 3 and 4 clearly demonstrate that the dioxin emissions from the incineration of the paperbased packaging materials are in the same range or lower than the dioxin emission of the biofuel and the used packaging. Furthermore the emission levels are one order of magnitude higher than the propane blank sample. The model waste pellets were found to have an emission three times higher than that of the biofuel. The paperbase fuel mixed with the model waste pellets had emission levels between the pure paperbase and the waste pellets emission as expected. No significant difference between the paperbased fuel A - H was noticed in the emission levels. The average values of the dioxin emission of the fuel A - H are compared to the emissions from biofuel and from MSW fuel in Fig. 2.

Table 3. Emission levels from the various combustion experiment.

Fuel Pellets	I-TEq ng/m^3	Σ PCBz µg/m^3	Σ PCPh µg/m^3	Σ PCB ng/m^3
A	0.8	0.5	13	27
B	0.9	0.2	22	31
C	0.7	0.2	7.8	42
D	0.6	0.4	8.5	26
E	1.2	1.4	110	38
F	0.5	0.3	4.0	25
G	0.4	0.5	35	64
H	1.2	0.2	12	34
Used packaging	0.7	0.3	27	17
Biofuel	1.0	0.7	18	16
Model waste	2.8	4.7	39	130

Chlorobenzenes: The same pattern as the emission of dioxins can be seen in the emission of the chlorobenzenes, see Table 3 and 4. The paperbases were found to generate very small emissions of chlorobenzenes, very close to the detection level and the blank level. The model waste pellets generate one order of magnitude higher levels. The emissions from the mixed fuels are found to be in the same range as the emissions from the model waste fuel. The used packaging fuel and the biofuel have emissions ranges of PCBzs in the same magnitude as the paperbase fuel. No significant difference between fuel A-H was noticed in the emission levels.

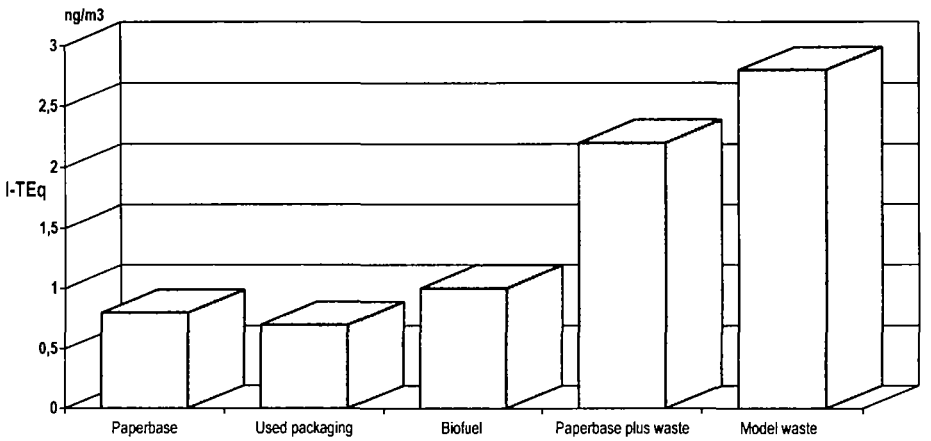

Fig. 2. Average values of chlorinated dioxins and dibenzofurans in the emission of the different fuels.

PCBs: The emissions of total PCBs with 4 to 10 a chlorine atoms show similarities to the PCDD/Fs and to the PCBzs. However, the emissions of PCBs in the paperbase fuel as well as in the biofuel are quite low and in the same range as the emission levels found in the blank sample from a combustion experiment using propane as fuel. This makes it difficult to determine the true formation of PCBs from the paperbase and the biofuel. The levels of PCBs in waste-, mixed waste- and paper fuel show levels distinctly above the blank samples. The DIN-congeners no 28, 52, 101, 138, 153 and 180 and the toxic congeners no 77, 81, 126 and 169 (coplanar isomers) show a larger variation and no noticeable trend. The levels of these PCB homologues are close to the detection levels, which result in higher errors in the quantification.

Chlorophenols PCPhs: Similar patterns as described above can be seen in the emission of chlorophenols, see Tables 3 and 4. The paperbased fuel, the used packaging and the biofuel all generate emission of chlorophenols in the same magnitude. The model waste pellets generate similar levels and the mixed fuels generate slightly higher emission levels of chlorinated phenols. The most dominant iso-

mers are the di and the tri chlorinated congeners. However, low recovery levels of the added spikes indicate significant losses during the sampling or the analytical procedure. The high emission level in the combustion of fuel E, 95% of the emission originates from one di PCPh isomer.

Table 4. Chemical analysis of the flue gas :

Fuel pellets	I-TEq ng/m^3	toxic PCB ng/m^3	ΣPCB ng/m^3	ΣPCBz µg/m^3	ΣPCPh µg/m^3
Paperbase (A-H mean value)	0.8	6,0	36	0.46	27
Paperbase plus model waste	2.2	12	89	3.4	90
Used packaging	0.7	1,6	17	0.3	27
Model waste	2.8	21	130	4.7	39
Biofuel	1.0	1,0	16	0.7	18
Blank (propane gas)	0.1	6,4	26	0.2	5

6. Conclusions

Tables 3 and 4 show that the main part of the chlorinated aromatic compounds formed during the combustion of municipal solid waste originates from other components in the waste than from the packaging materials studied. No significant increase in the emission levels of chlorinated organic compounds was observed from the addition of Al-foil or printing ink, within the tested levels se Tables 3 and 4. A positive influence of the printing ink, in terms of lower levels of chlorinated aromatics, is even suggested, although significant only for the PCDD/F and the PCB. No differences in dioxin formation were found between the bleached and the unbleached paper bases. From chemical analysis of the pellets and the fly ash, it was found that the major difference in these packaging material containing ink is a higher Cu - level. Other studies suggest that a higher Cu-content of the fuel will result in higher emissions of PCDD/Fs[6]. However, this study shows no increased emissions of PCDD/Fs when the copper in the paperbased fuel is increased 30 times. The synthetic model waste contains three orders of magnitude more Cu and one order of magnitude more Cl than the paperbased fuels and the combustion of this waste fuel results in significantly higher dioxin levels.

7. References:

1) Marklund, S., I. Fängmark, C. Rappe, N. Berge and B. Strömberg (1990). Use of an synthetic refuse in a pilot combustion system for optimizing dioxin emission. Part 1. *Chemosphere* 20, 1859-1866
2) Fängmark, I., L.-E. Wikström, S. Marklund and C. Rappe (1990).Studies on Sampling Methods for PCDDs and PCDFs in Stack Emission. *Chemosphere* 20, 1333-1340
3) Marklund, S., G. Söderström, K. Ljung, C. Rappe, M. Kraft and H.-P. Hagenmaier (1992). Parallel sampling using various sampling techniques at a Swedish MSW incinerator. *Waste.Manage.Res.* 10, 21-36
4) Marklund, S., C. Rappe, G. Söderström, K. Ljung, J.-P. Aittola, R. Vesterinen, H. Hoffren, C. Benestad, A. Jebens and M. Oehme (1989). "Internordic" method calibration for sampling and analysis of dioxins and other chlorinated organic compounds. In: International conference on municipal waste combustion volume 1. Conference proceedings. (T.G Brna and R.K. Klicius, Eds.), Minister of supply and services., Canada. p. 4C-1-4C-14.
5) Marklund, S. (1990). Dioxin Emissions and Environmental Immissions. A Study of Polychlorinated Dibenzodioxins and Dibenzofurans in Combustion Processes. Doctoral Dissertion, University of Umeå, Sweden,
6) Stieglitz, L., and H. Vogg (1988). Bildung und Abbau von Polychlordibenzodioxinen und -furanen in Flugaschen der Müllverbrennung. GIT-Supplement, Umweltanalytik Umweltschutz II, pp 4-11.