FORMATION AND DESTRUCTION OF PCDD/F INSIDE A GRATE FURNACE

Hunsinger, H., Jay, K. Vehlow, J.

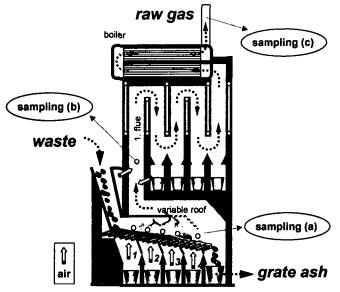
Institut für Technische Chemie Forschungszentrum Karlsruhe, D-76021 Karlsruhe, Postfach 3640, Germany

Introduction

Today's research in municipal solid waste incineration aims at the optimization of the economy of the whole process within environmental standards. If it is possible to reduce the formation of pollutants by controlled combustion the efforts in flue gas cleaning and residue treatment could be minimized. The reactions controlling the combustion process and influencing the formation of pollutants like PCDD/F are not known in detail. Therefore experimental investigations to describe local conditions like temperatures, concentrations of primary combustion products like CO, C_nH_m and particulate carbon as well as PCDD/F concentrations inside the furnace are needed.

The test facility TAMARA¹⁾ is well suited to acquire these data under defined operation conditions.

Experimental



Experimental work was performed within several test campaigns. The investigations described in this paper were carried out by burning different fuel fractions under comparable operation conditions. Each of the experiments was run over a period of 24 hours. Sampling took place 16 h after changing the fuel fraction to reach stable combustion conditions.

During the experiments flue gas was sampled at different locations inside the furnace shown in Fig. 1

Fig 1. TAMARA-furnace with sampling positions

Sampling (Fig.2) above the fuel bed (a) and inside the first flue (b) took place by means of cooled sampling probes with subsequent dust filtration and water condensation. The filter samples were analyzed for carbon and the condensates were used for the determination of H_2O concentrations.

Furthermore, the following gaseous compounds were monitored online: O_2 , CO_2 , CO, H_2 , CH_4 and Σ org. C by FID. To identify and quantify the major C_nH_m species at the positions above the fuel bed additional offline analyses were carried out by GC/MS using filter, condensate and separate gas samples. Sampling of PCDD/F in the flue gas at all three locations (a-c) was done by additional sampling trains using a filter/absorber combination.

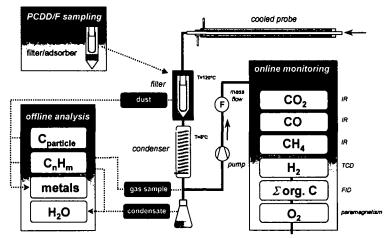


Fig.2: Sampling above the fuel bed inside the combustion chamber

Samples of the fuels and the grate ash leaving the furnace were also taken. The fuel was analyzed to estimate the calorific values, humidity, element concentrations (C, H, O, Cl, metals ...) as well as the PCDD/F concentrations.

Results

<u>Measurement above the fuel bed</u>. The characteristics of the individual concentration profiles in the flue gas leaving the fuel bed are quite similar for the different fuels. Only shifts of the location of the minimum/maximum concentration and the width of the distributions can be recognized.

As an example the concentration profiles calculated from the data obtained from the sampling points along the grate (a) are depicted in Fig 3 for a mixture of 75% municipal solid waste together with 25% RDF (refuse derived fuel).

The oxygen profile showed a marked minimum in grate zone 2 where the oxygen concentration tends to zero. This region is the major reaction zone. Here the incineration is incomplete and pyrolysis and gasification reactions take place. High concentrations of products of incomplete combustion (PICs) like CO, C_nH_m (Σ org.C), hydrogen and soot (C) are produced in this section. The concentrations of PCDD/F in the flue gas leaving the fuel bed showed partly very high concentrations especially of PCDF. The same relation of PCDD has also been found by Akimoto²⁾ at very high temperatures inside the combustion chamber of a fluidized bed incinerator. The concentration profiles of PCDD/F over the grate length showed a bimodal distribution. The two significant maximums were located in front and downstream of the oxygen minimum. At the oxygen minimum itself practically no PCDD/F were detected. In an oxygen free atmosphere and at temperatures in the range of about 900°C PCDD/F are known to be almost completely destroyed³⁾.

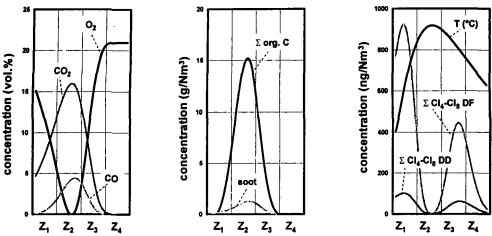


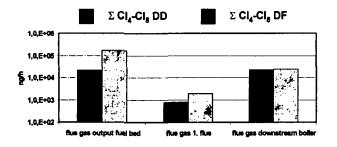
Fig 3: Concentration profiles in the flue gas above the fuel bed over the grate length

<u>Measurement inside the first flue</u>. Under the experimental conditions of an stoichiometric primary air ratio of about $\lambda_p \approx 1.5$ the burnout of the flue gas was almost completed at the end of the combustion chamber. The concentrations of CO and Σ org.C are in the range of the detection limit (<1mg/Nm³). The oxygen and CO₂ profile over the cross section of the first flue showed that the flue gas was well mixed.

In comparison to the measurements above the fuel bed the concentrations of PCDD/F were found to be lowered by nearly two orders of magnitude (fig.4).

These findings could be explained by results from numerical simulations of the flue gas burnout process by using the numerical code $FLUENT^{4,5}$. These calculations showed that the temperatures of the flue gas were increased while passing the combustion chamber by the burnout of the products of incomplete combustion (CO, C_n , H_m and H_2). Maximum temperatures reached up to 1100°C. The minimum residence time of the flue gas inside the combustion chamber was about 2s. Under these conditions most of the PCDD/F were destroyed.

<u>Measurement in the raw gas.</u> The concentrations of PCDD/F showed values below 1 ng TEQ/Nm³. Compared to the first flue, a significant increase of PCDD/F over the boiler section could be recognized.



These findings agree well with investigations carried out by Düwell⁶⁾.

A comparison of all mass flows of PCDD/F at the different positions of the flue gas described above are depicted in Fig. 4

Fig.4: Comparison of the mass flows of PCDD/F inside the furnace

Further experiments burning different fuels showed that inside the combustion chamber the formation of PCDD/F depends significantly on the fuel composition. Especially the content of halogens (and metals) play an important role. Burning bio mass fractions like natural wood chips or straw pellets resulted only in trace amounts of PCDD/F above the fuel bed. In contradiction to the measurements inside the combustion chamber the concentrations of PCDD/F found in the raw gas downstream of the boiler showed no influence of the fuel composition⁷⁾. The explanation of these results must be attributed to memory effects from fly ash deposits in the boiler section. They influence significantly the PCDD/F formation inside the boiler over a very long time. Similar effects were described by Lee⁸⁾.

Summary and Conclusions

From the investigations described above following conclusions could be drawn:

- High concentrations of PCDD/F, especially PCDF, are formed during the burnout process of the fuel bed. The formation reaction is mainly influenced by the fuel composition and furnace parameters. Fuels with low chlorine content result only in negligible concentrations of PCDD/F.
- Under stable combustion conditions characterized by an excellent flue gas burnout PCDD/F will almost be completely destroyed already inside the combustion chamber. "Cold strands" of unburned flue gas caused by instationary combustion conditions will result in high concentrations of PCDD/F in the raw gas.
- A second place of PCDD/F formation is the well known part of the boiler section. Here fly ash deposits containing residual carbon especially soot are responsible for the formation reaction. When interpreting raw gas PCDD/F measurements, memory effects caused by fly ash deposits should be taken into consideration. They are dominant for PCDD/F concentrations in the raw gas over a very long period of time. Therefore it is recommended to reduce fly ash deposits in the boiler section in order to minimize PCDD/F concentrations in the raw gas.

References

- 1) Hunsinger, H.; Jay, K.; Vehlow, J.; Seifert, H.: Proc. 7th Annual North American Waste-to-Energy Conf., Tampa, Fl. May 17-19, 1999 Silver Spring, Md.: SWANA, 1999, 199-212
- 2) Akimoto, Y., Nito, I. S., Inouye, Y.: Chemosphere, Vol. 34, No.4, pp 791-799 (1997)
- 3) Miller, H., Marklund, S., Bjerle, I., Rappe, C.: Chemosphere, Vol. 18, No.7-8, 1485-1494 (1989)
- 4) Frey, H.H.; Peters, B.; Hunsinger, H.; Vehlow, J.: 5th Internat.Conf.on Technologies and Combustion for a Clean Environment, Lisboa, P, July 12-15, 1999 Proc.Vol.1, 323-28
- 5) Fluent Manual (1999), Fluent Incorporated, Centerra Resource Park, 10 Cavendish Court, Lebanon, NH 03766
- Düwell, U., Nottrodt, A., Ballschmieder, K.: Chemosphere, Vol. 20, No.10-12, 1839-1846 (1990)
- 7) Hunsinger, H.; Kreisz, S.; Vehlow, J.; Seifert, H.: DIOXIN '98, Stockholm, S, August 17-21, 1998, Organohalogen Compounds; Vol.36, 193-96
- Lee, Ch. W., Kilgroe, J. D., Raghunathan, K.: Environmental Engineering Science Vol. 15, No.1, 1998 71-84