FORMATION OF PCDD/F DURING MUNICIPAL SOLID WASTE INCINERATION IN A GRATE FURNACE AT DIFFERENT MODES OF THE AIR SUPPLY

Hunsinger, H., Jay, K., Seifert, H.

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

Introduction

Aims of today's research in municipal solid waste incineration (MSWI) are the optimization of the economy of the whole process without changing environmental standards. If it is possible to reduce the formation of pollutants and to improve the quality of solid residues by controlling the combustion conditions the efforts in flue gas cleaning and residue treatment could be minimized.

The influence of furnace operating parameters on the formation rates of pollutants like PCDD/F and NO_x are not known in detail. Especially the question how the burnout efficiency of the flue gas and the grate ash correlates with requirements of low pollutant waste combustion indicates the need of detailed investigations.

One very important operation parameter in MSWI in grate furnaces is the mode of the combustion air supply. Detailed investigations of the combustion process ¹⁾ showed that shifts of primary to secondary air at a constant total stoichiometric air/fuel ratio influence the burnout characteristic of the fuel bed on the grate (drying, carbon burnout) as well as the flue gas burnout in the combustion chamber (temperatures, gas residence times) significantly.

The objective of this paper is to compare the different characteristics of carbon conversion caused by modifications of the air supply with the corresponding data of PCDD/F formation. On this way it should be possible to identify essential reactions and deduce recommendations to realize an optimized operation mode of municipal solid waste combustion in grate furnaces.

Experimental

Experimental work was carried out at the test plant TAMARA¹⁾. The furnace is equipped with a stoker grate (width: 0.8 m, total length: 3.2 m) divided into 4 primary air zones. Secondary air can be added at the entrance of the first flue. The geometry of the combustion chamber during the experiments was designed as center flow configuration.

During the whole duration of the test campaign the entire combustion air volume flow was kept constant at a total stoichiometric air/fuel ratio of $\lambda \approx 1.5$. Starting from complete air supply as primary air, the amount of primary air was reduced stepwise from a stoichiometric primary air/fuel ratio of $\lambda_p \approx 1.5$ down to $\lambda_p \approx 0.7$. The supply of secondary air was increased by the amount of reduced primary air.

The fuel burnt consisted of crushed and homogenized domestic waste (MSW) mixed with RDF (refuse derived fuel) at a ratio of 75/25. During all experiments the mixture had an almost constant lower calorific value of about 7.5 MJ/kg. The feed of fuel was kept constant at about 180 kg/h.

During all experiments temperatures and major constituents of the flue gas were measured online at several locations (B, C) in the process as shown in Fig. 1. PCDD/F, particulate carbon and heavy metals were sampled additionally at the respective locations. Details of the flue gas sampling procedures are described elsewhere ^{1, 2)}.

Sampling of the waste feed (A) and the grate ash (B) completed the measurements.

The experiments were started 3 days after start up of the furnace. During the whole duration of the campaign constant efficient combustion conditions without any malfunction of the furnace could be established. Sampling of each experiment started 16h after changing the air supply and after removal of the major parts of the fly ash deposits from the surface of the tube boiler by an mechanical cleaning device. The almost constant thermal capacity and constant total air supply resulted in constant temperature profiles over the boiler during all test runs. In this way undesirable influences caused by "memory effects" ^{2, 3)} or temperature shifts ²⁾ in the boiler on the measured PCDD/F concentrations in the raw gas could be avoided.



Figure 1. Test plant with sampling positions

Results

Measurements in the flue gas above the fuel bed along the grate length showed that in all experiments significant formation of PCDD and especially of PCDF during the burnout process of the solid waste takes place. This finding agreed well with earlier investigations ²⁾. Under controlled combustion conditions (high temperatures, long residence times and effective flue gas mixing) an almost complete destruction of the PCDD/F formed during fuel bed burnout takes place already inside the combustion chamber.

The second region of PCDD/F formation is the boiler. Here PCDD/F are formed at temperatures above 200°C by de-novo synthesis from particulate carbon ⁴) of the fly ash deposits. Under effective flue gas burnout (this means low CO levels in the raw gas) the reactions of the fly ash deposits in the boiler are dominant for the PCDD/F raw gas concentrations ²). Compared to the PCDD/F formed during fuel bed burnout which are characterized by a furan/dioxin ratio of F/D>>1, the PCDD/F formed in the boiler section show generally ratios of F/D1.

By shifting primary to secondary air the PCDD/F concentrations in the raw gas decreased with decreasing primary air ratio. Starting at $\lambda_n \approx 1.5$ with an TEQ concentration of about 1.6 ng TEQ/Nm³

the PCDD/F concentration were lowered by a factor of three to about 0.5 ng TEQ/Nm³ at $\lambda_p \approx 0.7$. Differences of the F/D ratios and of the homologue profiles could not be recognized.

The corresponding data of flue gas burnout efficiency represented by the raw gas concentrations of CO, $C_n H_m$ and the particulate carbon of the fly ash were found to be very low for each experiment. The measured values showed a slight tendency of decreasing concentrations of particulate carbon and of CO with decreasing primary air ratios. The trend of lowered PCDD/F concentrations parallel to decreasing particulate carbon contend of the fly ash would be explainable but since the concentrations of particulate carbon were in the range of the detection limit the correlation is not definite.

The low concentrations of unburned carbon of the fly ashes lead to low adsorption rates of PCDD/F on the fly ash. Always more than 95 % were found in the gas phase.

By lowering the primary air the velocity of carbon conversion of the fuel bed is reduced. This results in a shift and expansion of the combustion zone towards the grate end. At values of $\lambda_p < 1$ the burnout of the grate ash became more and more incomplete and the residual carbon (TOC) increased exponentially. The concentrations of PCDD/F in the grate ash were found to be well correlated with the TOC content. Mainly PCDF with a homologue pattern quite similar to those measured in the flue gas directly above the fuel bed could be detected.

The correlation of TOC and PCDD/F concentrations in the grate ash demonstrates clearly the requirement of an almost effective carbon burnout of this residue stream by sufficient air supply and residence time of the fuel on the grate.

The importance of these results is obvious when comparing the PCDD/F flows of both furnace output streams (grate ash and flue gas) together with the calculated total PCDD/F output of the furnace as shown in Fig. 2. Here all PCDD/F values are related to the fuel feed. It is obvious that at low primary air ratios the total PCDD/F output is dominated by the grate ash and at high primary air ratios by the flue gas. The additionally marked PCDD/F concentration of the fuel of about 30 ng TEQ/kg shows also that below $\lambda_p < 0.7$ the total PCDD/F output stream of the furnace exceeded the input values of the fuel and the combustion process changes from a sink to a source of PCDD/F. In this case PCDD which are prevailing in the fuel were replaced by PCDF in the grate ash.

The comparison of the PCDD/F concentrations in the raw gas with the corresponding levels of other pollutants like HCl, NO_x and SO_2 showed a complete contrary behavior. While PCDD/F decreased with decreasing primary air ratios the HCl concentration kept nearly constant and the NO_x and SO_2 concentrations increased. Since NO doesn't influence any known PCDD/F formation mechanism, the reason of decreasing PCDD/F concentrations might be effected by SO₂ which was



Figure 2. PCDD/F balance as function of λ_{n}

ORGANOHALOGEN COMPOUNDS Vol. 56 (2002)

increased quite similar to NO at low primary air ratios. These elevated SO_2 concentrations in the flue gas were caused by decreased Ca transfer rates out of the fuel bed to the fly ashes at low gas velocities inside the fuel bed. Reduced Ca concentrations in the fly ashes lead to reduced neutralizing capacities of the fly ashes and SO₂ remains to a higher extend in the gas phase.

The comparison of the Cl/S ratio calculated from the HCl and SO₂ concentrations in the raw gas and the PCDD/F concentrations indicates well decreasing PCDD/F concentrations at decreasing Cl/S ratios. The effect of reduced PCDD/F formation at lower HCl/SO₂ ratios, postulated by Griffin ⁵) must be taken in consideration.

The release of volatile heavy metals to the flue gas was maximized at a primary air/fuel ratio of about 0.8-1.0 caused by the highest average temperatures inside the fuel bed. Negative effects especially of the increased Cu concentrations in the fly ashes on the PCDD/F formation rates in the flue gas downstream of the boiler couldn't be detected.

Summary and Conclusions

The investigations showed that the mode of the combustion air supply effects pollution formation in a very complex manner especially in the flue gas. Optimized distribution of total air in primary/ secondary air in view of the burnout quality of the flue gas and the grate ash as well as minimized pollutant formation must be a compromise. Stoichiometric primary air ratios of about 1 were identified to guarantee low concentrations of unburned carbon and PCDD/F in the grate ash, excellent flue gas burnout, as well as acceptable concentrations of PCDD/F, NO_x and SO₂ in the flue gas in front of the flue gas cleaning system.

References

- 1. Hunsinger, H., Vehlow, J., Peters, B., Frey, H.H., Proc. of the Internat. Conf. on Incineration and Thermal Treatment Technologies (IT3), Portland, Oregon, May 8-12, (2000), CD-ROM, Irvine, Calif., The Regents Univ. of California
- Hunsinger, H., Jay, K., Vehlow, J., DIOXIN'2000, 20th Internat. Symp. on Halogenated Environmental Organic Pollutants and POPs, Monterey, Calif., August 13-17, 2000, Organohalogen Compounds, Vol. 46, pp. 86-89, Chemosphere, Vol. 46, (2002), pp. 1263-1272
- Lee, Ch. W., Kilgroe, J. D., Raghunathan, K., Environmental Engineering Science, Vol. 15, No.1, (1998), pp. 71-84
- 4. Stieglitz, L., Zwick, G., Beck, H., Roth, W., Vogg, H., 7th Internat. Symp. on Chlorinated Dioxins (DIOXIN'87), Las Vegas, Nev., October 4-9, 1987, Chemosphere, Vol.18, (1989), pp. 1219-26
- 5. Griffin, R.G., Chemosphere, Vol. 15, (1980), pp. 1987-1990