

## THE INFLUENCE FROM "BAD COMBUSTION" ON THE EMISSION OF CHLORINATED HYDROCARBONS.

**Strömberg, B.**  
Studsvik AB, S-611 82 Nyköping, Sweden

### ABSTRACTS.

Combustion experiments with propane and gaseous HCl in a laboratory reactor show that short periods of "bad combustion" yields high emissions of organic compounds (chlorinated as well as non chlorinated). The PAH is primarily formed in the high temperature zone during periods of bad combustion while the formation of chlorinated organic compounds is more dependent on the temperature and residence time in the cooling section.

### INTRODUCTION.

In combustion chambers parts exists with steep temperature and redox gradients where the combustion is less efficient especially with municipal waste and biomass as fuels. In 1987 results were presented from experiments with combustion of gaseous HCl and propane in a Meker burner. All the experiments were performed under oxygen deficiency conditions and sooting flames and yielded high amounts of chlorinated organic compounds (1).

The aim of the present project was to extend the investigation and study the effect on the emission of chlorinated compounds from short disturbances in an overall good combustion environment.

### EXPERIMENTAL.

The present experiments were performed in a small fluidized bed reactor earlier described in (2). The reactor is 100 mm in diameter with a bed volume of 0.65 l. Hydrochloric acid was fed to the reactor and mixed with the primary air. In order to simulate bad combustion the air was reduced by 40% for about 30 seconds 5 times during the sampling period. Temperatures at 11 different positions in the reactor and in the post combustion zone and analysis of oxygen, carbon dioxide, carbon monoxide and nitric oxide were measured every 30 seconds. The residence time for the gases in the cooling section was around 2.5 seconds. Flue gas samples were taken simultaneously close to the reactor outlet at a temperature of  $> 500^{\circ}\text{C}$  and at a point where the gas was cooled to  $250^{\circ}\text{C}$ . The method used is based on a method developed and validated for dioxin sampling (3) where a change of solvent from ethylenglycolmonoethylether to n-pentane made it possible to detect more volatile organic compounds.

Instruments used for analysis were a Hewlett-Packard GC (HP-5890) with an electron capture detector and a Finnigan Mat INCOS 50 massspectrometer. Columns used in both instruments were J&W DB-5.

# SOU

## Session 12

In the experiments, the chlorine content was high, 5% of the total fuel. This high feed was chosen in order to get easily detectable amounts of chlorinated compounds and to find the main components to investigate when lowering the chlorine content in the fuel.

### RESULTS.

Temperature measurements and gas analysis data show stable conditions during the experimental periods, except when lowering the air when CO-peaks appeared.

The results show differences in behaviour between higher and lower chlorinated benzenes, as illustrated in figure 1. The lower chlorinated benzenes seem to be formed already in high temperature processes while the higher chlorinated are formed mainly in low temperature processes, probably due to catalytic activity. Low temperature formation of chlorinated benzenes is earlier presented in (4).

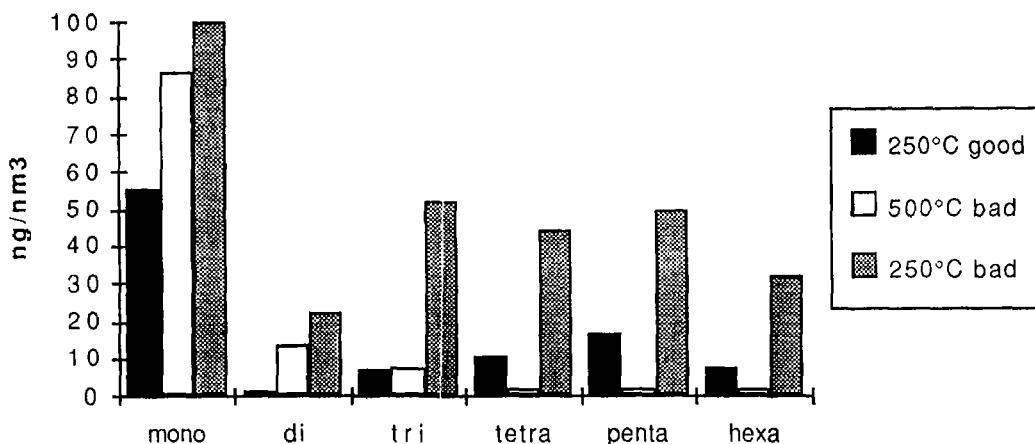


Figure 1. Emission of chlorinated benzenes in experiments with good and bad combustion.

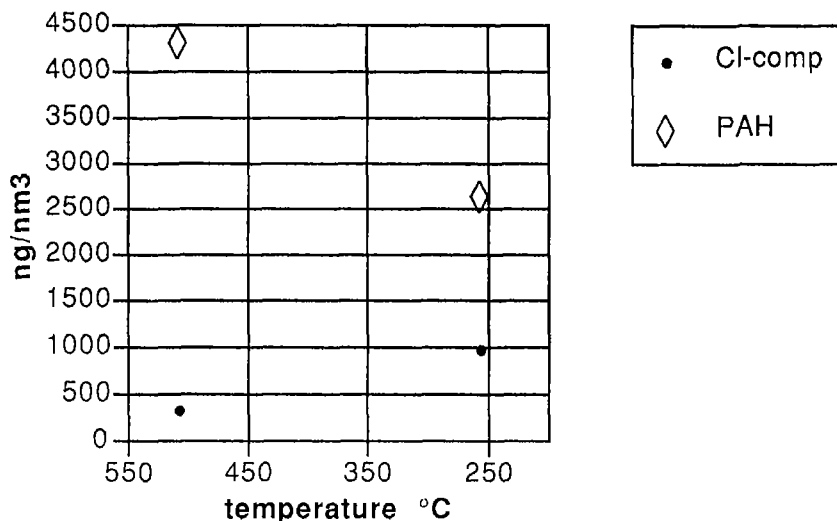


Figure 2. Emission of PAH and chlorinated compounds from "bad" combustion at high and low temperature.

In figure 2 the influence from temperature in the cooling section on the emissions of PAH and chlorinated compounds shows different trends. The PAH is present in the system already at high temperatures. The amount seem to decrease during the cooling process. Probably, these stable compounds will survive the relatively low temperatures present in the cooling section and the lower content is likely to be caused by deposition on walls and fly ash. The higher chlorinated benzenes like penta- and hexa- chlorobenzene may be retained in the cooling section and the "true" values for these compounds should be higher. The chlorinated compounds though, increases during the passage through the cooling section. This is in accordance with earlier results (5-6).

The presence of chlorinated phenols in the flue gas is interesting because we know that they quite easily can form more complex compounds like chlorinated dioxins, furans and PCB if time, temperature and suitable catalysts are present in the "right" combinations. Unsubstituted phenol and monochlorinated phenol are found in the flue gases at both high and low temperature while the higher chlorinated phenols only are found at the lower temperature, showing almost the same behaviour as the chlorobenzenes.

Other interesting compounds found in the flue gases are several unsaturated chlorinated hydrocarbons, for example tetrachloroethylene and butadienes with 2-6 chlorine atoms. The unsaturated alkenes and alkynes ought to be good precursors to aromatic compounds, especially with a ringforming catalyst as copper present. These compounds also increases in amount when cooling the flue gases. The amount found at 250 °C is 0.5  $\mu\text{g}/\text{nm}^3$  for tetrachloroethylene and about 10 times lower for the butadienes. At 500 °C the chlorinated butadienes are present in trace amounts if they can be detected at all, while the amount of tetrachloroethylene is 0.2  $\mu\text{g}/\text{nm}^3$ .

### CONCLUSIONS AND TECHNICAL ASPECTS.

Good combustion of highly chlorinated fuel results in relatively high amounts of chlorinated compounds in the flue gas. Short disturbances in the combustion increases the amount by a factor of 10, while the difference between good and bad combustion for the PAH's is about 1000. Other factors of importance for the emission of chlorinated hydrocarbons are the temperature- and time-profiles in the post combustion zone, which is in agreement with several other results.

The design of the combustion chamber and especially the post combustion zone is very important if the emissions of chlorinated organic compounds should be reduced. Hot-gas cleaning of the flue gases to reduce the amount of chlorine seems to be one important way to solve the problem in large units.

### REFERENCES.

1. Eklund G, Pedersen J R, Strömberg B. Formation of chlorinated organic compounds during combustion of propane in the presence of HCl. *Chemosphere* 1987;16:1 pp161-166
2. Marklund S, Fångmark I, Rappe C, Berge N, Strömberg B. Use of a synthetic refuse in a pilot combustion system for optimizing dioxin emission, part 1. *Chemosphere* 1990;20:10-12 pp 1859-65
3. Fångmark I, Wikström L-E, Marklund S, Rappe C. Studies on sampling methods for PCDDs and PCDFs in stack emission. *Chemosphere* 1990;20:10-12 pp 1333-1340
4. Strömberg B. Low temperature formation and minimization of chlorinated hydrocarbons. *Chemosphere* 1991;23: 8-10 pp 1515-1525
5. Marklund S, Fångmark I, Rappe C, Berge N, Strömberg B. Use of a synthetic refuse in a pilot combustion system for optimizing dioxin emission, part II. *Chemosphere* 1991;23:18-10 pp 1233-43
6. Öberg T, Warman K, Bergström J. Production of chlorinated aromatics in the post-combustion zone and boiler. *Chemosphere* 1989;19:1-6 pp 317-22