THE ROLE OF INORGANIC AND ORGANIC CHLORINE ON CHLORINATED ORGANIC COMPOUND EMISSIONS IN INCINERATION OF ALIPHATIC LIQUID FUEL

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1. Introduction

Toxic organic compounds have been reported to be formed in various incineration processes. Chlorine, catalysts and organic compounds are essential for these reactions. The function of inorganic and organic chlorine in these reactions is not known in detail. Many researchers have used fly ash samples and long residence times to study formation mechanisms. The circumstances of these investigations differ from the full scale incineration and also, from the pilot incineration studied in this paper. Aliphatic liquid as a basic fuel was incinerated in a laboratory scale pilot plant. Inorganic chlorine and organic chlorine mixed with basic fuel were used as additive chemicals. Sodium chloride (NaCl) and tetrachloroethylene (C_2Cl_4) were used as the sources of inorganic and organic chlorine. Combustion parameters were adjusted for optimum combustion and, consequently, the amount of particles in flue gases was low. The concentrations of chlorine in flue gases were high enough for possible formation reactions of organic chlorinated compounds in all of the chlorine input tests. The purpose of the aliphatic liquid fuel incineration tests was to study the effect of organic and inorganic chlorine on the formation of chlorinated organic compounds.

2. Experinmental procedure

Incineration tests were carried by burning aliphatic liquid fuel in a laboratory scale pilot plant (32 kW). Three tests were performed for organic chlorine (runs 3-5) and three test runs for inorganic chlorine (6-8) as an additive. Tests 1 and 2 were reference test runs where neither inorganic nor organic chlorine were added. The basic fuel includes of C_{10} - C_{13} aliphatic hydrocarbons.The sampling system and the details of the analysis are described elsewhere [1]. The distance between two sampling points used for organic chlorinated compounds was 1,5 m. The temperature difference between the sampling points 1 and 2 was about 30 °C. The retention times were 3,5 s and 5 s, respectively.

3. Results and discussion

Table 1. Test run parameters and gaseous compound concentrations. All values are arithmetic means of the total sampling time.

Test run	O_2 (wet- %)	T (°C) (point 1)	CO +H_2 (ppm)	NO_x (ppm)	HCl (mg/Nm3)
1 (reference test)	5,4	298	3	14	NA
2 (reference test + water)	5,8	294	63	16	1,25
3 (0,5 % organic chlorine)	5,7	273	1	48	5,0
4 (1,5 % organic chlorine)	5,0	270	56	44	9,4
5 (3,0 % organic chlorine)	4,9	269	73	38	18,5
6 (0,25 % inorganic chlorine)	6,3	272	130	28	90,7
7 (0,5 % inorganic chlorine)	7,0	256	284	34	108,2
8 (1,0 % inorganic chlorine)	8,1	241	460	38	225,7

NA= not analyzed

In inorganic chlorine tests the concentrations of C O+H_2 concentrations were high compared to organic chlorine tests because of higher amount of water input in inorganic than in organic chlorine tests. The total concentrations of organic chlorinated compounds

did not increase significantly when different amounts of chlorine were added as NaCl/water solution. The total concentrations of PCDD/PCDF compounds were similar in all tests. The concentrations of chlorophenols and chlorobenzenes increased from the level of 0,1 to 1,0 µg/Nm^3, but when compared to reference tests the increased concentrations were not statistically significant. Same isomers of chlorophenols increased when inorganic chlorine input was increased (Fig.1). Chlorobenzenes behaved similarly, but these compounds did not increase so strongly compared to chlorophenols. In inorganic chlorine tests hexadioxins, tetra-, hexa- and heptafurans were dominant (Fig.2). The similar congener distribution was observed, when biosludge was used as a fuel material[2] . Total concentrations of PCDD/F did not increase in inorganic chlorine input tests. In both tests furan concentrations were higher than dioxin concentrations. To conclude, inorganic chlorine has only slight effect on the total amounts of highly chlorinated organic compounds when no catalysts and particles were present.

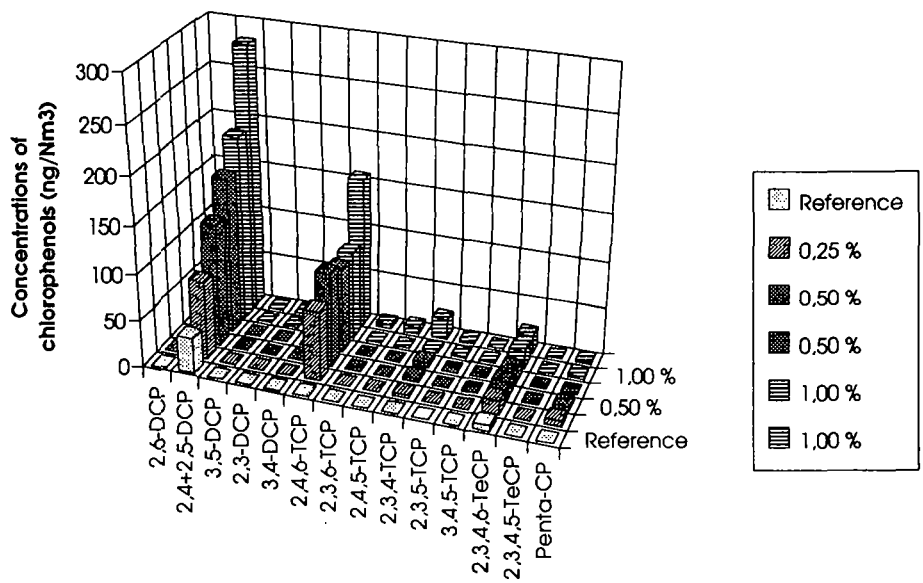

Figure 1. Concentrations of chlorophenols in inorganic chlorine tests.

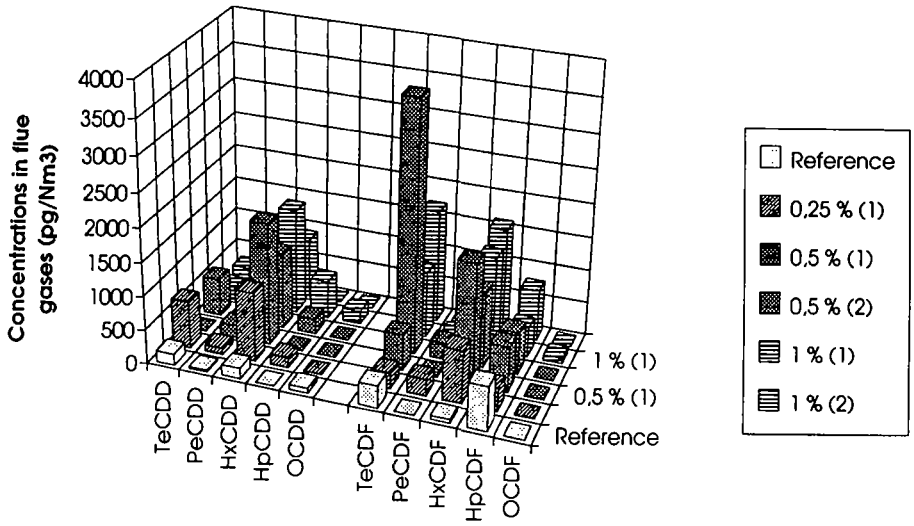

Figure 2. Concentrations of PCDD/Fs in inorganic chlorine tests.

In organic chlorine tests chlorophenol concentrations increased significantly from the level of 0,1 to 10 μg/Nm^3. Especially, 2,4-di-, 2,4,6-tri- and 2,3,4,6-tetraisomers increased (Fig. 3). The results showed that chlorophenols have some function when homogenous reactions take place in flue gases. These chlorophenol isomers were dominant also in inorganic chlorine tests. Total concentrations of PCDD/Fs were at the equal level in all the tests, but the total concentration levels of PCDD/Fs were higher in organic chlorine tests than in reference and inorganic chlorine tests. Thus, there is a possibility that organic chlorine also reacts with aliphatic or cyclic organic compounds forming short chain chlorinated hydrocarbons and, consequently, hydrogen chloride concentrations in flue gases were low. In organic chlorine tests penta- and hexadioxins and hexa- and heptafurans were dominant (Fig.4). Penta- and hexafurans levels increased compared to other congeners. To conclude, highly chlorine substituted organic chlorinated compounds, like PCDD/Fs, need at least an activator to be formed. Chlorine, neither inorganic nor organic together with aliphatic liquid fuel is not enough for PCDD/F formation, without any catalytic material.

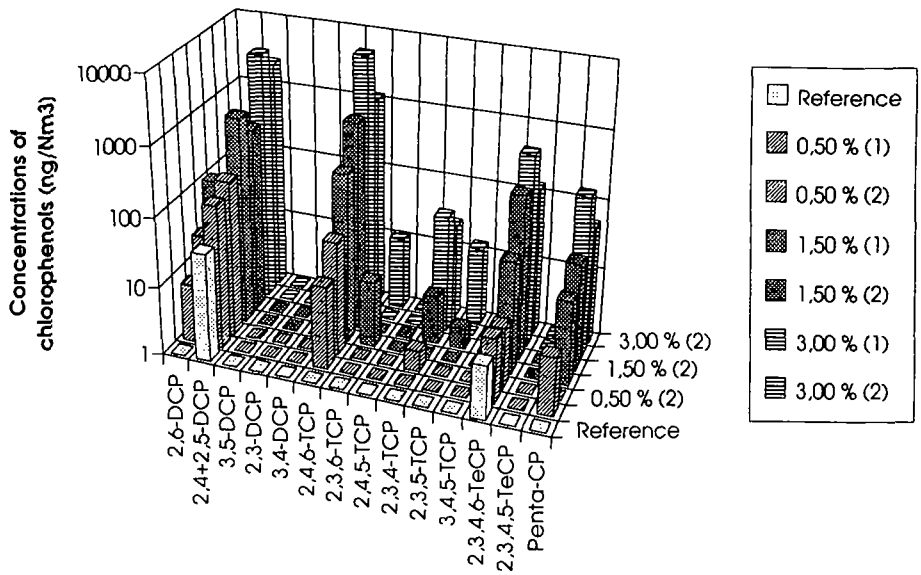

Figure 3. The concentrations of chlorophenols in organic chlorine tests.

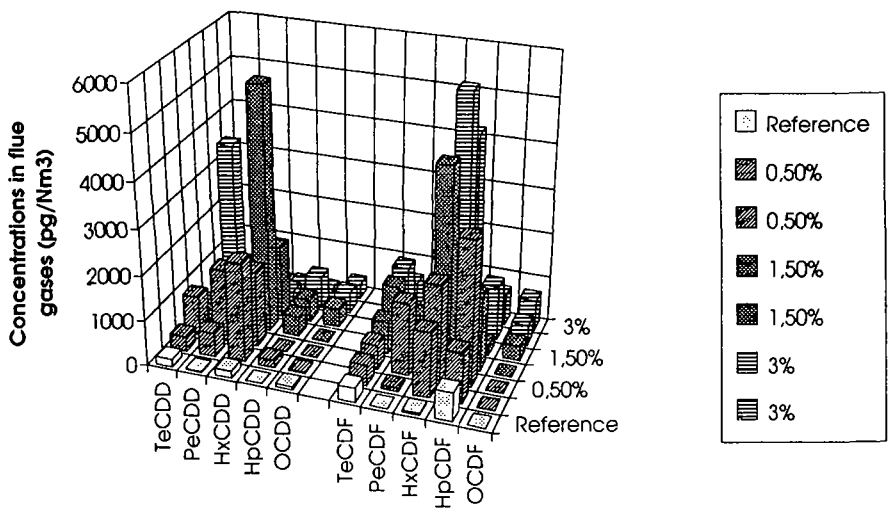

Figure 4. Concentrations of PCDD/Fs in organic chlorine tests.

The variation of Nordic toxic equivalents was observed in organic chlorine tests and the consistency of values was not good. All toxic equivalents were above the limit of 0,1 ng/ Nm^3 in organic chlorine tests and all below the limit of 0,1 ng/Nm^3 in inorganic chlorine tests.

4. Conclusions

When inorganic or organic chlorine were added to aliphatic fuel flow, chlorophenol concentrations increased in flue gases when organic chlorine was added. The isomeric distribution of PCDD/Fs, chlorophenols and chlorobenzenes did not change when organic and inorganic chlorine input was increased. On the contrary, the concentrations of isomers showed some variations. The increase of hydrogen chloride and hydrocarbons in flue gases did not have any effect on the concentrations of organic chlorinated compounds. Our result differ from the data reported by Takeshita, Akimoto [3] and Lenoir et al[4]. HCl concentrations in flue gases were higher in inorganic than in organic chlorine tests. In organic chlorine tests HCl concentrations in flue gases were low even though the input amount of chlorine was at the equal level in both tests. The possible explanation for low HCl concentrations in the case of organic chlorine addition is the chlorination reactions of tetrachloroethylene and small molecular organic (aliphatic, cyclic) compounds, not only the reactions of tetrachloroethylene and aromatic compounds. Further, increased concentrations of hydrocarbons and carbon monoxide did not have any effect on the formation of organic chlorinated compounds.

5. References

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