

CATALYZED FORMATION OF ORGANIC CHLORINATED COMPOUNDS IN COMBUSTION OF LIQUID FUEL

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1. Introduction

Catalyzed formation of chlorinated compounds has been known to be one of the most rapid and effective formation pathway in the combustion processes. The fact found in many experiment that the *de novo* formation occurs in the cooled flue gases, in the temperature area of 250-350 °C, and is involved the reactions with chlorine and carbon, promoted by copper ^{1,2)}. The possible precursor formation of PCDD/F compounds, through chlorophenols, chlorobenzenes, chlorinated phenoxy radicals and phenolate anions has also been reported ^{3,4)}. The gas phase or heterogeneous precursor formation of PCDD/Fs is rapid and controlled or promoted by the concentrations of possible precursors and gas kinetics ^{5,6)}. The distribution of PCDD/F compounds in the combustion of municipal solid waste favor the highly chlorinated congeners of PCDDs and the lower congeners of PCDFs. The possible distributions which differ from those patters tell us about the factors, which effect on the emissions of PCDD/F compounds. Those factors found may be the metals on the surface of fly ash particles or in the vapor phase, water vapor, other gaseous compounds, such as SO₂ and O₂, and also some experiment set-ups or techniques used ^{7,8,9)}.

2. Experimental procedure

Incineration tests were combusted in a 32 kW laboratory scale pilot plant. In the first test series copper, iron and tin were added to the flame as chlorides, and the concentration of hydrocarbons (CO+H₂) in the flue gases was varied from low to high. NaCl, representing inorganic chlorine, and tetrachloroethylene, representing organic chlorine, were mixed into a basic liquid fuel consisting of C₁₀-C₁₃ aliphatic hydrocarbons. The concentrations of organic chlorine and catalyst metals were 0.5 weight-% of the total fuel flow. The amount of inorganic chlorine in the total fuel flow was adjusted according to the catalyst metals. Due to the different types of metal chloride hydrates, the amounts of inorganic chlorine varied from 0.3 weight-% in the tin and copper tests to 0.9 weight-% in the iron test. The concentrations of the products of incomplete combustion (CO+H₂) in the flue gases were about 500-700 ppm in the incomplete combustion and 100-200 ppm in the complete combustion. In the second test series, copper, iron and manganese were added to the flame in the form of nitrates and inorganic or organic chlorine was mixed into the basic

liquid fuel. The concentrations of metals and chlorine used were 0.5 weight-% of the total fuel flow, combustion conditions were kept equal, the concentrations of CO+H₂ about 500 ppm.

3. Results of congener distributions

3.1 Copper combustion

In the complete combustion of copper catalyst the concentration levels of PCDD/Fs in the gas phase and in the particles were quite equal PCDD/PCDF ratios being 0.25 in the gas phase and 0.38 in the particles. Highly substituted dioxins and furans effect on this result, because of the concentration levels of tetra-, penta- and hexa substituted PCDD/F congeners were higher in the gas phase than in the particles, but totally, the higher chlorinated congeners were dominant compared to the lower ones, especially, in the flue gas particles. The concentration ratio of gas/particle was 0.34 in the complete and 0.004 in the incomplete combustion. Also in the poor combustion with copper the concentrations of particle-bound PCDD/Fs were dominant. The concentrations of hexa to octa congeners in the particles and tetra to hexa congeners in the gas phase were dominant. The concentrations of PCDD/Fs in particles, calculated in ng/g, were also high in the incomplete combustion compared to the complete combustion. PCDD/PCDF ratio in the incomplete combustion were 0.2 in the gas and 0.16 in the particle phase. PCDD/F conversion or the heterogenous reactions between the gas and the particle phase may be present in the flue gases in the incomplete combustion tests. The combustion conditions did not effect on the distributions of PCDD/F congeners in the particle phase, like slightly did in the gas phase. The distributions of PCDD/Fs in copper combustion is presented in Figure 1.

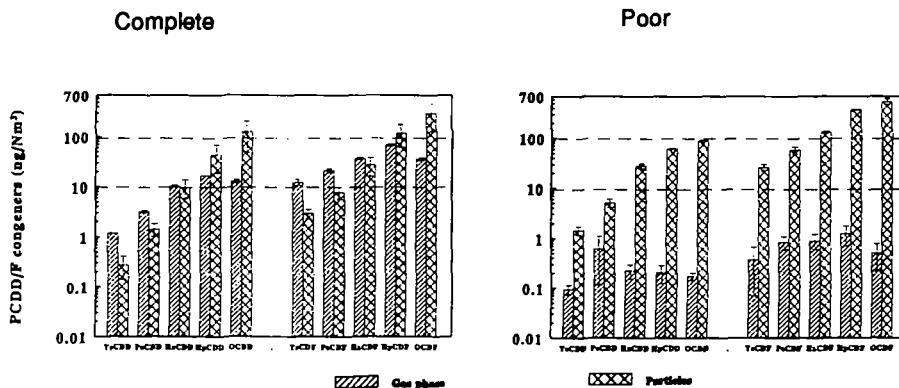


Figure 1. PCDD/F distributions in copper tests (complete combustion versus poor).

The concentrations of different PCDD/F congener were at the same level in the reference combustion without metals, the equal concentrations of tetra to octa were formed. This phenomena was observed also in our earlier experiment¹⁰. Present investigation also found tin not to affect on the formation of organochlorinated compounds, not either to the distributions of PCDD/Fs. The organic chlorine combustion with copper yielded similar congener distributions of PCDD/Fs in the poor combustion with copper and chlorine. In the gas phase the concentrations of tetra and penta congeners of PCDD/F were in higher level, whereas the concentrations of hexa to octa congeners were high in the particle phase. The formation rate of PCDD/Fs on the particle surfaces was very rapid and great in the organic chlorine combustion, where the gas/particle ratio was about 0.005, whereas in the inorganic chlorine addition the ratio was 0.09. PCDD/PCDF ratio in the organic chlorine addition was 0.17 in the gas phase and 0.38 in particles, and correspondingly, in the inorganic chlorine combustion the ratios were 0.30 and 0.64. The highly substituted congeners effected those results because of their high concentrations. On the other hand, the distribution similarity was also observed between the inorganic and optimized combustion tests. The results of those showed that the concentrations of lower substituted tetra-penta congeners were relatively high in the gas phase, whereas the levels of higher substituted hepta-octa congener were high in the particle phase.

3.2 Iron combustion

The concentrations of particle-bound PCDD/Fs were high in the combustion tests with iron, while also gas phase PCDD/Fs were formed in the optimized combustion. The levels of lower chlorinated tetra and penta congeners were relatively higher in the gas phase compared to the concentrations in the particles, whereas the concentrations of higher chlorinated congeners increased in the optimized combustion as opposite to the gas phase congeners in the poor combustion, where the dominant congeners were the lower chlorinated. This may be a consequence of low oxygen radical concentrations in the flue gases, whereas on the particle surfaces the effect of oxygen was minimal as shown in the optimized combustion. The formation of PCDD/Fs on the particle surfaces were increased dramatically in the cases of the poor combustion and in the addition of organic chlorine: the highly chlorinated congeners were dominant.

4. Conclusions

Combustion of aliphatic liquid fuel with chlorines and metal catalysts yielded great amounts of PCDD/Fs and the formation in the flue gases took place rapidly, under three seconds. For minutes required de novo synthesis is an impossible main reaction mechanism for PCDD/Fs, or de novo reaction should be rapid, below the one second in the temperature area of 250-350 °C. More obviously formation reactions may be the heterogeneous gas and particle "contact" reactions, also the compounds shift from one phase to the other as possible. It was also observed that metal catalysts promoted the formation of PCDD/Fs differently in the gas phase and on the particle surfaces. The chlorination effect of inorganic chlorides seemed to be unclear on the formation of gas phase PCDD/Fs, but obvious on the formation of particle-bound PCDD/Fs. The present experiment agrees with the temperature dependence on the concentration distribution between the gas and particle phase, but earlier studies in the real combustion plant disargee with

those results, in which the concentrations of PCDD/Fs in the gas phase were high at the temperature range 250-300 °C. The evaporation of PCDD/Fs in the sampling probe from particles to gas phase have earlier been noticed to be minimum at temperatures 120 °C¹⁰. In some investigations the dechlorination of PCDD/Fs were observed to be present even at the temperatures of 120 °C⁹. Followed to that, the question arised if some chemical or physical "inhibitor" or "catalyst" could effect on dechlorination and evaporation of PCDD/Fs over the thermodynamical facts.

5. References

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