

CARBON DIOXIDE- A PRECURSOR FOR DIOXINS ?

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ABSTRACTS

Experimental work show that chlorinated -alkenes, -benzenes, -phenols and -biphenyls can be formed from CO₂ and HCl at 300°C in a bed of silica sand with different catalysts. Several different conditions and additives to the bed were tested.

INTRODUCTION.

Many authors have experimentally studied the amount of PCDD and PCDF formed on the flyash with precursors, extra metal catalysts and different carrier gases added. (1-5) However, the chlorinated substances in the offgas from the flyash have been less examined and reported. "Good combustion" results in CO₂ and H₂O. According to the Fischer-Tropsch synthesis hydrocarbons can be formed from CO and H₂ with a suitable catalyst present. Hydrocarbons can also be formed from CO₂ in the presence of H₂ at 300° C with Al₂O₃-Ni/K as a catalyst. (6) The same reactions may occur in a municipal waste incinerator, in the cooling section for the flue gas after the furnace since flyash can be looked upon as a complex mixture of silica sand and metal catalysts.

The aim of the present work was to investigate if even simple species like CO₂ and CH₄ in flue gases could form chlorinated hydrocarbons at temperatures which can be found downstream a MSWI combustor. In addition efforts were made to determine the optimum conditions concerning the type and amount of catalyst and residence time.

EXPERIMENTAL.

The experiments were carried out in a Pyrex tube-reactor in which bed material with additives was heated electrically to 200-500°C. A carrier gas was forced through the bed, at a controlled rate. The carrier gas was bubbled through diluted HCl before entering the reactor. All the gas leaving the reactor was collected in a cooled impinger-bottle with n-pentane. 2µl of the pentane solution was injected directly without any clean-up procedures into a Hewlett-Packard HP 5890 gas chromatograph with an electron capture detector. Columns used were J&W DB-5 and GS-Q. The amount of chlorinated benzenes and alkenes were examined. Some samples were concentrated and analyzed with a Finnigan INCOS 50 mass spectrometer for identification of unknown compounds and confirmation of others.

The bed material consisted of silica sand and metal oxides or chlorides. Several catalysts were tested alone or in combinations. Catalysts tested were: CuCl₂, Cu(s), FeCl₂, FeCl₃, Fe₃O₄, Fe₂O₃, CrCl₃, SnCl₂, Al(s), AlCl₃, Al₂O₃, NiCl₂
As a carrier gas CO₂, CH₄, or a synthetic flue gas was used.

The synthetic flue gas contained: 10% CO₂, 500 ppm CO, 5% O₂, 250 ppm SO₂ and N₂.

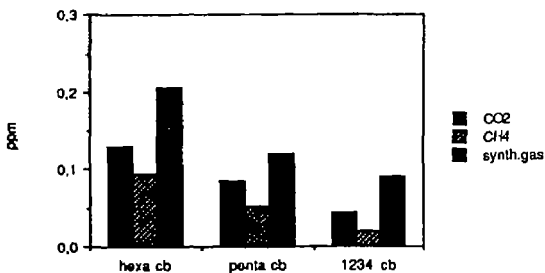
Extra carbon of different origin was mixed with the bed material with the purpose to study the importance of another carbon source.

The residence time was varied between 0.3 and 10 sec under otherwise identical conditions and the offgases was analyzed as described above.

RESULTS AND DISCUSSION.

When carbon dioxide is used as a carbon source and carrier gas, with Cu as catalyst, the dominating species, in the off gas, were chlorinated benzenes. Hexa- and pentachlorinated benzenes were formed in the highest amount. A change of carrier gas to either methane or synthetic fluegas gave similar results as with carbon dioxide. When the mass flow of carbon was kept constant for the three carrier gases, the amount of tetra to hexa chlorinated benzenes was almost identical in the off gas. This is shown in figure 1.

Figure 1. Yield of chlorinated benzenes with different carrier gases



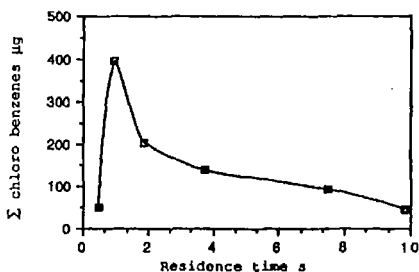
A basic experiment was set up with a bed of silica sand, no catalyst and a carrier gas consisting of CO₂ and HCl as described above. In this case no chlorinated benzenes above 0.02 ppb could be detected in the off gas. When CuCl₂ was added the amount of chlorinated compounds increased considerably. 0.02% Cu in the bedmaterial is enough to form detectable amounts of chlorinated benzenes. There is almost a linear correlation between the amount of chlorobenzenes formed and the amount of Cu added to the bed for reasonable concentrations. The same results could be seen with Cu₂O or Cu(s). It turned out that the optimum temperature for formation of chlorinated aromatic compounds was between 280°C and 300°C, with a sharp decrease on both sides. Therefore the remaining experiments were carried out at this temperature. This is also in accordance to several other investigations. (7-9) Iron, as oxide or chloride, alone as a catalyst resulted in low amounts of chlorinated benzenes but high amounts of chlorinated alkenes such as chlorinated ethylenes and -butadienes. A mixture of iron and copper catalysts in the bed resulted in both chlorinated benzenes and alkenes. Pure Al₂O₃ mixed with the silica sand had no effect on the formation of chlorinated species. When Al₂O₃ and copper was mixed with the bed material the amount of chlorinated hydrocarbons formed increased compared to the experiments when only Cu was added. Other metal oxides/chlorides had no effect on the

formation of chlorinated organic compounds under the conditions tested in this work.

When carbon, in any form except for activated carbon, was added to the bed material the number and amount of compounds detected increased dramatically. In this case of course extra carbon plus fragments of other organic molecules which can be chlorinated are available. Activated carbon on the other hand acted as an adsorbing agent and no chlorinated compounds could be detected in the off gas from the reactor.

Residence time have only a weak influence on the amount of chlorinated benzenes formed. Already at a residence time around 1 sec the yield, calculated as Σ chloro benzenes, seem to have reached its maximum. For shorter and longer times the yield decreases as can be seen in figure 2.

Figure 2. Yield of chlorobenzenes as a function of residence time.



CONCLUSIONS.

Under conditions which may occur in the cooling section of a MSW incinerator, pure CO_2 and hydrochloric acid can be precursors for chlorinated benzenes and other complex organic chlorinated molecules. Further it is obvious that the flyash and its constituents play an important role in the formation process. In the experiments metals acted as catalysts to different extent. One must however point out that even though CO_2 can form PCDD's with HCl present, the results when other carbon sources were added indicate that carbon containing molecule fragments must be considered to be the major carbon source for dioxins formed in the cooling path after an combustion chamber. Thus, better combustion leads to lower emissions, down to a certain base level.

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