

**The influence of different types of activated carbons  
on the formation of polychlorinated compounds  
in de-novo-synthesis**

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### 1. Introduction

One pathway to explain the formation of polychlorinated compounds in the colder zones in MWI-plants is the de-novo-synthesis, i.e. formation on fly ash from particulate carbon. Several papers have been presented over the last years<sup>1,2,3,4</sup>) and the assumption of an interaction between the low-temperature oxidation of carbon itself and the formation of polychlorinated compounds from carbon has been confirmed.

Different types of activated carbons in a fly ash-system were used as precursors and a correlation between carbon-oxygen surface complexes, low-temperature oxidation of carbon and the formation of organohalogen compounds was established.

### 2. Experimental

MWI fly ash from an electrostatic precipitator (ESP) was heated at 500 C for 6 h to remove the particulate carbon completely. After extraction with toluene and cyclohexane the fly ash was freeze dried and then mixed with different types of activated carbon.

The carbon content in the samples varied between 4.2-4.8 %.

Different techniques for activation were applied.

For the experiments two different series of carbon species were used:

- a) commercial activated carbon (A35/4, C40/4, D55/2 from Carbo-Tech in Essen), based on coal, activated in gasphase with steam.
- b) activated carbon, based on wood, modified by activation in the laboratory.

In a series of experiments Merck activated carbon (gas phase activated) was modified by strong oxidizing reagents ( $H_2O_2$ ,  $HNO_3$ ) as well as by chlorine ( $Cl_2$ ):

4 g of degased activated carbon (180 C, 70 mbar, 3 h) were stirred with 100 ml conc.  $HNO_3$  at 70 C for 24 h<sup>5</sup>). The formation of nitric gases was observed. In the case of the oxidation with  $H_2O_2$  the outgased carbon was stirred at 30 C for 3 h with 100 ml  $H_2O_2$ <sup>6</sup>).

The chlorination of the activated carbon with chlorine at 180 C for 24 h was carried out in a quartz tube<sup>7</sup>). The carbon was outgased in the quartz tube and afterwards chlorine gas was introduced to atmospheric pressure. After 24 h and cooling down to room temperature the procedure was repeated.

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The modified carbon samples were filtered, washed with bidistilled water and three times refluxed with bidist. water to remove all the physisorbed components. After drying at 110 C for 2 h the samples were degased and then mixed with the fly ash.

All thermal treatments were run for 2 h in a mixture of helium/oxygen (ca. 17-18 % oxygen). Volatile compounds were collected on XAD-16 resins which were changed every 30 min in the downstream flow. The determination of CO and CO<sub>2</sub> was performed continuously by an in-line massspectrometer.

Fly ash, XAD-resins and the quartz tube as well as the downstream quartz-fittings were seperately analysed for PCDD/F, PCIBz and PCIPh by HRGC-LRMS using a 30m 0,25mm I.D. DB-5 column. The measurements were made in SIM-mode.

Residual organic halogen (ROX)- and differential scanning calorimetry (DSC)-measurements were used for further interpretation.

Temperature programmed desorption (TPD) of carbon-oxygen surface complexes was performed in the same apparatus with oxygen-free helium and the in-line MS-measurement technique. Same amounts of activated carbon were used. The MS was calibrated using a calibration mixture containing the gases He, O<sub>2</sub>, CO and CO<sub>2</sub>. Spectral analysis was done with the help of a computer program from Leybold AG using the multicomponent analysis.

## 3. Results

### 3.1 Experiments with commercially activated carbons

The concentration of chlorinated compounds obtained in the experiments with carbon A35/4, C40/4 and D55/2 are presented in table 1.

Table 1: Concentrations in µg/g fly ash of organohalogen compounds from carbon A35/4, C40/4 and D55/2, calculated on a theoretical carbon content of 4 %.

	CARBO A35/4	CARBO C40/4	CARBO D 55/2
Σ PCIBz	37,0	29,1	12,5
Σ PCIPh	0,3	0,2	0,3
Σ PCDD	2,3	1,5	0,5
Σ PCDF	12,5	11,6	3,3
Σ PCDF/Σ PCDD	5,4	7,5	7,1
Σ Chlorinated C.	52,0	42,4	16,6

Generally the concentrations of organohalogen compounds of the different carbons showed a decrease from the A35/4 to the D55/2. Although the concentrations of the A35/4- and the C40/4-sample were nearly the same, the concentrations of PCDD/F and PCIBz of the D55/2-sample were only in the range of 30% of the concentration of the A35/4-sample.

This difference of the formation potential of the three carbons can be explained by means of the activation degree which increases from D55/2 to A35/4. The higher the activation the lower is the chemisorbed oxygen and therefore the lower is the concentration of functional surface groups. Elemental analyses showed that the oxygen content increases from 1.7% for the A35/4, 1.8% for the C 40/4 to 3.4% for the D55/2.

The formation of CO and CO<sub>2</sub> in an inert TGA-experiment analyzing the evolved gases fits very well in this scheme: 12(5)mg CO<sub>2</sub>(CO)/g carbon for the A35/4, 13(6)mg CO<sub>2</sub>(CO)/g carbon for the C40/4 and 22(7)mg CO<sub>2</sub>(CO)/g carbon for the D55/2 were analyzed during the temperature treatment from 120 C-950 C in a 5 bar nitrogen atmosphere.

### 3.2. Experiments with carbon activated by oxidizing agents

The objective of this investigation was to study the influence of oxidizing agents (H<sub>2</sub>O<sub>2</sub>, HNO<sub>3</sub>, Cl<sub>2</sub>) on the surface of the carbon specimen and the yield of organohalogen compounds.

Treatment with the above mentioned agents causes either the formation of carbon-oxygen surface complexes or the substitution of oxygen by chlorine. The surface complexes can be measured by temperature programmed desorption (TPD) of CO/CO<sub>2</sub>. In Fig. 1-3 the TPD-curves of the modified carbons are presented. The temperature programme was: 25 C→300 C(50K/min)-30 min-300 C→1100 C(50k/min)-50 min-.

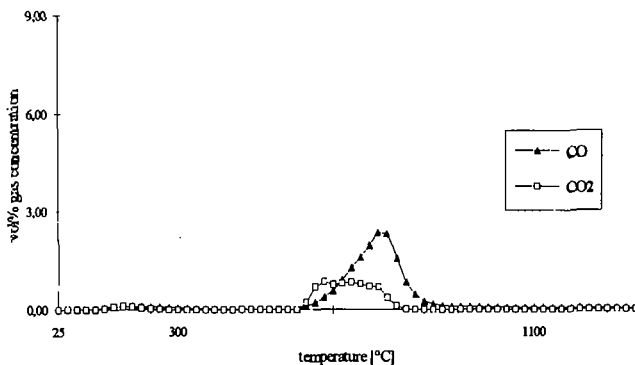


Fig. 1: TPD-curve of 1g activated carbon (Merck), untreated

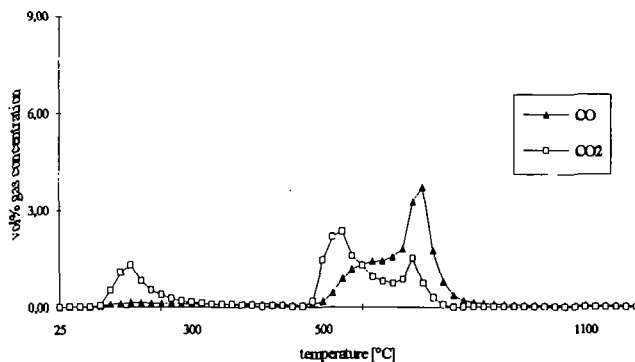


Fig. 2: TPD-curve of 1g activated carbon (Merck), H<sub>2</sub>O<sub>2</sub>-treated

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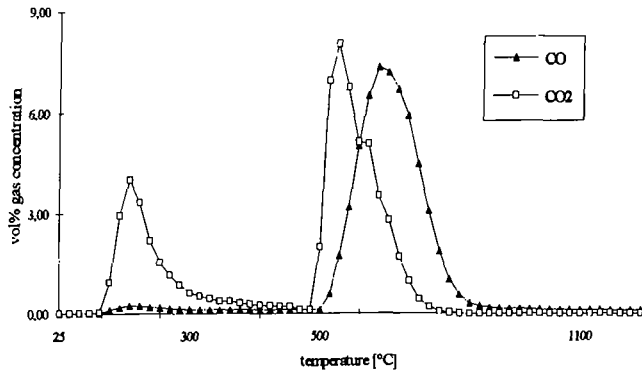


Fig.3: TPD-curve of 1g activated carbon (Merck), HNO<sub>3</sub>-treated

The TPD-measurements show that with increasing strength of the oxidizing agent the concentration of the carbon-oxygen surface complexes does increase as well.

An interesting observation is the low-temperature evolution of CO<sub>2</sub> in the case of the H<sub>2</sub>O<sub>2</sub>- and the HNO<sub>3</sub>-oxidized sample which can only be explained by carboxylic-surface groups, which undergo decomposition at temperatures of about 300 C.

The DSC-measurements of the untreated, the HNO<sub>3</sub>-treated and the Cl<sub>2</sub>-treated-sample showed a significant change in peak temperature in the carbon-oxygen oxidation reaction. Compared with the untreated sample (399 C) the peak temperature of the oxidized sample was shifted to a lower temperature (384 C), while the peak temperature of the chlorinated sample was shifted to a higher temperature (426 C).

The correlation between surface oxides measured by TPD and the shift to a lower peak temperature in the carbon-oxygen oxidation reaction shows that the surface functional groups have an influence on the low-temperature carbon gasification reaction.

The yield of organohalogen compounds with the modified carbon specimen is listed in table 2.

Table 2: Concentrations in µg/g fly ash of organohalogen compounds, calculated on a theoretical carbon content of 4 %.

	Merck, untr.	Merck, H <sub>2</sub> O <sub>2</sub>	Merck, HNO <sub>3</sub>	Merck, Cl <sub>2</sub>
Σ PCIBz	91,7	88,9	42,4	43,2
Σ PCIPh	0,6	0,6	2,8	1,7
Σ PCDD	4,8	4,6	2,5	5,5
Σ PCDF	25,9	22,2	11,7	18,0
Σ PCDF/Σ PCDD	5,4	4,9	4,7	3,3
Σ Chlorinated C.	122,9	116,2	59,5	68,4

The untreated activated carbon and the H<sub>2</sub>O<sub>2</sub>-oxidized sample show nearly identical results in the formation of organohalogen compounds. An explanation for this phenomenon is the fact that H<sub>2</sub>O<sub>2</sub> has a relatively low reaction rate for oxidizing surface structures of activated carbon, a fact which can also be taken from the TPD-measurements.

On the contrary the HNO<sub>3</sub>-oxidized sample showed a 50% decrease of formation of organohalogen compounds except in the formation of PCIPh, where especially the D2ClPhs are increased by a factor of ten. The 50% decrease is common to all chlorination degrees of PCDD/F and PCIBz.

AOX-measurements indicated an increase from approximately 300µg/g in the original mixtures to 560-600µg/g in the case of the reference and the H<sub>2</sub>O<sub>2</sub>-treated sample. In the case of the HNO<sub>3</sub>-treated sample the increase reached a maximum of 800µg/g.

An explanation for these results is the fact that strong oxidizing reagents are able to modify the surface of the carbon. Then either the low-temperature oxidation of carbon in the thermal treatment is favoured and the carbon structure is oxidized completely to CO and CO<sub>2</sub>, or the carbon-oxygen surface groups are substituted by chlorine resulting in a higher ROX of 800µg/g compared to 600µg/g.

In the Cl<sub>2</sub>-treated-sample the same amounts of PCDD and slightly lower amounts of PCDF compared to the untreated Merck and the H<sub>2</sub>O<sub>2</sub>-oxidized sample are found. We would have expected that the Cl<sub>2</sub>-treated-sample reacts much more slowly due to the strong C-Cl-bonds which were supposed to minimize carbon oxidation. An interesting observation was that preferably high chlorinated compounds like H7CDD/F, OCDD/F and H6ClBz are formed (between 80-90% of the PCDD/F are H7CDD/F or OCDD/F, compared to 22-25% in the case of the untreated Merck and the H<sub>2</sub>O<sub>2</sub>-oxidized sample).

#### 4. Conclusion

The comparison of the formation of polychlorinated compounds with the chemisorbed oxygen on activated carbons as a model substance for particulate carbon on fly ash shows:

- ① The formation of PCDD/F and PCIBz can be correlated with the activation degree obtained by gas phase activation with steam.
- ② Surface complexes have a positive effect on the low-temperature oxidation of carbon due to DSC-measurements of the modified carbons compared to the reference sample.
- ③ The higher the chemisorbed oxygen on a carbon the lower is the absolute formation of organohalogen compounds. This can especially be observed with compounds containing oxygen atoms in the structure like PCDD/F and PCIPh.

#### 5. Literature

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