

The Combustion Conditions and PCDD/F Emissions

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ABSTRACT

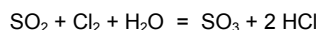
The main aim of this work is to find the influence of combustion conditions on formation of dioxins and furans. There is much inconsistent information to find on the topic in the literature. It is due to synergic effects of more parameters. In the study we sprayed diluted and concentrated sulfuric acid, hydrogen peroxide (combined with sulfur dioxide, too), and water into the flue gases from the combustion of undersize fraction charcoal at the temperature 600 °C. The charcoal was mixed with 1% of PVC resin. As a combustor we used 100 kW circulating fluidized bed (CFB).

Key Words: combustion, dioxins, furans, flue gas

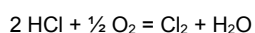
INTRODUCTION

In our work we tried to find the influence of water, sulfur compounds and hydrogen peroxide on formation of chlorinated dioxins and furans. There is a little and very inconsistent information to find on the topic in the literature Lenoir and Fiedler (1992), Lindbauer (1992, 1994), Schleihauf (1996). It is due to synergic effects of more parameters.

Touching sulfur compounds, we concentrated our effort on the effect of sulfur trioxide, respectively sulfuric acid for the prevailing part of experimental works is interested in the influence of sulfur dioxide on the formation of PCDD/F. We could find little information on this topic in the literature Lindbauer (1992, 1994). The classical theory, Griffin (1986), postulates that for a low Cl/S ratio in the gaseous phase the formation of PCDD/F is suppressed by reducing the necessary intermediate Cl₂ to HCl by the reaction:



This equation indicates that the addition of SO₃ would lead to increasing concentration of Cl₂ and, consequently, to an increase in PCDD/F amount. However, we have to consider that simultaneously the Deacon reaction takes place (even at the temperature > 400°C)



and thus the determination of total effect seems to be nontrivial.

Moreover, experimental results of Lindbauer (1992, 1994) show an inhibition effect of SO₃ for de novo synthesis. The authors give, that not the Cl/S ratio is the governing parameter, but the masking of catalytic dust particle surfaces due to conversion of present metals to sulphates by SO₃. Support for this opinion delivers the work done by Rigo and Chandler (1998). The authors state, on the basis of comparison of relative large amount of commercial data, that there is not a strong relationship between chlorine feed and flue gas PCDD/F content. It is alluring to say that in waste incineration is usually chlorine enough for de novo synthesis. The inhibition effect of H₂SO₄ on PCDD/F formation was also found by Grabic et al. (1999).

Also the influence of water in flue gas is mentioned in literature only marginally with inconsistent conclusions. Vogg (1995) gives that the higher content of water in fuel leads to poor burn-up and consequently to higher concentrations of carbon in fly ash, which results in increase of PCDD/F concentrations. The similar conclusion can be found in Lindbauer et al. (1992). Another

experiments mentioned in this paper give rise to the assumption, that effect of water spraying cannot be simply separated from the changes of other parameters, e.g. the addition of Ca(OH)₂.

In the study we sprayed diluted and concentrated sulfuric acid, hydrogen peroxide (combined with sulfur dioxide, too), and water into flue gases from the combustion of undersize fraction charcoal (mixed with PVC resin) at the temperature 600 °C. A set of experiments with the same additives (SO₂, H₂SO₄ and H₂O₂) was done by Grabic et al. (1999) with aim to find the influence of individual compounds to PCDD/F decrease. However, the possibility of application the data obtained in laboratory scale batch reactor for piloting of industrial plant is limited.

EXPERIMENTAL

The fluidized bed furnace of 100 kW power output is schematically depicted in Fig. 1. A ceramic shaft of square section, the bottom of which has the dimensions 30 x 30 cm, forms the body of the reactor. At the height 2 m above the distributor, the reactor is enlarged to a calming zone of 60 x 60 cm cross-section. The height of the whole reactor is 4 m. The part of ash with particles larger than 10 μm is separated in the hot cyclone (with efficiency 85%). The separated ash from hot cyclone is then pneumatically dosed to the fluid layer. Flue gas with smaller particles passes over cooling module and cold cyclone to the Venturi scrubber. The cooling module can be alternatively equipped by a cooler or by a nozzle. The sampling point for dioxin emissions is positioned in the output of cold cyclone, gas analysis in Fig. 1.

The experiments were started by the heating of the reactor space to 850°C with the use of gas burner. The feeding of charcoal 4mm diameter followed with gradual change to the recirculation fluidization. After two hours the steady state was reached in which the temperatures in reactor changed regularly only due to dosing of ash and coal. During the measurement the concentrations of CO, CO₂, SO₂ and O₂ in flue gas were determined. After finishing the experiment the sludge from scrubber was collected and analyzed together with scrubber water. The properties of the charcoal can be seen in the Tab. 2, whereas the average conditions of combustion are presented in the Tab. 1. We used the undersize fraction charcoal as model fuel with 1%wt. PVC resin. This undersize fraction is usually incinerated in blast furnaces as a cheap substitution of coke.

All experiments were made as "double experiments," it means that one experiment which takes about ten hours is divided in two parts and one parameter is changed in the second part of experiment, see Tab. 3. The comparison of results from different experiments seems not to be very reliable. In the first couple of experiments (1-1 and 1-2) the effect of water spraying in the flue gas was explored.

The experiment 1-1 was done with classical water cooler and experimental conditions were adjusted in such a way that the temperature profile was approximately the same as in experiment 2-2.

The temperature changed from about 600°C at the output of hot cyclone to about 200°C at the input of cold cyclone, see Fig. 2.

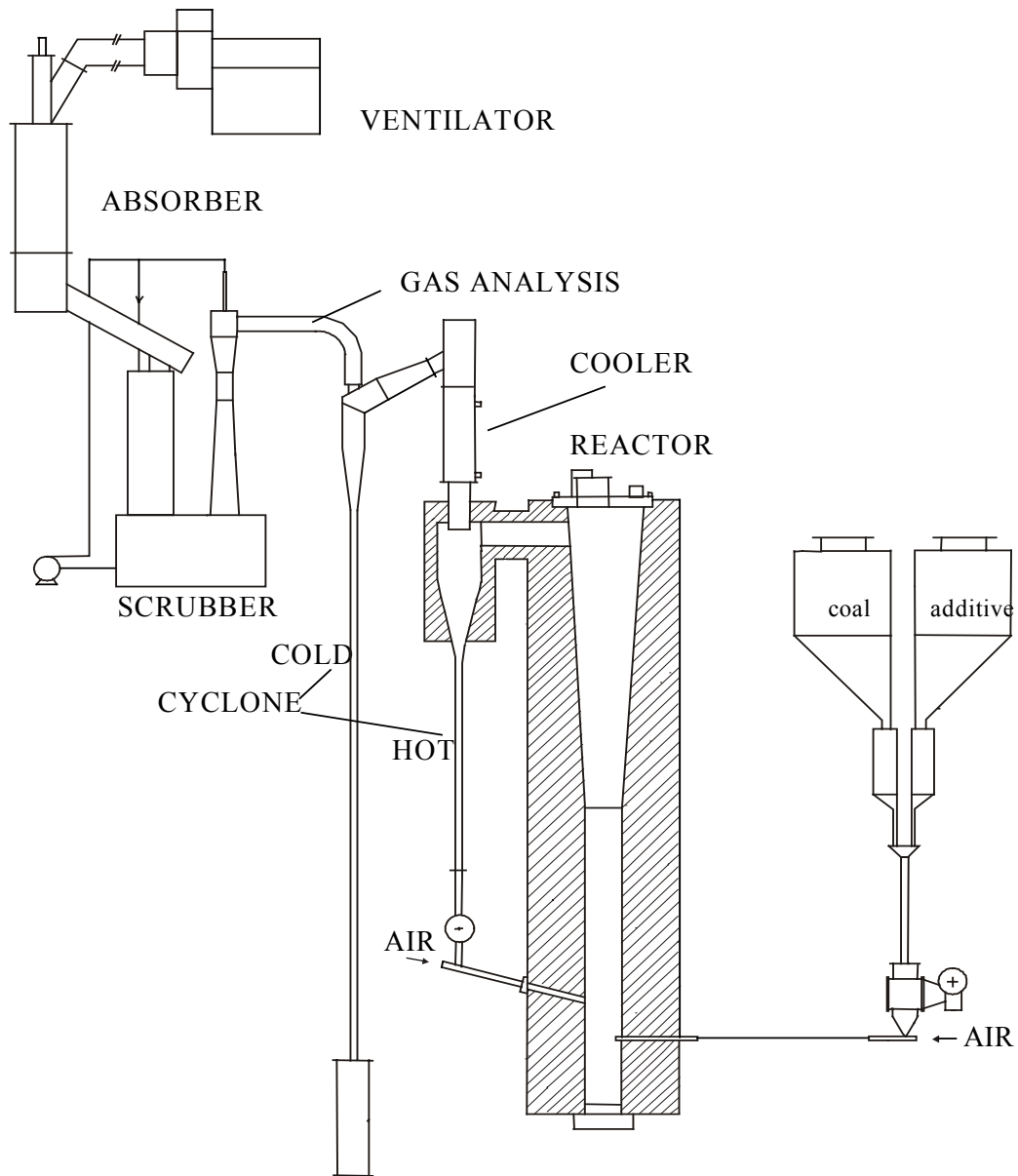


Figure 1 Experimental reactor

Temperature in chamber	$850^{\circ}\text{C} \pm 30^{\circ}\text{C}$
Temperature in cyclone	$580^{\circ}\text{C} \pm 30^{\circ}\text{C}$
C_{O_2}	4.8 - 12.4 % Vol.
C_{CO}	1 - 10 ppm
C_{NO_x}	130 - 140 ppm

Tab. 1 The conditions of combustion

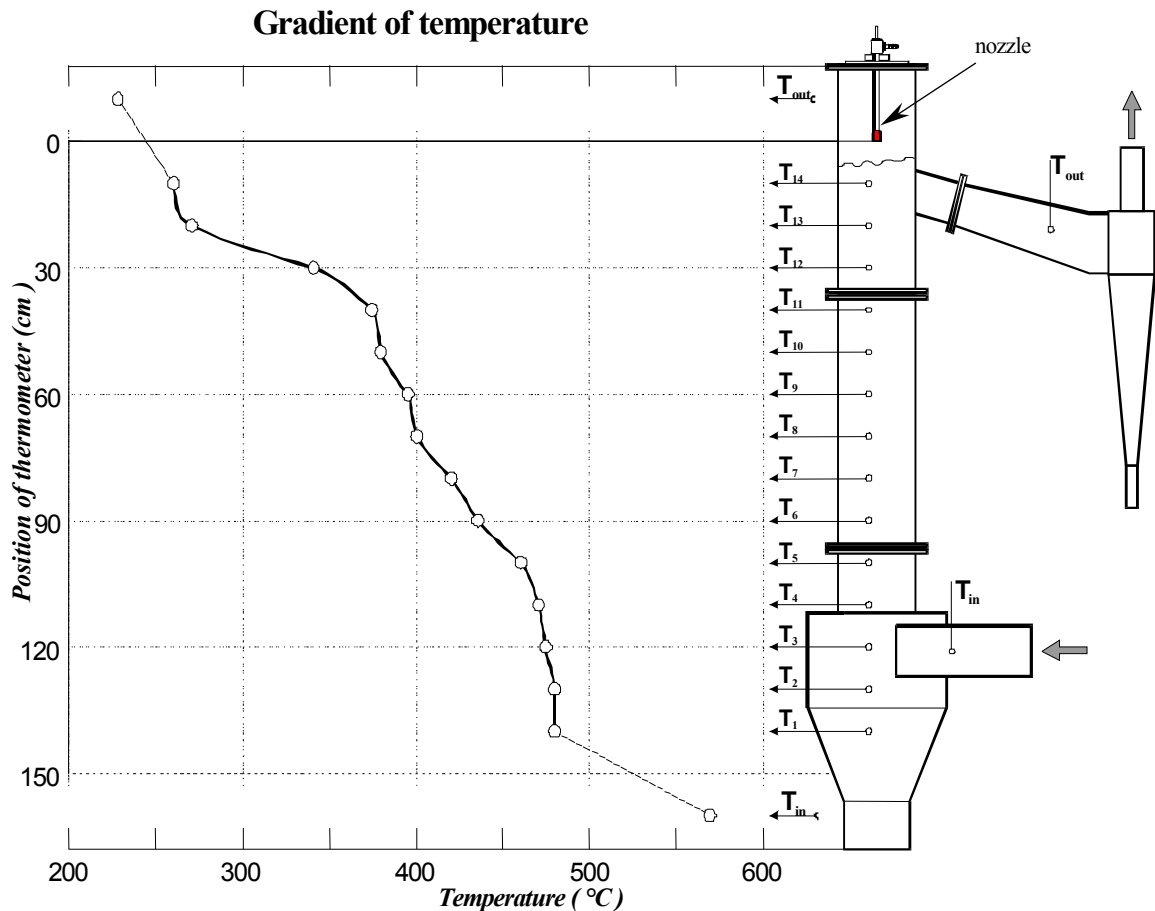
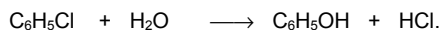
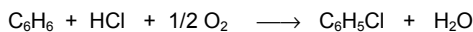


Figure 2 Gradient of the temperature during cooling of flue gas by nozzle

The measured values are present in the Figures 3-6. It can be seen from the Figures 3 and 4 that the spraying of water in flue gas with temperature gradient 600 – 200 °C has very strong effect on dioxin formation. The concentration of dioxins in flue gas increased three times (Fig. 3) compared with the experiment without water. High increase of PCDD is to see also on the fly ash (Fig. 4). The fact that water was sprayed into flue gas and could not influence the quality of combustion gives raise the conclusion that the water alone plays important role in de-novo synthetic reactions. The probable explanation may be the formation of phenols and consequently chlorinated phenols due to presence of water. Chlorinated phenols are known as precursors of dioxins. As an example can serve the Raschig-Hooker process for manufacture of phenol from benzene:



The measured values of PCDF in flue gas, Fig. 5, show that the level of furans slightly decreased.

Another interesting feature exhibits the distribution of congeners. We can observe that the relative concentrations of PCDD, PeCDD, TCDF and PeCDF in flue gas are higher than it is usual in samples from municipal incinerators. The probable explanation maybe

that there is lower residence time of flue gas in temperature window for our experimental reactor than it is usual in big industrial devices, thus there is not time enough for full chlorination of dioxins and furans. It is interesting to compare this fact with the trend of PCDD/F distribution on fly ash. Here we can see the shift to the higher chlorinated congeners, see Figures 4 and 6.

C	80,06 %
H	2,95%
S	0,015%
Cl	0,0085%
Cu	0,002%
Zn	0,003%
Pb	0,01%
Ash (800°C)	6,04%

Tab. 2 The properties of charcoal

The result corresponds well with supposed mechanism of de-novo synthesis as catalyzed reaction on the surface of fly ash.

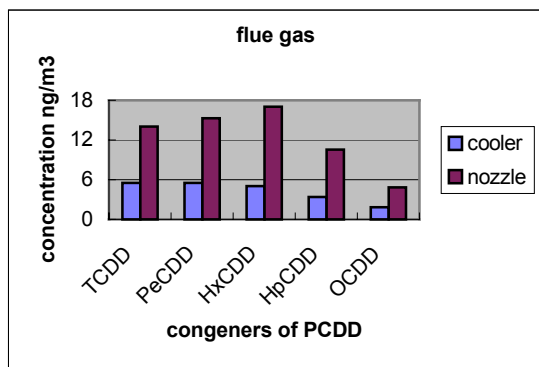


Figure 3 Concentration of PCDD congeners in flue gas

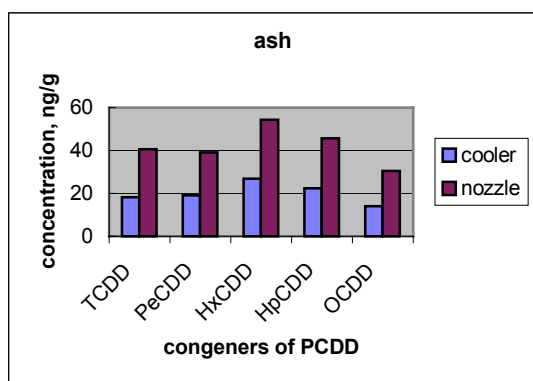


Figure 4 Concentration of PCDD congeners on fly ash

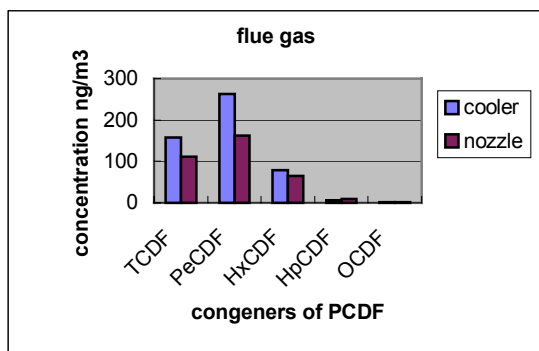


Figure 5 Concentration of PCDF congeners in flue gas

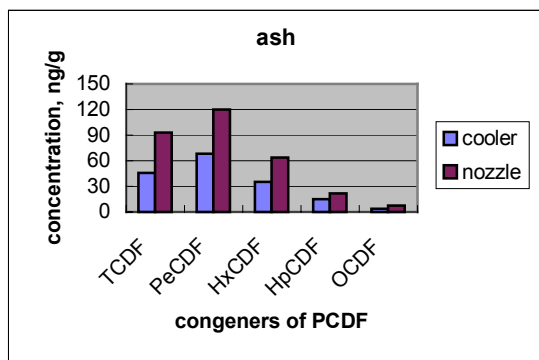


Figure 6 Concentration of PCDF congeners on fly ash

In the next experiments (2-1 and 2-2) the effect of diluted sulfuric acid was investigated. Experiment 2-1 consisted of water spraying into the flue gas and diluted sulfuric acid (2% wt. in 10l/h) was used in experiment 2-2. The molar ratio S:Cl in flue gas of the experiment 2-2 was about 1,3. The sum of PCDD/F for the experiment with sprayed water (2-1) was 575 ng/m³ whereas the same sum for diluted sulfuric acid decreased to the value 225 ng PCDD/F m⁻³ (in toxic equivalent 7.1 ng TEQ/m³ vs. 3.6 ng TEQ/m³). From these results it follows that diluted acid caused much smaller increase of dioxins than in the case of pure water 1.31 vs. 3 (in ng/m³). However, it is very difficult to differentiate between the influence of water and acid. The experiments 3-1 and 3-2 demonstrate the effect of concentrated sulfuric acid on PCDD/F formation. In the experiment 3-1 was used only the cooler without dosing any additive into the flue gas (blank experiment). The concentrated sulfur acid (98% wt.) was dosed in the experiment 3-2 in front of the cooler (at the temperature about 600°C). The flow rate of concentrated acid was 0.5 l/h. This amount corresponds to the stoichiometric ratio S/Cl=3 in flue gas. The results of experiment can be seen in the Figs. 7 and 8.

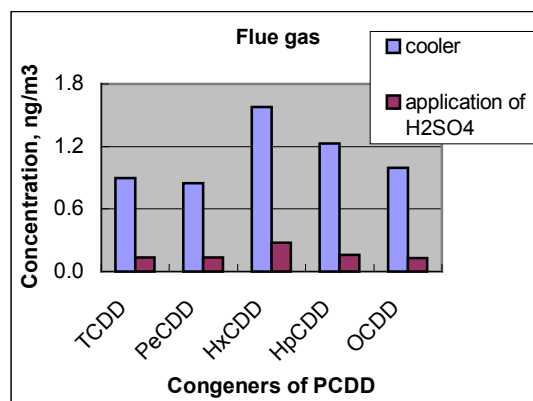


Figure 7 Concentration of PCDD congeners in flue gas

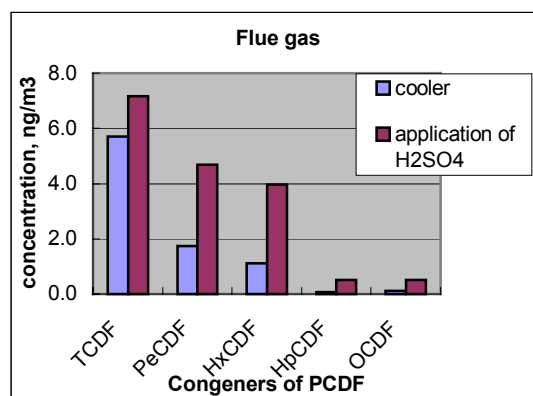


Figure 8 Concentration of PCDF in flue gas

We can see that application of concentrated sulfuric acid led to drastic dropping of PCDD concentration in flue gas. In sum of TEQ we obtain the following values:

Blank experiment	0.49 ng TEQ/m³
Experiment with H₂SO₄	0.12 ng TEQ/ m³

The fourth set of experiments, 4-1 and 4-2, was concentrated on the effect of lime addition to the fuel. The lime was added to the fuel in the experiment 4-2 in stoichiometric ratio to Cl. The comparison shows the

decrease of PCDD/F on about one third in the presence of lime.

In the last double experiment, 5-1 and 5-2, we investigated the effect of hydrogen peroxide. In the first part, the hydrogen peroxide (30% wt.) was dosed at the input of hot cyclone with the aim to improve the burn-off of fuel. The amount of peroxide was determined on the basis of average amount of rest carbon in flue ash.

We reached the value 2.7 ng TEQ/m³ that indicates high efficiency of H₂O₂ for dropping of PCDD/F emissions. In the next experiment SO₂ was added in such a way that the molar ratio S:Cl was about 2:1. The level of dioxins and furans decreased in this case on the value 0.86 ng TEQ/m³. The high efficiency of this process can be explained by reaction of SO₂ to H₂SO₄ and, as we believe, partially up to Caro's acid Grabic et al. (1999).

The general summary of experimental conditions is done in the Table 3.

No. of experiment	Characteristic
1-1	Coal +1%PVC + cooler
1-2	Coal +1%PVC+H ₂ O (nozzle)
2-1	Coal +1%PVC + cooler
2-2	Coal+1%PVC+2%H ₂ SO ₄ (nozzle)
3-1	Coal +1%PVC + cooler
3-2	Coal +1%PVC+98%H ₂ SO ₄ + cooler
4-1	Coal +1%PVC+2%H ₂ SO ₄ (nozzle)
4-2	Coal +1%PVC+2%H ₂ SO ₄ (nozzle) + Ca(OH) ₂
5-1	Coal +1%PVC+H ₂ O ₂ + cooler
5-2	Coal +1%PVC+H ₂ O ₂ +SO ₂ + cooler

Tab. 3 The characteristic of experiments

CONCLUSIONS

The spraying of water in flue gas with temperature gradient 600 – 200 °C has very strong effect on dioxin formation. The concentration of dioxins (in ng/m³) increased three times compared with the experiment without water. The probable explanation may be the formation of phenols and consequently chlorinated phenols due to presence of water. Chlorinated phenols are known as precursors of dioxins.

The application of diluted sulfuric acid (with the same flow rate as water in the experiment 1-2) leads to essentially lower increase of dioxins. This is probably due to inhibition effect of acid. The strong effect of concentrated acid for dropping of PCDD/F may prove the blocking of catalytic efficiency fly ash surface due to formation of metal sulfates (we found 9.1 wt% of SO₄ in fly ash). However, the chemical destruction of PCDD/F by concentrated acid can not be excluded.

The influence of calcium hydroxide on PCDD/F formation at combustion of charcoal with 1%PVC was found significant.

Good results in decreasing of PCDD/F were found at the use of hydrogen peroxide squirt to output flue gas.

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