

PCDD/F IN FLUE GAS AND IN BOTTOM ASH OF LIGNITE DOMESTIC COMBUSTION
AND THE ROLE OF THE SALT CONTENT OF THE BURNED BRIQUETTES

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Abstract:

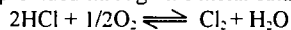
Lignite briquettes with different salt contents ("normal"-coal: 300 ppm w/w, "salt"-coal: 2000ppm w/w) were burned in a common type of a house heating facility. The content of polychlorodibenzo-dioxins and -furans (PCDD/F) in the bottom ash and in the flue gas were determined. Both values were significantly higher for the "salt"-coal briquettes. Making considerations about the mechanism of the formation of PCDD/F and taking in account a wide variety of additional analytical parameters the assumption was proved that the higher chlorine content (of the "salt"-coal briquettes, respectively) is responsible for it. The evaluation of the homologue profiles and the isomer distribution shows that the mechanism of the formation of PCDD/F in the flue gas is equal for both coal sorts whereas the mechanisms of the formation of these compounds in the bottom ashes are different. On the base of the quantitative results an assessment of lignite domestic heating as source of PCDD/F is given.

1. Introduction

Natural lignite can contain considerable amounts of salt. If lignite briquettes are combusted a potential exists for the formation of PCDD/F. For the PCDD/F content in the flue gases of the combustion two theories of the formation have been proposed:

- Condensation of PCDD/F from precursor compounds formed in the gas phase at higher temperatures (700°C-900°C) (Ballschmiter et al. /1/).
- DE NOVO-synthesis of PCDD/F from chemically unrelated carbon sources and inorganic chlorides in the presence of air, water and a metal catalyst at lower temperatures (300°C) (Stieglitz, Vogg /2/). Investigations of Nottrodt et al. /3/ indicate that the DE NOVO-synthesis is of higher importance. In the bottom ash the DE NOVO-synthesis only produces the PCDD/F.

A source of the free "in situ" chlorine, which is the precondition for all formation processes of organochlorine compounds, may be provided through the metal catalyzed (CuCl₂) DEACON-reaction:



This was implicated by Griffin /4/ and demonstrated by others./5,6/ These points of view lead to the assumption that the content of salt of the lignite briquettes is relevant for the PCDD/F formation

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during their combustion. The domestic burning on the base of lignite briquettes with a chlorine content up to 2500 ppm w/w is still of considerable importance in Eastern Germany. /7/

The present paper should provide information about how the flue gas and the bottom ash are polluted with PCDD/F and how the chlorine content influences its formation qualitatively and quantitatively.

2. Experimental

A house-heating facility (tiled stove with air circulation) with a heating power of 9 kW was chosen to carry out the investigations. The isokinetic sampling of the flue gas (including particulate matter) and the trapping of PCDD/F was conducted according to the VDI-method 3499 Bl.3 VE. To control the combustion-process the temperature of exhaust, the gas-draught (pressure inside the chimney), the velocity of flow, the position of the throttle valve and the humidity of the exhaust gas were determined. The following concentrations were measured continuously in the flue gas; concentration of carbon dioxide, carbon monoxide, oxygen, sulphur dioxide, total hydrocarbons (THC).

The clean-up is similar to the procedure described in VDI-Richtlinie 3499. Briefly, this procedure entails a series of liquid chromatographic clean-up sequences, which include a celite column, a basic alumina column and a combination silica gel column containing acid modified, base modified and neutral silica gel and silver nitrate/silica-gel. Samples originating from lignite combustion are quite filthy and strongly loaded with a great variety of organic matrix compounds. For that reason we have used two additional cleaning steps.

The analysis was carried out by HRGC/HRMS. Two different types of columns were used for the gaschromatographic separation of the PCDD/F: an RTX-2330 cross-bound polar (90% biscyanopropyl-10% phenylcyanopropyl) stationary phase capillary column and a DB-5 nonpolar (5% phenyl-, 95% methylpolysiloxane) capillary column. Using different analytical techniques (e.g. RFA, ISE, ICP-AES and specific analysers) the additional parameters listed in table 2 were determined. The experimental section is described elsewhere in detail. /8/

3. Results and Discussion

3.1. Quantitative evaluation of the results

In the table below the quantitative results of the PCDD/F measurements are summarized.

table 1: quantitative results	"salt"-coal	"normal"-coal
emission concentration [pg TE/m ³]	109	15
specific emission [ng TE/kg fuel]	2,24	0,34
ash content [ng TE/kg ash]	4,8	18,2

The values represents the average of three samples for each briquett sort. Regarding to the calculation of the toxikological equivalents (NATO/CCMS) the values base on the evaluation of the single 2,3,7,8-congeners and the homologue groups. By comparing the values of both the briquett sorts it is obvious that during the combustion of "salt"-briquettes significantly more PCDD/F are formed than in the case of the "normal"-briquettes (seven times higher for the flue gas emission and four times higher for the ash content). The combustion of the briquettes represents a technical process with various factors influencing the formation of PCDD/F.

table 2: selected peripheral parameters

	parameter	"salt"-coal	"normal"-coal
briquettes	C [wt %]	63,1	65,8
	Cl [ppm w/w]	2000	300
	Cu [ppm w/w]	2,9	3,0
	S [wt %]	7,9	4,2
	heating value [kJ/g]	28,6	29,2
	dust emission [mg/m ³]	90	93
	ash component [wt %]	13,3	10,7
fly ash/ fly dust	C [wt %]	3,2	10,1
	Cl [ppm w/w]	4500	590
	Cu [ppm w/w]	12	48
	S [wt %]	13,2	3,9
flue gas	CO [mg/m ³]	3780	1650
	THC [mg/m ³]	260	81
	SO ₂ [mg/m ³]	2490	1560
	HCl [mg/m ³]	48,4	0,38
	H ₂ O [%]	1,8	1,2
	O ₂ [vol%]	16,5	16,0

The briquettes, the flue gas and the emission dust were analyzed with different methods for a wide variety of peripheral inorganic and organic parameters. A selection of these parameters is depicted in table 2: Together with the GC/MS results of PCDD/F they form a new, expanded data set. This set was investigated for possible correlations, which might causally be related to PCDD/F formation during the thermal process:

- Relation between PCDD/F and CO:

There is a controversy in the literature on whether PCDD/F and CO flue gas concentrations are correlated. This relation was investigated in various studies for different combustion processes with different feed materials (waste incineration /9/, co-combustion of mixed plastics and coal /10/, model experiments /11/). From these studies it can be concluded that a correlation, if observed at all, mainly holds for poor combustion conditions. As a consequence, the correlation between PCDD/F and CO is not significant or at least weaker than between PCDD/F and other aromatic compounds. In agreement to this the results of this work (depicted in the following table) show, that the CO flue gas concentration cannot be responsible for the higher PCDD/F-emission of "salt"-briquettes. Admittedly the average value for the "salt"-briquette combustion is higher but there is no correlation within the samples of each briquette sort. The THC (total hydrocarbon content) values can be interpreted similarly.

table 3: selected flue gas emissions of the single samples

fuel	"salt"-briquettes			"normal"-briquettes		
	1	2	3	4	5	6
PCDD/F [pg TE/m ³]	87	134	106	13	21	10
CO [mg/m ³]	2360	4960	4020	1200	1010	2700
THC [mg/m ³]	219	215	338	102	84	56
O ₂ [vol%]	16,7	17,0	15,9	15,7	16,3	15,9

- Relation between PCDD/F and O₂:

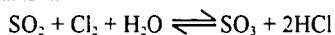
The average concentrations of O₂ does not differ significantly between the samples of both coal sorts (see table 3) and the concentration level is so high that the oxygen supply is not the limiting factor for the formation of PCDD/F. There is no correlation between PCDD/F and O₂ in our measurements.

- *Relation between PCDD/F and H₂O*

The average humidity in the flue gas of the "salt"-briquettes is approx. 50% higher than this of the "normal"-briquettes. Although model experiments with MWI fly ash show that a higher concentration of H₂O yield higher contents of PCDD/F but the humidity was ten times higher than in our measurements and the homologue profiles were changed to dominant tetra-hexachlorinated PCDD/F. Comparing the profiles of "salt"- and "normal"-briquettes (figure 1) in our experiment there is no significant change. The increase of the PCDD/F-fluegas concentration is much stronger than in the model experiments mentioned above. That is why it can be concluded that the different humidity in the flue gas is not the main cause for the stronger PCDD/F-formation during "salt"-briquet combustion.

- *Relation between PCDD/F and S/SO₂*

The influence of S/ SO₂ is contrarily discussed in the literature. Stieglitz and Vogg /12/ and Junk and Richard /13/ reject such an influence whereas Griffin does not rule out the possibility of an influence according to the following mechanism:



This reaction would inhibit the release of the free "in situ" chlorine, which is essential for the formation of PCDD/F. Consequently the PCDD/F formation during "salt"-briquet combustion should be weaker because the "salt"-briquettes as well as the bottom ash contain more sulphur than in the case of the "normal"-briquettes. The SO₂-concentration in the flue gas is also higher. Our measurements produced the opposite result. If the SO₂-influence exists it is superposed by another effect.

- *Relation between PCDD/F and dust emission*

A higher dust emission (dependent on the feed material) could feign a stronger PCDD/F formation. This effect cannot be responsible for the different PCDD/F emission of "salt"- and "normal"-briquettes because the corresponding dust emission is nearly the same.

- *Relation between PCDD/F and copper*

Copper strongly influences the PCDD/F formation. Two mechanisms are proposed:

1. the catalytic effect for the DEACON process /14/
2. direct redoxreactions /15,16/

The different PCDD/F-flue gas emission cannot be correlated with the copper content because both briquet sorts show the same value. The copper level of the bottom ash is significantly higher but low in comparison to fly ash samples from a MWI. Surprisingly the copper content of the bottom ash of the "salt"-briquettes is considerably lower than the corresponding value of the "normal"-briquettes. Possibly the intensified formation of copper chlorid and its evaporation could be the cause. Nevertheless the PCDD/F content in the "salt"-briquettes-ash is higher. Consequently another factor must overcompensate the effect of the copper.

- *Relation between PCDD/F and chlorine*

The bottom ash of both coal sorts amounts approximately twice as much chlorine than the briquettes. This enrichment is in accordance with the expectations. A comparison of both the coal sorts shows that the chlorine content is approx. seven times higher for the "salt"-briquettes and their bottom ash respectively. (table 2) These chlorine values are in close accordance with the PCDD/F contents in the flue gas and in the bottom ash. Concerning the flue gas emission the value for the combustion of the "salt"-briquettes is seven times higher, regarding to the content of the bottom ash the value is four times higher.

From this investigations it can be deduced that the higher PCDD/F emission of the "salt"-coal combustion is caused by the higher chloro content of the "salt"-briquettes.

All other alternative approaches to explain this difference were found to be non-relevant because the corresponding parameters do not differ significantly (e.g. dust emission, Cu content, O₂-concentration) or the available data were inconsistent with the expected correlations (S-content, CO-, SO₂-, H₂O- concentration, THC).

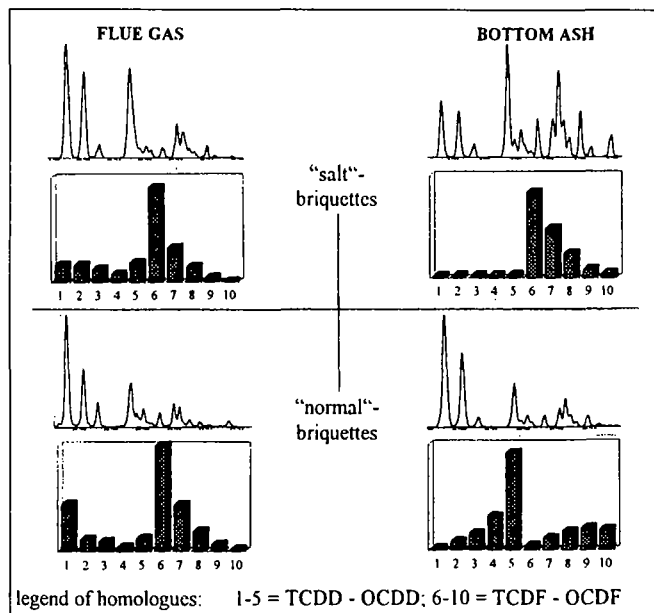
3.2. Estimation of the lignite domestic heating as a source of PCDD/F in the new german federal states

The annual PCDD/F-input from lignite domestic heating based on the flue gas emissions was estimated to be minimal 1.2 g TE/a and maximal 3.0 g TE/a for the German New States. The details of the calculation are described elsewhere./8/ The tendency is that the portion of lignite domestic heating will not be too well related to the total emission summed over the entire area of the new german federal states.

Regarding to the PCDD/F-contents of the bottom ash it can be stated that they are not relevant from a toxicological point of view (risk assessment). The values are lower than the limit for soils being used for agricultural purposes (5 and 40 ng TE/kg). /17/

3.3. Qualitative evaluation of the homologue profiles and isomer distribution pattern

figure 1: The homologue profiles and the TCDD-mass fragmentograms



In figure 1 the homologue profiles and the isomer distribution pattern of tetrachlorodioxins for both briquette sorts and for the flue gas emission and the bottom ash are presented. There is no essential difference concerning the flue gas emissions of both briquette sort. Therefore it can be concluded that the mechanism of formation is similar. In contrast the patterns of the bottom ashes are quite different. The homologue profile of the "salt"-coal ash is predominated by the tetrachlorofurans whereas the most abundant isomer in the homologue profile of the "normal"-coal ash is the

octachlorodioxin. The major isomers in TCDD-mass fragmentogram of the 'salt'-coal ash are the 1,3,6,8- and the 1,3,7,9-TCDD whereas the isomer distribution pattern of the 'normal'-coal ash is more even. The isomer distribution pattern can be explained in different ways:

-Explanation by different isomerization and condensation of precursor compounds (phenoxy radicals, chlorophenols). Characterization of the distribution by superposing two extrem patterns, the so called "2,3-" and "2,6-" types. /18,19/

-Result of thermodynamic product distribution. If the free Gibb's energy of formation of PCDD/F determines the isomer distribution, the pattern should be dominated by a few isomers only, while at lower temperatures the distribution is more even. /20/

The different profiles and distribution pattern indicate that the PCDD/F-formation occurred under different conditions. Both profiles and patterns are reported in the literature for bottom ash. /21,22/ The cause for that is possibly the stronger slagging due to the higher salt content of the ash of the 'salt'-briquettes. This influences the thermic history and the access of oxygen (air) and for that reason the formation of PCDD/F.

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