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PCDD/F Prevention by Novel Inhibitors: Addition of Inorganic S- and N-Compounds in the Fuel before Combustion

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The objectives of this work were to study the addition of sulfur and nitrogen containing compounds to the fuel before the combustion, to examine their capacity for preventing PCDD/F emissions, to investigate their influence on the PCDD/F homologue patterns and to determine the most effective additive concentration used for inhibition. Various sulfur and nitrogen containing solid compounds were mixed with Refuse Derived Fuel (RDF) in proportions of 10% w/w of the fuel, and the mixtures were combusted in a lab-scale reactor at 1000 °C. Analysis and quantification of PCDD/F showed that inorganic sulfur containing compounds significantly affected PCDD/F emissions, resulting in more than 98% reduction of toxic compounds. However, urea presented a lower prevention capacity and resulted in about 28% reduction of PCDD/Fs. High PCDD/F prevention efficiencies, about 96%, were also obtained during the combustion of a mixture containing 1% w/w of amidosulfonic acid (ASA) used as the additive. In addition, the presence of sulfur and nitrogen containing compounds affected the PCDD/F formation pathways, as it was observed from the PCDD/F ratios and the homologue profiles. The PCDD/F prevention ability of sulfur containing compounds is discussed; it could be attributed to the formation of sulfur–copper complexes.

Introduction

The presence of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/F) in the flue gases emitted during combustion of municipal solid wastes represents a serious problem due to the adverse health effects caused by these toxic compounds. Today it is known that PCDD/F are mainly formed through heterogeneous reactions taking place in the downstream regions (200–400 °C) of HCl-containing flue gases waste combustion processes (1). Furthermore, it has been proved that metal ions in the fly ash, primarily copper species, play an important role in the

formation mechanisms acting as catalysts (2, 3). Due to the toxic nature of these compounds, stringent stack emissions limits of 0.1 ng TE/ m³ have been set for the flue gas by several European countries, and much research effort is paid on methods for PCDD/F emissions control (4–6). A large number of emission control techniques is concerned mainly with the “end of pipe” or secondary measures such as wet/dry scrubbing, fabric filtration, activated carbon adsorption. This approach is focused on the removal of PCDD/F from flue gases after their formation by means of gas cleaning devices, increasing their installation and operation costs.

A second approach, the so-called primary measure technique, has been developed for toxic emissions reduction. This technique includes measures and actions for controlling the PCDD/F formation, such as optimization of the combustion processes (7). This approach may include the addition of some selected compounds in the post combustion zone aiming in reducing the formation of PCDD/F and their precursors; it is known as inhibition and differs from the flue gas cleaning methods as it deals with the prevention of PCDD/F (8).

Various inorganic and organic compounds have been studied for their PCDD/F prevention ability. One group includes basic compounds such as NH₃, CaO, NaOH, KOH, and Na₂CO₃ which might change the acidity of the fly ash surface (9, 10). Another group of inhibitors includes compounds that are likely to form some kind of complexes with the transition metal species, responsible for catalyzing the PCDD/F reaction pathways. Sulfur compounds such as Na₂S, Na₂S₂O₃, CS₂, SO₃ and SO₂ are capable of reducing the PCDD/F concentration (11, 12). Furthermore, low PCDD/F emissions have been observed during coal combustion, which were attributed to the high sulfur content of coals (13, 14). A postulated role of sulfur is to react with the copper catalytic sites, as sulfur is known for its poisoning ability of metals and especially copper (15). In this way, sulfur alters the form of copper sites and presumably their ability to produce Cl₂ through the Deacon process reaction (16, 17). It has been proposed, in addition, that SO₂ may sulfonate the phenolic PCDD/F precursors, thus preventing subsequent chlorination and biaryl synthesis (17), or convert the primary chlorinating agent, Cl₂, into a form (HCl) less likely to undergo aromatic substitution reactions forming PCDD/F precursors (18). In general, sulfur compounds have been added in various stages i.e., injected into the combustion chamber or into the boiler section or introduced in the form of high-S containing coals. However, the effects on PCDD/F emissions were not always observable or controllable, while the mechanisms of toxic emissions prevention have not been well developed and proved (6).

Functionalized amines (ethanolamine, EDTA, trimethylamine) can also be effective as inhibitors (8, 9, 19). A complex reaction with the copper catalytic sites is the most likely manner in which the functionalized amines work (20). Among the nitrogen containing compounds, urea has been examined for its PCDD/F inhibiting ability, by addition to the fly ash or by injection in the form of aqueous solutions in the post combustion zone (21, 22). Inhibition activity of urea was explained as a result of interactions between the catalysts and the inhibitor involving the formation of stable inactive compounds or strongly bonded organometallic complexes. Urea with its amino-functional group may form some surface nitride complexes with the metal species as shown by surface spectroscopy (imine, cyanides and azides), resulting in the irreversible deactivation of the catalytic sites (20).

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TABLE 1. Composition of the Artificial RDF

no.	simulating component	compound	content, % w/w
1	paper	cellulose	28
2		lignin	7
3	plastics	poly(vinyl chloride), PVC	1
4		polyethylene, PE	7.5
5	rubber	tetramethylthiuram disulfide	0.5
6	metals	iron, Fe	5.25
7		AlCl ₃	0.5
8		CuCl ₂	0.25
9	biodegradable materials	potato starch	25
10	meat and bone residues	glycin	25

In most of the studies presented here, the experiments were performed in laboratory scale conditions, where fly ash samples were impregnated with the inhibitors and the reactants, and were heated to the desired temperature. However, in full-scale studies, the inhibitors were injected into the flue gas at the post combustion zone. By such a method, PCDD/F inhibition potential is affected by several operating parameters such as the location and the temperature of the inhibitor injection, the contact surface area between the active metal sites and the inhibitor molecules and the concentration of the compound. In addition, the nonadsorbed and nonreacted inhibitors present in the flue gas could also cause problems as some inhibitors are toxic themselves or can be transformed into other organic/inorganic chemicals which are toxic and corrosive (6). Furthermore, the introduction of an organic compound in the post combustion zone could result in high increase of CO concentration in the stack gases, due to problems during combustion process. Preliminary studies using this technique with various amines added to the post combustion zone and applied on a pilot scale reactor showed positive results (23). However, all attempts for scale-up on a full scale plant using the same inhibitors failed completely due to a number of technical difficulties and problems such as oxidation of the inhibitors to CO.

In this study, we performed a series of experiments for the prevention of PCDD/F formation, by mixing various nitrogen and sulfur containing inorganic compounds initially with the raw solid fuel before the combustion. The objectives of this work were to study the ability of various low cost materials to prevent PCDD/F formation when added to the fuel prior to the combustion, to determine the most effective dioxin preventing compound, to investigate the influence of additives on PCDD/F distribution and homologue patterns and to examine the effect of the additive concentration on the PCDD/F prevention capacity.

Experimental Section

The fuel used in this study was an artificial Refuse Derived Fuel (RDF), produced by mixing a number of chemically pure compounds. The manufacturing of this fuel was considered necessary in order to minimize variations in the chemical composition of a natural RDF and to improve the homogeneity of the sample (24). Effort was taken in the composition of the artificial fuel to reflect the major components of municipal solid wastes (25). The concentration of model compounds used for the production of the artificial RDF is shown in Table 1. The model compounds in the form of powder were mixed and stirred overnight, to prepare a sample with a uniform and constant concentration.

Five different compounds were examined for their PCDD/F preventing capacity in a concentration of 10% w/w of the total sample amount. An amide (urea, p.a. grade, Merck)

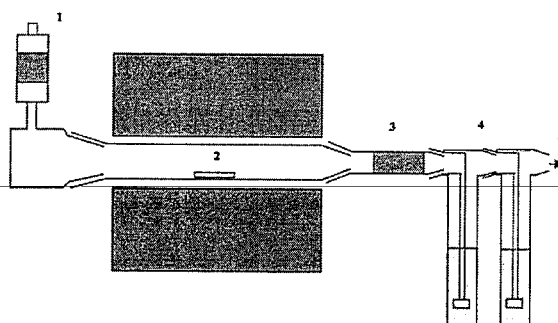


FIGURE 1. Flow diagram of the combustion unit (1-inlet with activated carbon filter, 2-sampling boat, 3-quartz wool filter, 4-toluene traps, 5-connection to flow control unit and to vacuum pump).

was used as representative of nitrogen containing compounds, while the three sulfur-nitrogen containing compounds included amidosulfonic acid (ASA), hydroxylamine-O-sulfonic acid (HOSA), and sulfamide (SA, p.a. grade, Merck); in addition pure sulfur (S₈) was used. To examine the combined action of sulfur and nitrogen, a mixture was prepared (S/U), containing pure sulfur, urea and the fuel, in a % weight ratio of 3.5:6.5:90, respectively. Furthermore, the effect of the additive concentration on PCDD/F prevention capacity was studied by preparing samples containing 1 and 5% w/w amidosulfonic acid (ASA 1% and ASA 5% respectively). Each compound was added to the fuel in appropriate amounts before the combustion experiment, and the two components, i.e., the fuel and the inhibitor, were mixed for 1 h.

A laboratory scale horizontal reactor was used, to achieve reproducible and easily repeatable combustion experiments, and is shown in Figure 1. The laboratory reactor consisted of a quartz tube with ID = 4.5 cm and length 140 cm. A quartz wool filter was placed downstream the reactor and was used for solid particle collection. Two impingers containing 300 mL of toluene and immersed into an ice-bath were connected after the quartz wool filter, for the removal of PCDD/F from the reaction gases. This system could be easily cleaned between the combustion experiments in order to minimize any memory effects and to facilitate the achievement of similar experimental conditions. An isothermal high temperature heating zone, about 10 cm long, was maintained at the middle of the quartz tube. Furthermore, a 50 cm long post combustion zone was achieved at the outlet of the reactor, where the temperature was reduced from the reaction temperature to a temperature of about 200 °C.

Before each combustion run, the quartz glass wool filter was spiked with ¹³C-labeled PCDD/F, and the system was checked for gas leakages. Experimental procedure included preheating of the furnace to 1000 °C, placement of about 5 g of the fuel in the high heating zone, and combustion under an air flow of 1 L/min for 15 min. This reaction time was necessary for complete combustion of the sample, as it was deduced from the analysis of the unburned carbon content in the ash. A quartz wool filter was used for the removal of solid particles, while two toluene traps immersed in an ice bath, downstream the quartz reactor, were used for the PCDD/F removal from the gas phase. At the end of each combustion run, glass components were disconnected, and the remaining ash was withdrawn from the reactor. The outlet part of the quartz reactor and the quartz wool filter were Soxhlet extracted with toluene for 24 h. Cleanup of extracts was performed by a procedure involving application of the extracts in a silica column, an acid mixed column, and an alox column. Identification/quantification of PCDD/F was

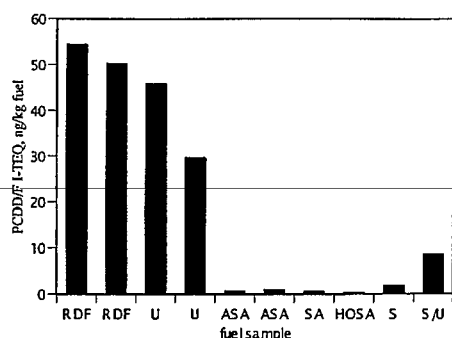


FIGURE 2. PCDD/F I-TEQ values during combustion of RDF and RDF mixtures (RDF-single component experiments, U-mixture with urea, ASA-mixture with amidosulfonic acid, SA-mixture with sulfamide, HOSA-mixture with hydroxylamine-O-sulfonic acid, S-mixture with sulfur, S/U-mixture with sulfur and urea).

performed using a HRGC/HRMS (MAT 95 Finnigan), according to methods described in details in previous work (26). PCDD/F collection efficiency on the quartz wool filter and the toluene traps has been estimated to be more than 90%, while recovery rates of PCDD/F were in the range from 65 to 90%. Duplicate combustion experiments were carried out in order to examine the ability to reproduce the experimental runs and to confirm the reproducibility of the results.

Results and Discussion

The results of PCDD/F I-TEQ emissions corresponding to the combustion of RDF and its mixtures with the various additive compounds are shown in Figure 2, and the corresponding emission values of homologues are given in Table 2. High PCDD/F concentrations, more than 50 ng I-TEQ/kg RDF, were found during the single RDF combustion experiments. The average PCDD/F concentration during RDF combustion was estimated to about 3.6 ng I-TEQ/m³; this value is similar to emission values observed during the combustion of a synthetic fuel in a pilot incinerator ranging from 0.9 to 270 ng/Nm³ according to the experimental conditions (7). In addition, similar PCDD/F concentrations have been measured in the flue gases from a hazardous waste incinerator (2.9 ng/Nm³) (27) and from a municipal waste incinerator (3.0 ng/Nm³) (28), indicating the good operating conditions of the used reactor, which simulate the operation of pilot and full scale incinerators.

The addition of urea in the fuel before the combustion resulted in a slight decrease of the PCDD/F emissions. The average PCDD/F I-TEQ value of urea mixture combustion was about 38 ng/kg RDF, corresponding to a prevention efficiency of about 28%. Duplicate combustion experiments, which were performed with RDF and RDF-urea mixtures, resulted in slight variations in the emission values from their means, ranging from 4% for single RDF runs to 21% for the

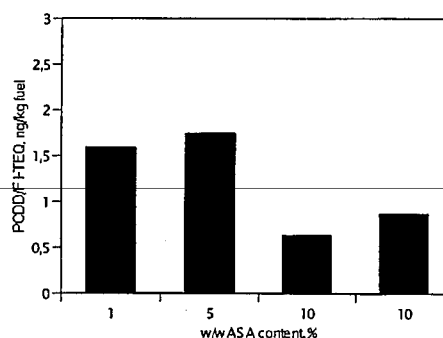


FIGURE 3. The effect of amidosulfonic acid concentration on PCDD/F emissions.

RDF-urea tests, ensuring the quite good reproducibility of the experimental results and the achievement of similar conditions during each run.

The addition of sulfur containing compounds in the fuel mixture resulted in significant reduction of total PCDD/F concentration and I-TEQ values as well. PCDD/F I-TEQ values measured during combustion of these mixtures were lower than 1 ng/kg RDF resulting in prevention efficiencies higher than 98%. In the case where the inhibitor was added in the form of neat sulfur, PCDD/F emissions measured were about 2 ng/kg RDF, resulting in a prevention efficiency of more than 96%. Sulfur is known for its poisoning properties to metal catalysts, as in electrophilic halogenation reactions, where sulfur can effectively block Fe/Cu metal catalysts and cease the chlorination reaction (15). Moreover, in the presence of sulfur, heavy metals are converted into stable metal sulfides at low temperatures (29). However, urea was less effective in reducing toxic emissions, in accordance to a previous work where combustion of natural RDF with urea resulted in limited reduction of PCDD/F emissions (24).

The sulfur containing inorganic compounds were added in a proportion of 10% in the fuel mixture. However, a very small amount of sulfur should be enough for preventing PCDD/F formation. Accordingly, to examine the PCDD/F prevention capacity of the additives, two additional combustion experiments were performed. In these tests, the most efficient inhibitor, amidosulfonic acid, was added in amounts of 1 and 5% w/w in the total fuel sample, and the results from PCDD/F emissions are included in Figure 3. As it is shown, low PCDD/F I-TEQ values of about 1.7 ng/kg RDF were observed during the combustion of mixtures containing low amounts of sulfur compounds, resulting in increased inhibition efficiencies, higher than 96%.

The distribution of total dioxins and furans amounts emitted during the various combustion experiments is shown in Figure 4. As it is shown in this figure, for RDF combustion, furans dominated over the dioxins, and the ratio PCDD:PCDF was varied from 1:22 to 1:29. These ratio values are higher than the corresponding values deduced from the emission

TABLE 2. Emission Values (ng/kg fuel) during the Combustion of Various Fuel Mixtures

	RDF	RDF	U	U	ASA	ASA	SA	HOSA	S	S/U	ASA 5%	ASA 1%
TCDD	84.8	60.5	58.3	41.1	1.9	3.7	1.1	2.7	8.4	22.4	4.2	5.7
PeCDD	29.7	19.9	20.9	11.8	1.6	0.3	0.2	0.6	4.1	7.4	3.7	4.1
HxCDD	9.7	5.2	3.4	2.6	1.5	0.9	0.3	0.8	9.4	7.6	8.4	5.3
HpCDD	4.7	1.8	1.5	1.0	1.1	0.7	0.6	0.6	4.1	9.6	7.6	4.1
OCDD	17.1	3.2	4.6	1.9	2.8	1.6	1.0	1.6	6.6	7.0	7.7	8.4
TCDF	2535.5	2043.8	2180.9	1104.2	16.9	18.5	23.4	6.5	21.6	307.0	25.0	23.2
PeCDF	586.6	543.8	522.5	212.1	1.9	2.3	1.2	0.8	6.7	63.7	6.6	7.3
HxCDF	112.0	100.4	84.9	34.4	2.3	2.7	1.4	1.5	5.7	13.6	6.7	4.4
HpCDF	13.4	8.7	6.5	3.1	1.0	0.6	0.6	1.8	2.0	4.2	5.4	2.0
OCDF	7.1	3.2	1.9	1.2	1.7	1.2	1.1	1.0	1.5	2.0	3.0	0.9

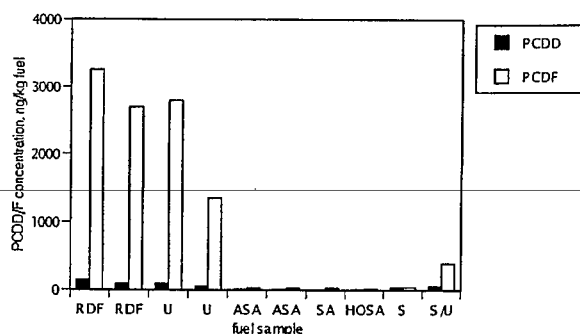


FIGURE 4. PCDD/F distribution during RDF and RDF mixtures combustion.

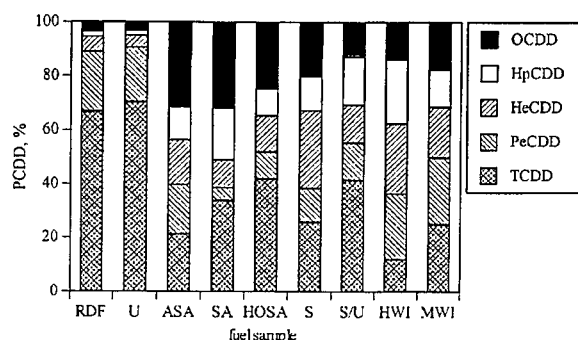


FIGURE 5. PCDD homologue patterns during lab scale (RDF and RDF mixtures) and full scale (hazardous and municipal waste incinerators, HWI and MWI respectively) combustion runs.

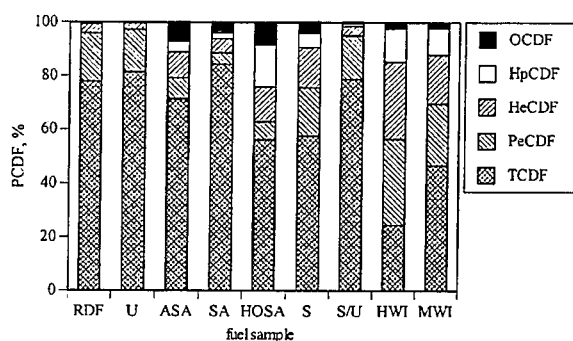


FIGURE 6. PCDF homologue patterns during lab scale (RDF and RDF mixtures) and full scale (hazardous and municipal waste incinerators, HWI and MWI respectively) combustion runs.

data of waste incinerators where PCDD/F ratios are lower than 1:10 (27). Similar ratio values were obtained during combustion of the RDF-urea mixtures, where the PCDD/F ratios varied from 1:22 to 1:32, in accordance to previous results where the addition of urea did not change the proportion of PCDD and PCDF amounts (24). However, during combustion of fuel mixtures containing sulfur compounds, the furan concentrations were only up to eight times higher than the corresponding dioxin concentrations. Apparently, the addition of these compounds not only resulted in reduction of the total PCDD/F emissions but also affected the formation mechanisms of the toxic compounds.

The homologue profiles of PCDD and PCDF emitted during the combustion of RDF and its mixtures are shown in Figures 5 and 6, respectively, where the various homologues are presented as proportions of the total amount of the corresponding dioxins and furans. The homologue profiles

of PCDD/F emissions from a hazardous waste incinerator (HWI) and a municipal waste incinerator (MWI) have been included in these figures for comparison reasons (27, 28). As shown in these figures, lower chlorinated dioxin homologues (tetra- and pentachlorinated isomers) prevailed over the higher ones for the combustion tests of RDF and RDF-urea mixtures. However, as it was already observed in Figure 4, addition of sulfur containing compounds resulted in different homologue profiles where all chlorinated substitutes presented a significant contribution. In all the cases where an inhibitor had been added to the fuel, an increase of the contribution of the octachlorinated homologues to the profiles had been observed. Taking into account that the octachlorinated isomers are first formed through condensation reactions of polychlorinated precursors, while the other dioxins are subsequently produced through dechlorination of the higher chlorinated isomers, or chlorination of the lower ones (mono- to trichlorinated), it is possible that the use of sulfur compounds suppresses the dechlorination/chlorination reactions (30). Similar results were obtained from the furan homologue profiles, Figure 6, where the presence of the inhibitors resulted in the increase of the higher chlorinated isomers contribution. However, the content of the tetrachlorinated homologue was the highest of all the isomers in all the cases.

The homologue profiles from the hazardous waste incinerators indicated the prevalence of the penta- to heptachlorinated homologues over the other isomers. Nevertheless, in the homologue profiles for the municipal waste incinerator the lower chlorinated isomers prevailed over the higher ones, indicating that emission characteristics are greatly affected by the properties of the fuel and the combustion conditions.

These preliminary results showed that the technique of inorganic sulfur and nitrogen containing compounds addition to the fuel prior to the combustion, might be an innovative, effective and low cost prevention technique of PCDD/F formation. The addition of ASA in only 1% w/w to the fuel has been shown to be the most efficient way to effectively reduce PCDD/F concentration to more than 95%. The application of this method in full scale combustion units will result in suppression of their cost, as the installation and operation of expensive processes such as activated carbon adsorption and wet scrubbing will not be necessary anymore. However, from a practical point of view, the transition of lab-scale experiments to pilot and full-scale units is not easy to be accomplished, as the formation of chlorinated compounds is affected by the properties of the fuel and especially by the combustion conditions and the type of the incinerator. The primary ideas deduced from this study were the determination of an effective PCDD/F preventing compound, which, upon addition in the fuel before the combustion, should be able to reduce PCDD/F emissions. As a result this compound could contribute in the efforts for avoiding the use of the more complicated methods where inhibitors are injected in the post combustion zone. The proposed technique of precombustion addition seems to be very promising, as it could be easily applied in industrial scale, requiring only minor modifications of the fuel feeding device in existing plants.

Apparently, further experiments are necessary in pilot and full-scale combustion reactors, to examine the properties of these compounds, to determine the most efficient inhibitor concentration, to exploit the mechanism of inhibition and to study the effect of the additives on the emissions of other gases and chlorinated compounds (SO_2 , PCB, chlorinated phenols and benzenes). The selection of the inhibitor should be made carefully, taking in mind that it should survive through the harsh combustion environment, block the catalytic sites and not provide any undesirable byproducts.

Acknowledgments

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