

Inhibition of PCDD/F and PCB formation in co-combustion

M. Pandelova^{a,*}, D. Lenoir^a, K.-W. Schramm^{a,b}

^a GSF-Forschungszentrum für Umwelt und Gesundheit, Institut für Ökologische Chemie,
Ingolstädter Landstr. 1, D-85764 Neuherberg, Germany

^b TUM, Wissenschaftszentrum Weihenstephan für Ernährung und Landnutzung,
Department für Biowissenschaften, Weihenstephaner Steig 23, D-85350 Freising, Germany

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Abstract

Co-combustion of coal-solid waste mixtures in pilot and laboratory-scale combustors with emphasis on monitoring of toxic chlorinated hydrocarbon emissions such as polychlorinated dibenzo-*p*-dioxins and -furans (PCDD/F) and polychlorinated biphenyls (PCB) is elaborated. The objective of the work is to investigate the so-called primary measures technique. Twenty different thermally resistant inorganic compounds were added directly to the fuel as inhibitors of PCDD/F formation. The fuel-types used in this study included lignite coal, pre-treated municipal solid waste and polyvinyl chloride (PVC). Principle component analysis (PCA) provides the basis for a feasible discussion about the efficiency of 20 inhibitors on PCDD/F and PCB formation. The study showed that the metal oxides group investigated had no inhibitory effect. Although the single N- and S-containing compounds, used as additives for the type of lignite coal, solid waste and PVC fuel, are not very effective as inhibitors, all other N- and S-containing substances are capable to strongly reduce PCDD/F and PCB flue gas emission. The most effective inhibitors are (NH₄)₂SO₄ and (NH₄)₂S₂O₃. (NH₄)₂SO₄ present at 3% of the fuel can reduce the PCDD/F emissions to 90%. Its low cost and high efficiency favour them as useful for full-scale combustion units.

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1. Introduction

Co-firing of solid waste with coal in power plants is a promising technique for countries lacking waste incinerators because of special environmental and economical reasons. The energy efficiency of coal for electric power, coupling of heat and local heating in power plant is substantially higher as compared to the waste used as fuel in municipal waste incinerators. Although incineration of small percentage of solid waste used as substituted fuel has become an important method in coal power plants. The potential of such a substituted fuel type is high enough for proposed co-firing of waste with coal and could help to reduce the waste disposal, preserve fossil fuel coal resources, and reduce uncontrolled burning at dumping sites or backyard burning in all countries. Co-combustion of solid waste and coal also reduce the emissions of greenhouse gasses such as CO₂ and CO. Despite, the application of this process poses some environmental risks due to the chemical nature of the compounds formed from solid

waste during co-combustion. For example, high concentrations of polychlorinated dibenzo-*p*-dioxins (PCDD), polychlorinated dibenzofurans (PCDF) and polychlorinated biphenyls (PCB) are produced during waste incineration [1]. The United States Environmental Protection Agency (EPA) in 1994 report that dioxin is a potential human carcinogen and exposure to dioxin can cause immune system damage and interfere with regulatory hormones [2,3]. Last few years, control over the release of dioxins into the atmosphere has become more widespread, which has led to an increasing consensus in Europe for an emission limit in flue gas of 0.1 ng/m³ based on the toxic equivalents (TEQ) value [4].

Recently, it has been shown that mixed oxide catalysts based on TiO₂/V₂O₅/WO₃ lead to the destruction of chlorinated aromatic compounds, such as monochloro-, 1,2-dichloro-, and 1,2,4-trichlorobenzene in a laboratory-scale fixed bed reactor and a waste incineration plant [5]. The catalytic oxidation of 1,2-dichlorobenzene has been investigated over a series of transition metal oxides (i.e. Cr₂O₃, V₂O₅, MoO₃, Fe₂O₃ and Co₃O₄) supported on TiO₂ and Al₂O₃ [6]. Based on the idea to block the catalytic active sides of copper species many researchers have used nitrogen compounds like amines or alkanolamines as inhibitors in order to reduce the PCDD/F emissions

* Corresponding author. Tel.: +49 89 3187 2932; fax: +49 89 3187 3371.
E-mail address: pandelova@gsf.de (M. Pandelova).

[7–9]. Organic amines like ethanolamine, triethanolamine and monoethanolamine are successfully used to prevent the formation of PCDD/F from pentachlorophenol on fly ash [10]. Other inhibitors have the ability to complex with or bind to metal ions, which catalyses the PCDD/F formation. The experimental results suggest that the reaction of Cu (II) with SO₂ to form CuSO₄ in the presence of oxygen renders the catalyst less active and leads to decreasing PCDD formation. Inactivity is also due to the reduced ability of Cu (II) and Cu (I) species to promote a second catalytic step of biaryl synthesis [11]. Urea and some sulfur and nitrogen compounds such as hydroxylamine-*o*-sulfonic acid, amidosulfonic acid, sulfur and sulfamide have been successfully used as inhibitors in a laboratory-scale experiment with a refuse-derived fuel [12,13].

In this study, a laboratory-scale furnace is used to perform a series of experiments aiming to prevent the formation of PCDD/F by the use of inhibitors. The objective of this work is to identify the most effective low cost and low toxicity inhibitors for PCDD/F, making them applicable for use in full-scale combustion units.

2. Materials and methods

2.1. Reagents

The types of fuel used in this study are lignite coal from Puertollano (Spain), pre-treated municipal solid waste (Rethmann Plano GmbH), and used polyvinyl chloride (PVC) (waste from ground carpet). The lignite coal content from the total fuel mixture was 80% by weight percentage. Such a high amount of lignite coal was chosen because of the interest in coal combustion. Although addition of solid waste supposes to be sufficient for dioxin formation, in the laboratory scale furnace the emissions were still not very high. Thus, the addition of PVC to the lignite coal/solid waste mixture was necessary to generate a PCDD/F-level that can be potentially reduced by inhibitors at least 3 orders of magnitudes. The chlorinated compounds were 20% by weight of the fuel mixture with a 13.3:6.7 ratio of the solid waste to PVC. In the inhibitor experiments, the inhibitor is added as 10% of the fuel. The rest 90% fuel used is homogenised very well with additives in the sampling boat. Although addition of solid waste to the coal has been reported to be optimal for dioxin formation, the dioxin emissions concentration in the laboratory-scale furnace was not very high. Thus, the addition of PVC to the lignite coal/solid waste mixture was mandatory. Twenty different compounds were investigated as inhibitors (Table 1).

The two most effective inhibitors for PCDD/Fs and PCBs formation were also tested at an amount of 5%, 3% and 1% of the fuel.

2.2. Apparatus

For the experiments a laboratory-scale horizontal split-tube furnace (Split Tube furnace (3-zone) type HZS & TVS, Carbolite, England) (Fig. 1) is used. The laboratory reactor dimension are set by quartz tube of i.d. = 14 cm and a length of 150 cm, 3/4

Table 1
Alphabetic indicator of inhibitors used for laboratory scale experiments

A	Without inhibitor
B	TiO ₂
C	ZrO ₂
D	Na ₂ MoO ₄ ·2H ₂ O
E	Al ₂ O ₃
F	H ₂ NSO ₄ H
G	NaVO ₃
H	H ₂ NSO ₃ H
I	S
J	H ₂ NSO ₂ NH ₂
K	Pomace ^a
L	[(CH ₃) ₂ N] ₃ P(O)
M	N(CH ₂ CH ₂ OH) ₃
N	Na ₂ WO ₄ ·2H ₂ O
O	P ₂ S ₅
P	Na ₂ S·H ₂ O
Q	Cr ₂ O ₃
R	(NH ₄) ₂ SO ₄
S	(NH ₄) ₂ HPO ₄
T	(NH ₂) ₂ CO + S
U	(NH ₄) ₂ S ₂ O ₃

^a Residue of olive oil production.

of the length of which was placed into the heating zone of the furnace. When the desired temperature was achieved the sampling boat was pushed from the cooled part of the quartz tube to the middle of the heated zone.

The combustion experiments were performed according to the same procedure each time in order to achieve reproducible results. The flue gases occurring during the experiment were trapped into three impingers in series each filled with 70 mL toluene. The first impinger was previously spiked with 100 μL CEN-sampling PCDD/Fs standard. The air flow was 2 L/min, the furnace temperature was 400 °C, the duration of the experiment was 30 min and the weight of the sample was 10 g.

2.3. Dioxin measurement

After combustion experiment terminate the sample was processed for further specific clean-up steps [14,15]. The tetra- to octachloro-isomers of PCDD/F and the tetra- to hepta-PCB were identified and quantified in pg/g combusted material.

2.4. Statistical analysis

Statistical Package 3.11 g, Kovach Computing Service [16] was used for the principle component analysis (PCA). PCA reflected the effect of the 20 different inhibitors on the PCDD/F

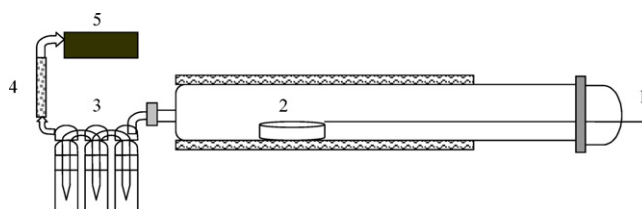


Fig. 1. Scheme of the laboratory scale furnace (1: inlet with air flow, 2: sampling boat, 3: toluene impingers, 4: glass wool filter, 5: vacuum pump).

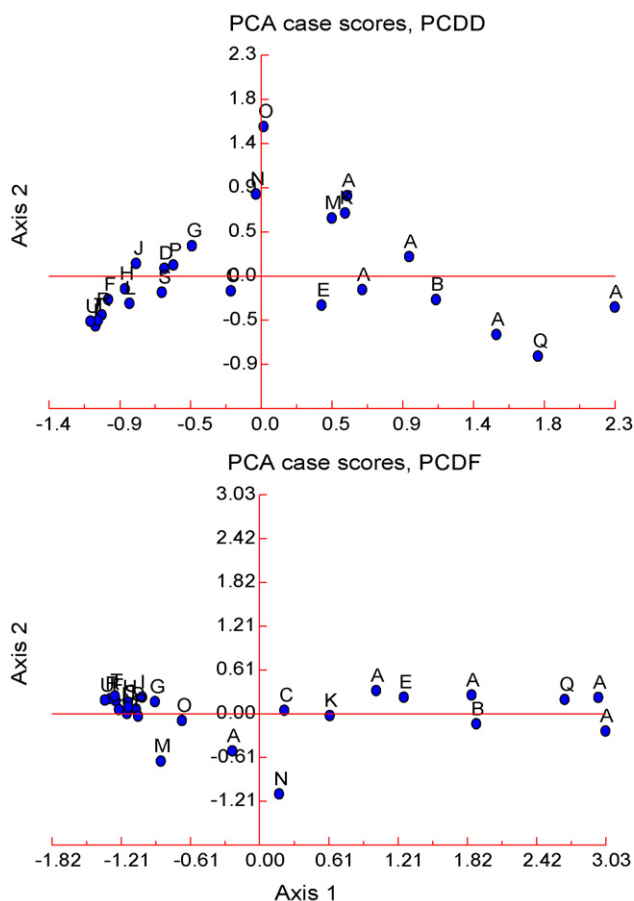


Fig. 2. Score plots of PCDD and PCDF of 5 samples treated without any inhibitor and 20 samples with 10% of different inhibitors.

congener patterns emitted. No transformation of the data was performed during the statistical analysis.

3. Results and discussion

PCA was used in order to give a better view of the similarity between the samples using the concentrations of PCDD and PCDF congeners. The statistical score plot for the laboratory-scale experiment with 20 inhibitors is shown in Fig. 2.

The matrix for PCDDs consisted of 37 variables (PCDDs congeners) and 25 cases (samples) and the matrix of PCDFs was comprised of 63 variables (PCDFs congeners) and 25 cases (samples). In both score plots two main groups of samples were observed. The samples without inhibitor are placed on the right side of the multidimensional space. Neighbouring these toxic samples are some other points, which can be attributed to the metal oxide inhibitors Cr_2O_3 , TiO_2 , Al_2O_3 and pomace. In addition they also belong to the samples with higher concentrations. The samples with lower concentration of PCDD/Fs became located on the left side of the score plots. Between both groups and near to the ordinate axis and, N-, S- and metal oxide inhibitors such as P_2S_5 , $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$, $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ and ZrO_2 were placed. These four compounds were additives that manifested low inhibitory effects or samples with high variation in the PCDD/Fs amount. A highly agglomerated group

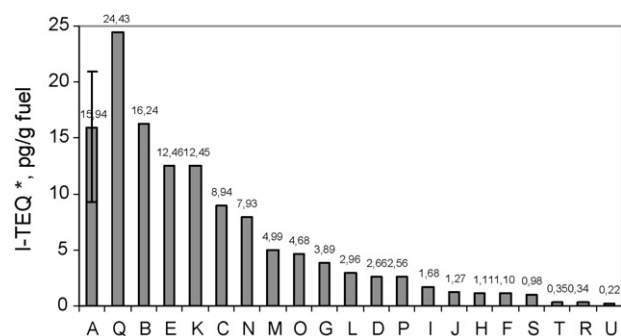


Fig. 3. I-TEQ* (pg/g fuel) values of the flue gas during thermal treatment of lignite coal, solid waste and PVC for the samples without inhibitor and 20 different compounds used at 10% inhibitor of the fuel. *Sum PCDD/F and PCB.

especially in the case of PCDF, is on the left hand side. It represent samples with 10% inhibitor concentration, where all inhibitors were N- and S-containing compounds, and others such as NaVO_3 , $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{HPO}_4$, $[(\text{CH}_3)_2\text{N}]_3\text{P}(\text{O})$, S and $\text{Na}_2\text{S} \cdot \text{H}_2\text{O}$. The points were very close to each other, which was explained by the similarity in their pattern and the amount of PCDD/Fs formed. The N- and S-containing compounds were placed much more to the left in the score plot. This effect correlated with the tendency observed on Fig. 3, where the same compounds showed a strong inhibitory effect for the international toxic equivalent (I-TEQ) of PCDD/Fs and PCBs concentrations in the flue gas.

The total amounts of PCDDs, PCDFs and PCBs generated during experiments with a mixture of lignite coal, solid waste and PVC were substantial enough to investigate the effect of inhibition. The average I-TEQ of the sum of PCDD/Fs and PCBs was about 16 pg/g fuel or about 2.5 ng/Nm^3 (Fig. 3). Such experiments were performed five times and the results showed a relatively low standard deviation of about ± 4.96 . The experimental results with 10% inhibitor showed very different I-TEQ values; some of the compounds such as Cr_2O_3 , TiO_2 , Al_2O_3 , and pomace led to similar and/or greater amounts of PCDD/Fs and PCBs than the samples without inhibitor (Fig. 3).

Other additives such as $\text{H}_2\text{NSO}_3\text{H}$, $\text{H}_2\text{NSO}_4\text{H}$, $(\text{NH}_4)_2\text{HPO}_4$, $(\text{NH}_2)_2\text{CO} + \text{S}$, $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_2\text{S}_2\text{O}_3$ showed a very strong inhibitory effect in the flue gases. $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_2\text{S}_2\text{O}_3$ exhibited stronger inhibitory effects on PCDD/F and PCB formation with respectively 0.34 and 0.22 I-TEQ pg/g fuel and cause emission reduction up to 98–99% (Fig. 3). Therefore, experiments, wherein these inhibitors were studied at 5%, 3% and 1% of the total fuel weight, were performed in triplicate (Fig. 4). In addition, the experiment without any inhibitor was repeated in order to obtain an actual value during that time of the investigation. The average calculated concentration for the sum PCDD/F and PCB I-TEQ was 17.5 pg/g with a maximum value of 20.5 pg/g and minimum value of 12.7 pg/g. $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_2\text{S}_2\text{O}_3$ were effective inhibitors at 10% and 5% of the fuel for PCDD/Fs and PCBs (Fig. 4). If the percentage of these substances was decreased further, the formation of chlorinated micropollutants was also increased. According to Fig. 4, $(\text{NH}_4)_2\text{SO}_4$ might also

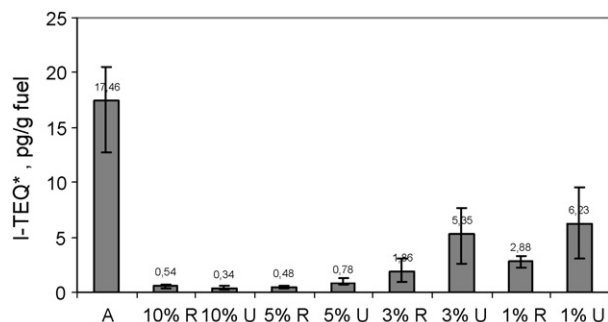


Fig. 4. I-TEQ* pg/g fuel in the flue gas for the samples without inhibitor (A) and with inhibitor R and U at 10%, 5%, 3% and 1% of the fuel. *Sum PCDD/F and PCB.

have reduced the PCDD/Fs and PCBs in flue gas emission at 3% but not as effectively as at higher percentages.

4. Conclusion

High concentrations of PCDD/F and PCB are detected during the co-combustion of lignite coal and solid waste when a small amount of PVC is additionally added to the mixture. Recent laboratory scale study manifest also that PVC once converted to HCl may contribute to PCDD/F formation. However, another experiment of co-combustion of coal and PVC in bubbling fluidised bed boiler suggested that an increase in PVC content of 1–2% resulted in a decrease of PCDD/F emissions in the flue gas as well as in the particle phase [17]. Current results showed that the metal oxides group investigated herein had no inhibitory effect. Some of the additives such as Cr_2O_3 , Al_2O_3 and TiO_2 even increased the PCDD/F emissions. It seems that the transition metal, such as copper, iron or one of the oxides of these metals can also promote the *de novo* reaction. They produced very high amounts of the most toxic congeners and high amounts of other less chlorinated PCDD/Fs and PCB. Some other substances belonging to the metal oxides groups such as NaVO_3 , $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ showed low inhibitory effects, especially for PCDDs. These substances were active for catalytic oxidation. Their chemical structure consisted of a strong oxide base such as VO_3^- , MoO_4^{2-} , WO_4^{2-} . Probably due to that base, a better performance of incineration during the experiments occurred. However, these additives did not reduce sufficiently PCDD/F and PCB formation.

Relatively low inhibitory effects are observed for the compounds containing either S or N. Despite sulphur present at 10% of the fuel shows great reduction of PCDD/F and PCB formation. Further, all other N- and S-containing compounds seemed to be able to strongly reduce PCDD/Fs and PCBs flue gas emission if used as a 10% additive to a fuel containing lignite coal, solid waste and PVC. In our study, we showed that sulphur and nitrogen compounds like $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_2\text{S}_2\text{O}_3$ were the

most efficient inhibitors. $(\text{NH}_4)_2\text{SO}_4$, present at 3% of the fuel, could reduce the PCDD/F and PCB emissions by 90%. These compounds are low cost and non-toxic materials, making them applicable for use in full-scale combustion units.

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