PRIMARY MEASURES FOR REDUCTION OF PCDD/F IN CO-COMBUSTION OF LIGNITE COAL AND WASTE: EFFECT OF VARIOUS INHIBITORS

[a]Pandelova, M., [a]Lenoir, D., [a,b]Kettrup, A., [a]Schramm, K.-W.

[a] GSF-National Research Center for Environment and Health, Institute of Ecological Chemistry, Ingolstädter Landstr. 1, D - 85764 Neuherberg, Germany
[b] Technische Universität München, Lehrstuhl für Ökologische Chemie und Umweltanalytik , D.-.85350 Freising - Weihenstephan, Deutschland

Introduction

Co-firing of solid waste with coal in incineration plant is a promising technique, which could help reduce toxic gas emissions and waste disposal, utilize solid waste energy content, and preserve fossil fuel resources. Due to it's application some environmental caused by the chemical nature of the solid waste can appear. High amounts of polychlorinated dibenzo-*p*-dioxin and furans (PCDD/F) may be formed during the waste incineration.

PCDD/F emissions from flue gas can be controlled by primary and /or secondary measures in order to comply with the limit value of 0.1 ng/m^3 TEQ. Primary measures include adjustment of the operation conditions (temperature, turbulence, air flow, residence time) and focus on the additives of selected compounds which can inhibit the formation of PCDD/F completely. Secondary measures lead mainly into the use of flue gas cleaning systems, electrostatic precipitators (ESP), activated carbon adsorption and fabric filters. Compared to primary measures, secondary measures are much more expensive. During their use toxic solid residues are produced which can cause additional problems.

Recently, many inhibitors of PCDD/F-formation are investigated. This type of compounds are NH_3, CaO, KOH, and Na_2CO_3 [1, 2]. Their mechanism might be attributed to the change of the acidity of the fly ash surface [3] . Some other inhibitors are believed to interact with metal ions, which catalyse PCDD/F formation. Experimental results suggest that the reaction of Cu (II) with SO_2 to form $CuSO_4$ renders the catalyst less active and decrease PCDD/F formation. Activity can also be reduced by the decreased ability of Cu (II) to promote a second catalytic step of biaryl synthesis [4]. Urea and some sulphur and nitrogen compounds as hydroxylamine-o-sulfonic acid, amidosulfonic acid, sulfur and sulfamide are successfully used as a inhibitors in laboratory scale experiments in combustion with refuse derived fuel (RDF) [5, 6]. Functionality of ethanolamine, triethanolamine and monoethanolamine to prevent the formation of PCDD/F from pentachlorophenol on fly ash have been also observed despite the increase of CO concentration in the flue gas [7, 8, 9]. The decomposition of 1,2-dichlorobenzene as a model reaction is experienced with titanium-supported vanadium catalyst (VOx/TiO_2) for catalytic destruction of PCDD/F [10]. The surface species of series of transition metal oxides (i.e. Cr_2O_3, V_2O_5, MoO_3, Fe_2O_3 and Co_3O_4) supported on TiO_2 and Al_2O_3 are proofed as potential intermediates for the oxidation of 1,2-dichlorobenzene [11].

In this study, a series of experiments in laboratory scale condition for the prevention of PCDD/F formation by most of the already used inhibitors were performed. Some other new inhibitors with

similar and different chemical structure were also included. We selected thermally stable inorganic compounds which were added directly to the fuel. The aim of this work is to elaborate some of the most effective inhibitors for PCDD/F, with low cost and less toxic properties. Investigations about the behaviour of PCDD and PCDF-pattern is also developed, as well as the corresponding treatment PCDD/F-results by means of multivariate statistical methods.

Methods and Materials

The fuel-types used in this study are lignite coal from Puertollano (Spain), pre-treated municipal solid waste (Rethmann Plano GmbH) and PVC (waste from ground floor). The weight percentage content for the lignite coal is 80% and for the chlorinated compounds is 20% as 13.33:6.66 respectively for the solid waste and PVC. In case of inhibitor experiments, the inhibitor is present as 10 % of the fuel. Before the experiment each fuel is stirred by the help of mechanical mortar in order to generated an average particle size of less then 1mm. For the solid waste, the mixing procedure is performed after 30min cooling of the larger pieces in liquid nitrogen.
Four different type groups with 20 compounds are used as inhibitors:

- Metal oxides group - 8 different substances
- N-contents group – 3 different substances
- S-contents group – 3 different substances
- N- and S-contents group – 6 different substances

A laboratory scale horizontal split-tube furnace is used for the experiments. The laboratory reactor consisted of a quartz tube with ID=14cm and a length of 150cm, which is placed into the heatable zone of the furnace with around 3/4 parts of its total length. From the cooled part of the quartz tube the sampling boat is pushed to the middle of the heated zone. The flue gases occurring during the experiment are trapped into 3 impingners in series, each of them filled with 70ml toluene. The fist impingner is previously spiked with 100µl CEN-sampling standard. The combustion experiments are performed according to the same procedure each time in order to achieve comparable results. The furnace temperature examined is 400°C, the air flow is 2L/min, the weight of the sample is 10g and the duration of the experiment is 30min. To avoid memory effects the furnace is cleaned mechanically with solvents after each experiment: toluene and acetone and heated afterwards at 850°C for 2h with a gas flow 2l/min. Frequently blank samples are generated.
After completing the experiment, the toluene solution is spiked with CEN- internal standard mixture of (^{13}C) – analogues of PCDD/F, reduced by evaporation and placed at the top of the first sandwich chromatography column. The organic interferences are eliminated by employing other columns with aluminium oxide. The extract is finally evaporated by a gentle stream of nitrogen to 25 µl. The vial for this purpose is previously spiked with 25 µl CEN- recovery standard for PCDD/F. The sample is analysed with HRGC/HRMS. The tetra- to octachloro- isomers of PCDD/F were identified and quantified.

Results and Discussion

The total amounts of PCDD and PCDF generated during experiments with lignite coal, solid waste and PVC are high enough to investigate substantial inhibition. The average measured value of the sum of PCDD/F is around 11111 pg/sample. Such type of reference experiments without inhibitor are performed five times. The experimental results with inhibitors showed very different values for PCDD/F. Metal oxides show no inhibitory effect, while inorganic compounds with N- and S group show strong reduction of PCDD/F-values by a factor of 98-99%.

Statistical Package 3.11g, Kovach Computing Service is used for the principle component analysis (PCA) and pattern analysis. The current analysis is performed separately for PCDD and PCDF. The statistical results of the laboratory scale experiments with 20 inhibitors are visualized by score plots (Fig.1). Samples with similar PCDD/F emission are located close to each other in the score plot, while those which have divergent emission or congeners or both pattern are located further apart. The matrix for PCDD consist of 37 variables (PCDD isomers) and 25 cases (samples) and the matrix of PCDF is represented with 63 variables (PCDF isomers) and 25 cases (samples).

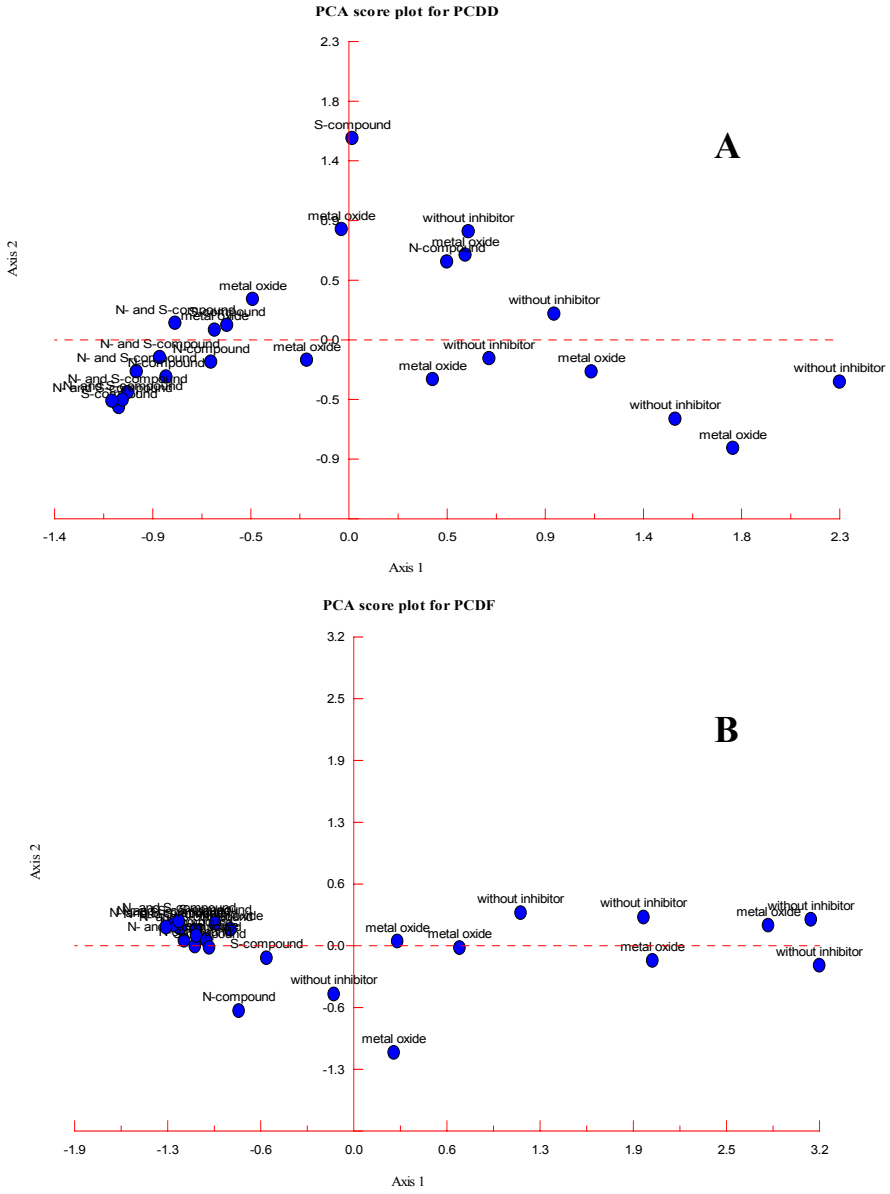

Figure 1: Score plot for PCDD (A) and PCDF (B) of Principle Component Analysis.

Two main groups of samples are observed in the score plot. One of it is placed right and the other left of the ordinate axis. The samples without inhibitor are found in the right side of the multidimensional space. Neighboured to this toxic samples are also some other points located which can be attributed to the metal oxide inhibitors. However, they also belong to the higher concentrated PCDD/F samples. Near to the ordination axis and in the middle of the both groups are some other inhibitors from the N-, S- and metal oxide group plotted. They represent samples with low inhibitor effects or samples with high variation of PCDD/F amount. The agglomerated group especially for PCDF score plot is the left one, representing samples containing the lowest PCDD/F amount with inhibitors used from all N-and S-compounds and few N-, S- and metal oxide substances. The points are very close each other which can be explained by their similarity in their pattern and their amount formed.

Conclusions

The primary idea of this study is to examine substances which can be added to the waste and can deactivate dioxin and furan formation. The preliminary results show that N-and S-compounds can be successfully used as preventive additives for PCDD/F formation. The pattern of 2,3,7,8-substanted compounds are of main interest to be decreased. Their effective reduction is about 98-99%; low cost and less toxic properties make them applicable for further experiments in pilot and full scale incineration plants.

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