Co-combustion of coal and waste in power plants poses both environmental and economic challenges, especially because of the high polychlorinated dibenzo-p-dioxin and furan (PCDD/F) emissions from solid waste. In this study, we performed a series of experiments focusing on the prevention of PCDD/F formation by the use of various inhibitors added to the fuel before combustion. A mixture of lignite coal, solid waste, and poly(vinyl chloride) (PVC) was thermally treated in a laboratory-scale furnace at 400 °C. Twenty different additives were investigated at a level of 10 wt % of the total fuel during the experiments. We have divided them into four general groups according to their chemical nature: metal oxides, N-containing compounds, S-containing compounds, and N- and S-containing compounds. The resulting values showed a significant reduction of PCDD/F levels when N- and S-containing compounds were used as additives to the fuel. Principle component analysis (PCA) was used to illustrate the effect of the 20 different inhibitors on the congenter patterns emitted. As a result, the most effective inhibitors for PCDD/F formation in flue gases were determined to be (NH₄)₂SO₄ and (NH₄)₂S₂O₃; they are inexpensive and nontoxic materials. Both compounds can suppress the formation of toxic compounds such as PCDD/Fs by more than 98–99%, and the most toxic PCDD/F congeners were not detectable in most of the samples. Thus, these compounds were also studied as a lower percentage of the fuel. (NH₄)₂SO₄ resulted in a greater than 90% reduction of PCDD/F even when composing only 3% of the fuel combusted. However, less than 5% (NH₄)₂S₂O₃ resulted in far weaker inhibition. The PCDD/F homologue distribution ratio for samples with varying percentages of (NH₄)₂SO₄ and (NH₄)₂S₂O₃ was also investigated. Higher percentages of the inhibitors produced a lower percentage of lower chlorinated PCDDs. The opposite effect was found for PCDFs.

Introduction
The increasing costs of municipal waste management and disposal options in recent years, combined with the desire of many developed countries to utilize organic waste material from landfill depots, has interested some power plants in using coal together with this waste for energy production. The technology of co-firing fossil fuel, biomass, and waste has been promising for many years. It could cause reduction in greenhouse gas emissions such as CO₂ and CO while improving waste quality and enabling the utilization of waste energy, thus preserving fossil fuel resources (1). Coal waste co-combustion is also especially attractive for countries that do not have waste incinerators.

However, 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 and furans (PCDD/Fs) are produced during waste incineration (2). According to a report released in 1994 by the United States Environmental Protection Agency (EPA), dioxin is a potential human carcinogen, and exposure to dioxin can cause immune system damage and interfere with regulatory hormones (3, 4). Over the past 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 equivalent (TEQ) value (5). Emission factors from power plants fueled with various kinds of coal have been applied. Measured stack emissions were far below 0.1 ng of international toxic equivalent per cubic meter (I-TEQ/ m³) for all plants in Germany (6). In 1989 and 1990, power plant dioxin emissions were determined to have an annual 5 g of I-TEQ value, whereas waste incinerators showed amounts of 400 g of I-TEQ.

PCDD/F emissions from flue gas can be controlled by so-called primary and/or secondary measures to comply with the limit of 0.1 ng/m³ TEQ. Primary measures include the adjustment of operation conditions (temperature, turbulence, airflow, and residence time) and the addition of selective compounds that can substantially inhibit the formation of PCDD/F (7, 8). The influence of parameters such as water, carbon monoxide, and carbon dioxide; amount of gas-phase chlorine; reaction temperature; and reaction time in the flue gas has been investigated (9). Overall, the most significant parameter in the formation window of the postcombustion zone for PCDD/Fs has been determined to be the reaction temperature; 300–400 °C maximizes the production of PCDDs, and 400–500 °C is optimal for PCDFs (9). Secondary measures stress the use of flue gas purifying systems, electrostatic precipitators (ESP), activated carbon adsorption, and fabric filters (10). The use of secondary measures allows toxicologically relevant residues to be produced and collected, but the disposal of this residue causes further environmental risks. The installation and maintenance of secondary measures is much more expensive than primary measures and is not economical for coal power plants.

In recent years, many additives such as NH₃, CaO, KOH, and Na₂CO₃ have been investigated for their effect on PCDD/F emission gas reduction during incineration (11, 12). These compounds are basic, and their mechanism can be explained by a change in the acidity of the fly ash (13), which can lead to loss of aromatic chlorine by base-catalyzed elimination. Other inhibitors have the ability to complex with or bind to special metal ions, which catalyze the PCDD/F formation. The experimental results suggest that the reaction of the Cu (II) compounds with SO₂ in the presence of oxygen to form CuSO₄ renders the catalyst less active and leads to decreasing PCDD formation. Inactivity is also due to the reduced ability of the Cu (II) and Cu (I) species to promote a second catalytic step of biaryl synthesis (14).
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 (15, 16). Urea and sodium ammonium hydrogen phosphate dissolved in a water–methanol phase have also been investigated as inhibitors of PCDD/F generation. These substances are injected into the flue gas stream and the cause reduction of PCDD/Fs in the particle-phase by up to 90% with sodium ammonium hydrogen phosphate and 70% with urea (17). Organic amines such as ethanolamine, triethanolamine, and monoethanolamine prevent the formation of PCDD/Fs from pentachlorophenol on fly ash (18–20).

Supported transition metal oxides and vanadium-containing multicomponent oxides were investigated for oxidative catalytic destruction of PCDD/Fs. Among the catalysts tested, the V–Mo–O/TiO2 catalysts have shown good activity for the oxidation of PCDD/Fs in flue gas emitted from municipal solid waste incineration (21). It has been shown that the 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 waste incineration plant (22). The catalytic oxidation of 1,2-dichlorobenzene has been investigated over a series of transition metal oxides (Cr2O3, V2O5, MoO3, Fe2O3, and Co3O4) supported on TiO2 and Al2O3 (23). The chromium oxide catalyst supported on TiO2 and Al2O3 is also examined in a fixed-bed flow reactor system. The prevention potential of these compounds of PCDD/Fs formation is more than 93–95% (24).

In this study, we used a laboratory-scale furnace to perform a series of experiments designed to prevent the formation of PCDD/Fs by the use of inhibitors. These inhibitors were chosen based on previously successful additives and other compounds. The aim of this work was to identify the most effective inhibitors of PCDD/F formation that were cost-effective and had low toxicity. Congener patterns of PCDD/Fs were analyzed by means of statistical methods.

**Experimental Procedures**

**Reagents.** The types of fuel used in this study are lignite coal from Puertollano (Spain) (25), pretreated municipal solid waste (Rethmann Plano GmbH) (26), and used poly(vinyl chloride) (PVC) (waste from ground carpet). The lignite coal was 80 wt% of the total fuel. Such a high amount of lignite coal was chosen because of the interest in coal combustion. The chlorinated compounds were 20 wt% of the fuel mixture with a 13.3:6.7 ratio of solid waste to PVC. The type and ratio of the fuel used in this study were similar to that currently used by coal power plants. Although the addition of solid waste to coal has been reported to be optimal for dioxin formation, the dioxin emissions concentration in the laboratory-scale furnace has been reported to be less than 1 mm. For the solid waste, the mixing procedure was performed after cooling the larger pieces in liquid nitrogen for 30 min. This procedure preserved the composition of the solid waste during homogenization.

The 20 different compounds (Table 1) investigated as inhibitors can be divided into four main groups according to their chemical nature and structure: (1) metal oxides: chromium (III) oxide (Cr2O3) (Merck); titanium (IV) oxide (TiO2) (Merck); sodium (meta) vanadate (NaVO3) (Fluka); zirconium (IV) oxide (ZrO2) (Merck); aluminum (III) oxide (Al2O3) (IGC-EcoChrom); sodium molybdate dihydrate (Na2MoO4 · 2H2O) (Fluka); and sodium tungstate dihydrate (Na2WO4 · 2H2O) (Fluka). (2) N-containing: di-ammonium hydrogensulfophosphate (NH4H2PO4) (Merck); triethanolamine ([CH2OHCH2OH]3N) (Merck); and hexamethyldiphosphoramide ([(CH3)2N]3P(O)) (Sigma-Aldrich Chemie). (3) S-containing: sulfur (S) (Sigma-Aldrich Chemie); phosphorus (V) sulfide (P2S5) (Merck); and sodium sulfide (Na2S · H2O) (Merck). (4) N- and S-containing: hydroxylamine-O-sulfonic acid (HNSO4H) (Merck); amidosulfonic acid (H2NSO3H) (Sigma-Aldrich Chemie); sulfamide (H2NSO2NH2) (Sigma-Aldrich Chemie); ammoniumthiosulfate ((NH4)2H2SO3) (Merck); urea + sulfur ((NH2)2CO + S) (1:1) (urea, techn.); and ammoniumsulfate ((NH4)2SO4) (Merck).

Pomace, a residue of olive oil (27), was also tested as an inhibitor of PCDD/F formation in such a fuel mixture.

**Apparatus.** A laboratory-scale horizontal split-tube furnace (Split Tube furnace (3-zone) type HZS and TVS, Carboline, England) (Figure 1) was used for the experiments. The laboratory reactor consisted of a quartz tube with i.d. = 14 cm and a length of 150 cm, 3/4 of the length of which was placed into the heating zone of the furnace. The dimensions of the sampling boat were 3.5 cm × 15 cm. The sampling boat was pushed from the cooled part of the quartz tube to the middle of the heated zone when the desired temperature was achieved.

The trace organics in the flue gases produced during the experiment were trapped into three impingers in series, each filled with 70 mL of toluene (Figure 1). The first impinger was previously spiked with 100 μL of CEN-sampling PCDD/F standard. Each experiment was performed according to the same procedure every time to achieve reproducible results. The furnace temperature was 400 °C, the air-flow was 2 L/min, the weight of the sample was 10 g, and the duration of the experiment was 30 min. After each experiment, the amount of fly ash residue was determined with a balance. The final residue was measured to be about 5 g or about 50% of the total sample. No further analyses of the fly ash were made after the experiment. The inlet of the air-flow and the outlet of the vacuum pump were controlled with standard rotameters (ROTA). There were no precooling steps of the air. In our experience, with the type of fuel used herein, combustion at higher temperatures such as 500 and 600 °C yields lower PCDD/F concentrations. Thus, higher temper-
Dioxin Measurement. Once the experiment of thermal treatment was completed, the sample was processed by further PCDD/F specific cleanup steps. The volume of the sample was reduced by evaporation and placed at the top of the first sandwich chromatography column, which had been spiked with a CEN—internal standard mixture of 13C-labeled PCDD/Fs. Organic interferences were eliminated by employing columns containing aluminum oxide and Florisil. The extract was finally evaporated to 25 mL by a gentle stream of nitrogen. The vial for this purpose had been previously spiked with 25 mL of CEN—recovery standard for PCDD/Fs. Quantification of PCDD/Fs was performed on a high-resolution gas chromatograph (60 m Rtx-2330 polar capillary column, Restek) coupled with a high-resolution mass spectrometer (MAT 95, R 10 000 Finnigan) (HRGC/HRMS). The tetra- to octachloro-congeners were identified and quantified in a pg/g combusted material.

Statistical Analysis. Kovach Computing Service, Statistical Package 3.11 g (30), was used for the principle component analysis (PCA). PCA was used to classify variables and elucidate relationships between them. The results of the PCA were visualized by a score plot. Samples with similar PCDD/F emissions were located close to each other in the score plot, while those that have divergent emission patterns were located further apart. A detailed description of the PCA method can be found elsewhere (31, 32). The analysis reflected the effect of the 20 different inhibitors on the congener patterns emitted. The current analysis was performed separately for PCDDs and PCDFs.

Results and Discussion

The total amounts of PCDDs and PCDFs 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 was about 15 pg/g fuel or about 2.5 ng/Nm3 (Figure 2). Such experiments were performed 5 times, and the results showed a relatively low standard deviation. The experimental results with 10% inhibitor showed very different I-TEQ values; some of the compounds led to similar and/or greater amounts of PCDD/Fs than the samples without inhibitor (Figure 2). Other additives showed a very strong inhibitory effect in the flue gases. Two compounds could reduce the PCDD/Fs emission up to 98–99%.

Principle Component Analysis. PCA was used to give a better view of the similarity between the samples using the concentrations of PCDD and PCDF congeners. The matrix for PCDDs consisted of 37 variables (PCDDs congeners) and 25 cases (samples), and the matrix of PCDFs is comprised of 63 variables (PCDFs congeners) and 25 cases (samples). No transformation of the data was performed during statistical analysis. The statistical score plot for the laboratory-scale experiments with 20 inhibitors is shown in Figure 3.

Two main groups of samples were observed in both score plots. The further left the sample is located in the statistical plot, the lower the concentration of PCDD/Fs is. The samples without inhibitor were found on the right side of the statistical plot in Figure 3. Neighboring these toxic samples were other points that could be attributed to the metal oxide inhibitors Cr2O3, TiO2, Al2O3, and pomace. However, they also belong to the samples with higher PCDD/F concentrations. Near to the ordinate axis and between both groups, N-, S-, and metal oxide inhibitors such as P5S9, N(CH2CH2OH)3, Na2WO4,2H2O, and ZrO2 were plotted. These four compounds were additives that manifested low inhibitory effects or samples with high variations in the PCDD/F amount. A group that was highly agglomerated, especially in the case of PCDF, is on the left-hand side. It included samples with 10% inhibitor concentration, where all inhibitors were N-and S-containing compounds, and others such as NaVO3, Na2MoO4,2H2O, (NH4)2HPO4, [(CH3)2N]3P(O), S, and Na2S-H2O. The points were very close to each other, which is explained by the similarity in

FIGURE 2. PCDD/F I-TEQ (pg/g) 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.

FIGURE 3. Score plot of PCDD and PCDF of five samples treated without any inhibitor and 20 samples with 10% inhibitor.
their pattern and the amount of PCDD/F formed. Here, the N-and S-containing compounds were placed much more to the left in the score plot. This effect correlated to Figure 2, where the same compounds showed a strong inhibitory effect for I-TEQ PCDD/F concentrations in the flue gas.

17 Toxic PCDD/F Congeners. It is generally accepted that only 17 out of the 210 dioxin and furan congeners are toxic (3). The toxicity rating of these congeners is reflected by their toxic equivalent factor, or TEF. The TEF of the most toxic congener, 2,3,7,8-TCDD, is defined as 1. Table 2 shows nine of the most effective inhibitors of PCDD/F formation and presents a comparison to the samples without inhibitor according to their mass concentration value (pg/g) for the 17 most toxic PCDD/F congeners. In Table 1, the limit of detection is listed for all samples.

Since 2,3,7,8-TCDD is the most toxic dioxin, the inhibition of the formation of it was critical. The inhibitors that resulted in concentrations below the detection limit for this congener were H2NSO3H, S, H2NSO2NH2, (NH4)2S2O3, (NH2)2CO + S (1:1), and (NH2)2SO4. These were also samples with low PCDD/F values. Almost all examples with inhibitor additives showed values below the detection limit for 1,2,3,7,8-PeCDF, 1,2,3,4,7,8-HxCDD, and 1,2,3,7,8,9-HxCDF. The HpCDD and OCDD concentrations were slightly higher as compared to the less chlorinated congeners for the nine most effective inhibitors. These congeners were attributed to a low TEF that contributed less to the final I-TEQ value.

The TEF value for 2,3,4,7,8-PeCDF, the most toxic congener among all PCDD congeners, is 0.5. The smallest detectable value of this congener was found using (NH2)2CO + S (1:1), (NH2)2SO4, and (NH2)2S2O4 as inhibitors. The latter two inhibitors showed concentrations below the detection limit or negligible amounts for all other PCDF congeners. (NH2)2CO + S (1:1) together with H2NSO3H and S also exhibited very low or undetectable concentrations of PCDF congeners. All samples had amounts below the detection limit for 1,2,3,7,8,9-HxCDF.

The average amounts of the 17 toxic congeners in the samples without inhibitor were much higher than in those with inhibitor. The abundance of the 2,3,7,8-TCDD and 2,3,4,7,8-PeCDF congeners made them sufficiently toxic for further inhibition experiments. According to Figure 2 and Table 2, (NH2)2SO4 and (NH2)2S2O4 were the best inhibitors of PCDD/F formation. Both compounds are inexpensive and nontoxic materials.

Experiments with Varying Amounts of Inhibitor. (NH2)2SO4 and (NH2)2S2O4 showed stronger inhibitory effects than the other substances and resulted in an approximately 50-fold reduction of PCDD/F I-TEQ values (Figure 2). The differences between the samples without any inhibitors and these substances were promising. Therefore, further experiments were performed in which these substances constituted a lower fraction of the fuel. Experiments wherein these inhibitors were studied at 5, 3, and 1% of the total fuel weight were performed in triplicate (Figure 4). In addition, the experiment without any inhibitor was repeated to obtain an actual value during that time of the investigation. The standard deviation of the pattern was calculated on the basis of six measurements. The average calculated concentration for PCDD/F I-TEQ was 16.4 pg/g with a maximum value of 30.6 pg/g and minimum value of 10.4 pg/g. The variation for PCDD/F I-TEQ was 16.4 pg/g with a maximum value of 30.6 pg/g and minimum value of 10.4 pg/g.
It became obvious that in the samples with (NH₄)₂SO₄ and lignite coal, solid waste, and PVC in laboratory scale experiments, samples with and without inhibitor during thermal treatment of (NH₄)₂S₂O₃ occurred in experiments with (NH₄)₂SO₄. The TCDF formation in the flue gases of lignite coal, solid waste, and PVC. This method was less sophisticated than others in which sulfur and nitrogen compounds such as (NH₄)₂SO₄ and (NH₄)₂S₂O₃ were the most efficient inhibitors. (NH₄)₂SO₄, (NH₄)₂S₂O₃ were the most efficient inhibitors. Some of the additives such as Cr₂O₃, Al₂O₃, and TiO₂ even increased the PCDD/F emissions by catalyzing the de novo formation. They produced very high amounts of the most toxic congeners and high amounts of other less chlorinated PCDD/Fs. Some other substances belonging to the metal oxides groups such as NaVO₃, Na₂MoO₄·2H₂O, and Na₂WO₄·2H₂O 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 V₂O₅, MoO₃, and WO₃. Probably due to that base, a better performance of incineration during the experiments occurred. Regardless, these additives did not reduce PCDD/F formation sufficiently.

Relatively low inhibitory effects were also observed for the N-containing substances. The samples of this group of additives were located between the two extremes of the score plot. The inhibition behavior of triethanolamine was investigated with FTIR analysis. Ethanolamine can undergo intermolecular dehydroamination reactions. Bromobenzene or the benzene precursors were displaced from the catalytically active sites, which were blocked by ethanolamine.

A greater reduction of PCDD/F formation could be obtained for the S-containing substances present at 10% of the fuel. Sulfur showed a very strong inhibition of PCDD formation. It is known that sulfur is converted into SO₂ and reduces Cl₂ to HCl, therefore, dioxin formation can be reduced (33). The rest of the S-containing compounds most likely inhibited PCDD/F formation in flue gases by this mechanism. Although the compounds containing either N or S were not very effective as inhibitors, those containing both N and S seemed to be able to strongly reduce PCDD/Fs flue gas emission if used as a 10% additive to a fuel containing lignite coal, solid waste, and PVC. The mechanism has been shown to be a complex interaction of the inhibitors with the catalytically active sites of the fly ash (18). In our study, we showed that sulfur and nitrogen compounds such as (NH₄)₂SO₄ and (NH₄)₂S₂O₃ were the most efficient inhibitors. (NH₄)₂SO₄ present at 3% of the fuel, could reduce the PCDD/F emissions by 90%. These compounds are inexpensive and nontoxic materials, making them applicable for use in full-scale combustion units.

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**Literature Cited**


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