

The effect of sulfur on the inhibition of PCDD/F formation during co-combustion of coal and solid waste

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Introduction

Co-combustion of solid wastes with coal is a promising technique used to reduce landfilled wastes, utilizing waste the energy content ¹. However, solid wastes often contain chlorine and other substances, which upon combustion may result in the production of extremely toxic compounds like polychlorinated dibenzo-p-dioxins and dibenzofurans ². These compounds are of great environmental interest, with significant human health effects ³. As a result their removal from flue gases has been the subject of extended research. It is known that these compounds are formed through heterogeneous reactions taking place in the downstream regions of chlorine-containing flue gases waste combustion processes (200±400°C) ⁴. Furthermore, it has been proved that metal ions in the ash, primarily copper, play an important role in the formation mechanisms acting as catalysts ^{5,6}. Several researchers developed various techniques for the minimization of PCDD/F emissions. These techniques include measures for controlling PCDD/F formation, such as: adjustment of the operation conditions (air flow, temperature, residence time), addition of certain compounds in the post combustion zone, inhibiting their formation ^{7,8}. The former approach is focused on the removal of PCDD/F from gases, using gas cleaning installation while the latter approach is characterized by high installation and operating costs, while the efficiency is greatly affected by the operation condition.

An alternative technique is the addition of certain compounds preventing the formation of PCDD/F. Various compounds have been proposed for their inhibition ability of PCDD/F formation, including sulphuric and nitrogen containing substances ^{9,10,11}. Sulfur compounds may form some kind of complexes with metal species, reducing thus their ability for catalysing the PCDD/F formation pathways ¹². Sulfur inhibitory capacity has been attributed to reaction with copper catalytic sites, altering their form and presumably their ability to produce Cl₂ through the Deacon process reaction ¹³. Another second postulated role of sulfur is to undergo homogeneous reactions, converting the primary chlorinating agent, Cl₂, into a form (HCl) less likely to undergo aromatic substitution reactions forming PCDD/F precursors ¹⁴.

The objectives of this work were the measurement of PCDD/F emissions during co-combustion of different fuel mixtures, and the study of the effect of sulfur addition to the fuel on PCDD/F formation.

Materials and Methods

The fuels used in this study were an artificial Refuse Derived Fuel (RDF), produced by mixing chemically pure compounds, and a mixture of coal and artificial RDF, in ratios coal/RDF 80/20. A South African Coal and a Low Volatile sample were used in the combustion tests. The composition of the artificial RDF, assimilating typical municipal solid wastes is shown in Table 1, while the proximate and ultimate analysis of the South African coal, is shown in Table 2. Fuel mixtures were prepared by stirring overnight, in order to improve the homogeneity of the sample. Pure sulfur was used as the inhibiting compound, in concentration of 10% w/w for all tests, while additional tests were made using single ARDF sample and sulfur in concentration 1 and 5% w/w.

Table 1. Composition of the Artificial RDF

A/a			Content, % w/w
1	Paper	Cellulose	28
2		Lignin	7
3	Plastics	Polyvinylchloride, PVC	1
4		Polyethylene, PE	7.5
5	Rubber	Tetramethylthiuram, TMTD	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		Glycin	25

Table 2. Proximate and Ultimate Analysis of South African Coal

Proximate Analysis	%
Moisture	1.3
Volatile Matter	37.6
Ash	13.1
Fixed Carbon	48.0
Ultimate Analysis	
Carbon	67.1
Hydrogen	4.2
Nitrogen	1.9
Sulphur	0.6

A laboratory scale horizontal reactor was used, in order to achieve easily repeatable combustion experiments. The flow diagram of the reaction system is shown in Figure 1. The reactor consisted of a quartz tube with 4.5 cm ID and 120 cm length, which was placed in a horizontal type tubular furnace. Solid particles were collected in a glass wool filter placed downstream the reactor, while three impingers containing a total of 250 mL toluene were connected to the experimental rig for trapping PCDD/F from the gas phase. Before each combustion test, ^{13}C -labeled internal PCDD/F standard was spiked into the toluene traps. At the end of each experiment the system was cleaned using a mixture of toluene, hexane and dichloromethane in order to avoid memory effects from the previous tests.

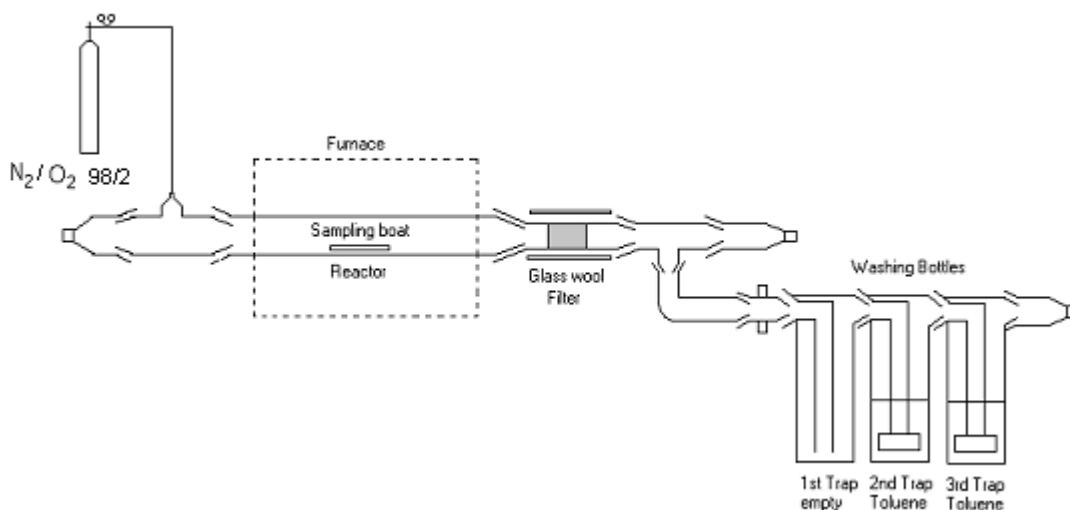


Figure 1. Flow diagram of the combustion unit

The procedure included preheating the furnace to 900°C and feeding 2L/min of a gas mixture containing 2% v/v O_2 in N_2 . At the set temperature, 3gr of fuel sample were introduced at the furnace, and combustion took place for 15 minutes.

At the end of each combustion run, the glass components were disconnected and the remaining ash was withdrawn from the quartz tube. The outlet part of the reactor and the quartz wool filter were Soxhlet extracted for 2h in toluene, while the glass wool of the filter was spiked with ^{13}C -labeled extraction standard and Soxhlet extracted for 24h with toluene. Clean up of samples was performed by a procedure involving application of the extracts in an alox column, an acidified silica column and a silica column¹⁵. The identification and quantification of PCDD/F was made using a HRGC/HRMS (MAT 95 Finnigan). Duplicate experiments were carried out for all tests in order to confirm the reproducibility of the results.

Results and Discussion

The composition of the fuel mixtures used for the co-combustion tests are shown in Table 3. The PCDD/F emissions measured during combustion of the fuel mixtures are shown in Figure 2. In all cases, PCDD/F were mainly extracted from the solid particles, which were collected at the outlet of the reactor and at the quartz wool filter. The average PCDD/F concentration during ARDF combustion was about 60 ng/kg. Co-combustion of South African Coal, and a Low Volatile coal with 20% ARDF, resulted in PCDD/F I-TEQ emissions of about 27 and 100 ng/kg respectively.

Table 3. Fuel Mixtures

	Fuel Mixture	Symbol	Concentration
1	ARDF	a	100
2	SAC_ARDF	b	80/20
3	LVC_ARDF	c	80/20
4	ARDF with S	d	90/10
5	SAC_ARDF with S	e	72/18/10
6	LVC_ARDF with S	f	72/18/10

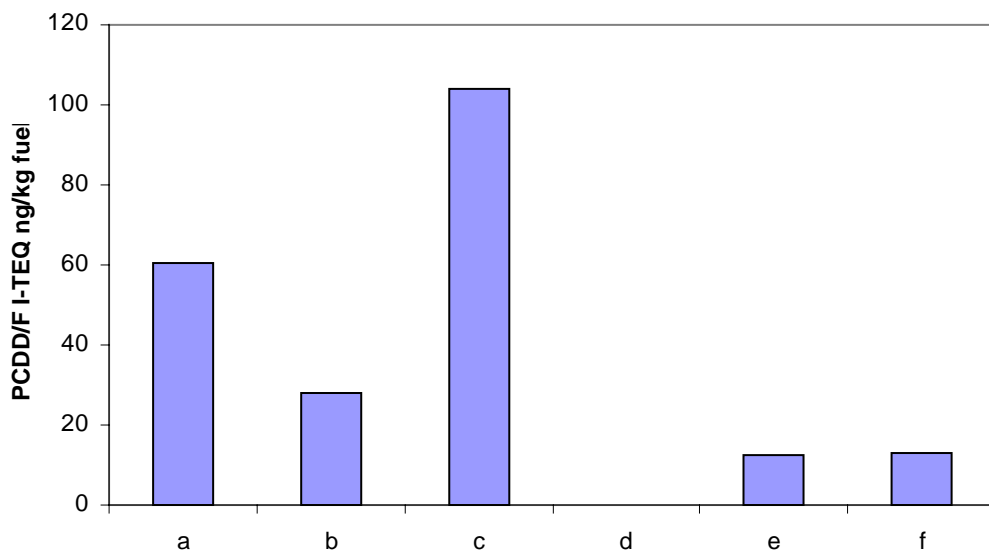


Figure 2. PCDD/F I-TEQ emissions during co-combustion of different fuel mixtures with and without Sulfur

The addition of 10% sulfur in the fuel before combustion resulted in almost 100% reduction of PCDD/F emissions. Additional tests were performed using lower sulfur content in the artificial RDF fuel, which resulted in considerable PCDD/F reduction. Sulfur resulted in 65% reduction of PCDD/F when it was added in amount of 1% w/w and by 85% when added in 5% w/w.

The PCDD/F I-TEQ value during combustion of the South African coal - ARDF mixture (80/20% w/w) was about 28 ng/kg fuel, while the addition of 10% of Sulfur resulted to a reduction of the emissions to an average of 13 pg/g. Similar reduction was observed during the addition of 10% sulfur to the Low Volatile Coal - ARDF mixture, and the emissions were decreased from 100 to 20 ng/kg fuel. As a result the addition of sulfur in the fuel before combustion, resulted in significant restriction of PCDD/F formation in all cases. Furthermore, addition of lower sulfur amounts in ARDF presented a considerable PCDD/F reduction reaching up to 85%.

The PCDD/F homologue patterns emitted during combustion of the three fuel mixtures with and without sulfur are shown in Figures 3 and 4, respectively. It seems that in case of furans, lower chlorinated homologues, especially the tetra-chlorinated ones, prevailed over the higher, while sulfur did not affect strongly the congeners distribution. However, congeners distribution presented a different pattern for PCDDs. Dioxin homologues presented similar concentration; penta- and hexa- being the higher ones the addition of sulfur, led to production of higher chlorinated homologues (Hepta- and Octa-dioxins). As a result, it seems that sulfur enhanced the chlorine substitution in existing structures.

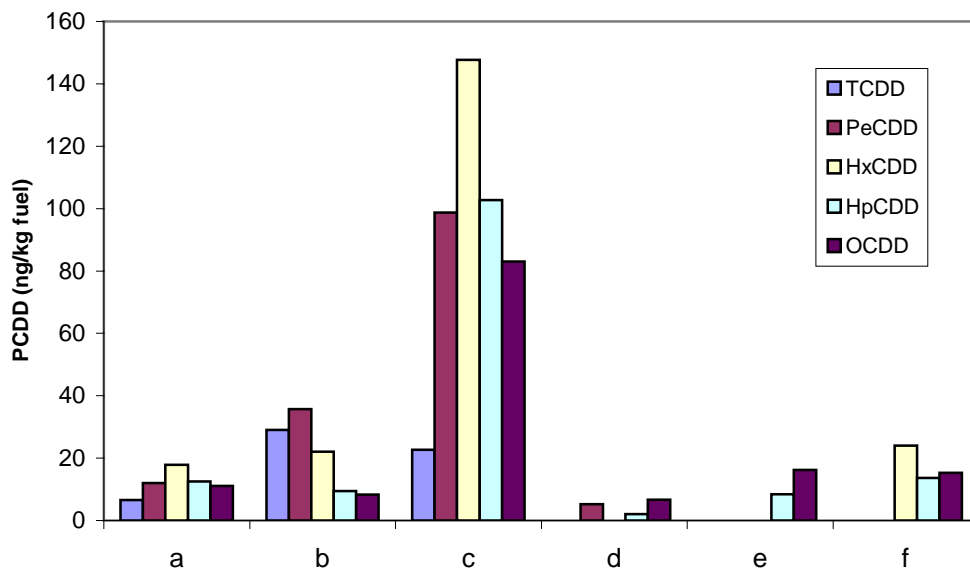


Figure 3. PCDD homologue pattern

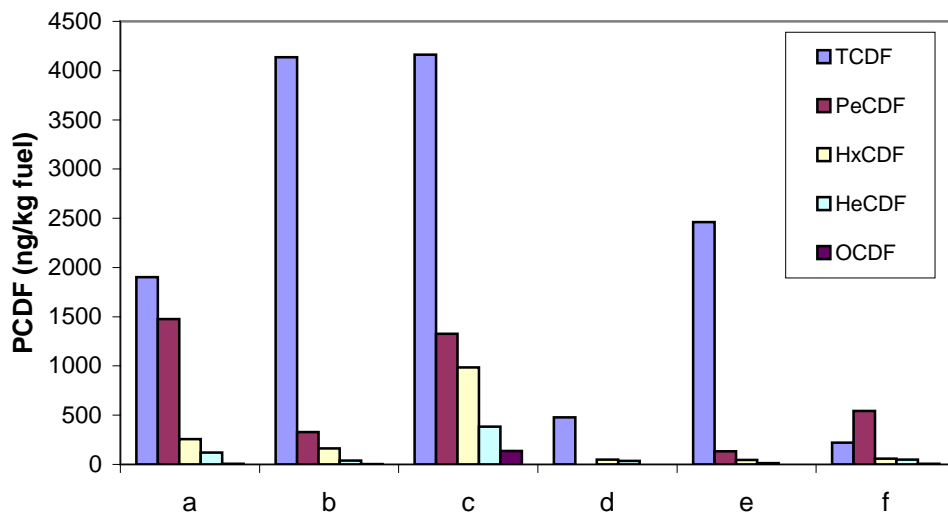


Figure 4. PCDF homologue pattern

The primary idea deduced from the current study is the addition of a low cost inhibitor in the fuel, prior to the combustion, in order to prevent PCDD/F emissions and to avoid the use of more complicated and expensive methods, where inhibitors are injected in the post combustion zone. The results showed that this technique might be effective, although additional work is required in order to examine the efficiency of sulfur compounds in full scale co-combustion units.

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