

## Recent studies of inhibition of PCDD/F formation in thermal processes

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### Introduction

The *de novo* synthesis is an important pathway for PCDD/F formation in thermal processes, which occurs in the post-combustion zone (between 200-400°C). Therefore, many studies have been focused on the effect of inhibitors of formation. Present work reviews recent studies related with the inhibition of PCDD/Fs during thermal processes.

### Discussion

It is well known that one of the most significant pathways of generation of PCDD/Fs is during post-combustion zone (between 200-400°C) from precursors or by *de novo* synthesis on the surface of fly ash particles. For this reason, some researchers suggested reducing the residence time in this temperature range by a rapid cooling of the flue gases<sup>1</sup>, although the rapid cooling in the post-combustion zone is difficult due to the high volume of flue gas in full-scale incinerations<sup>2</sup>. Consequently, recent studies have been focused on the effect of inhibitor addition. Some of these studies are shown in Table 1.

Since the post-combustion zone is the main critical point of the formation of PCDD/Fs, many researchers have been carried out experiments at the temperature range of post-combustion zone with model fly ash and inhibitors<sup>3-7</sup>. In addition, other researchers have been studied the effect of inhibitors on the combustion of biomass, waste, or a mixture of both<sup>8-16</sup>.

The most common additives for inhibition of PCDD/F formation in thermal processes are the N- and S-containing compounds, and alkaline sorbents.

In selective catalytic reduction (SCR) technology, NH<sub>3</sub> is injected into the post-combustion zone and NO is reduced into N<sub>2</sub>. Some studies have shown that it is also effective in the decomposition of PCDD/Fs<sup>17-20</sup>. For instance, a recent study showed high removal efficiencies of PCDD/Fs and NOx (97.2% and 90.3%, respectively)<sup>18</sup>, although, the inconvenient of this technology is its high cost.

NH<sub>3</sub> can also be injected into the high-temperature combustion zone, and simultaneous reduction of NOx and PCDD/Fs is observed<sup>8</sup>.

Some recent researches also studied the inhibitory effect of the gaseous SO<sub>2</sub> and the results obtained were also quite significant<sup>6,9</sup>.

Since the efficacy of gaseous SO<sub>2</sub> and NH<sub>3</sub>, some waste with high nitrogen and/or sulphur content could be a low cost inhibitor of PCDD/F formation. For example, some authors have studied the effect of the drying or decomposition gases of sewage sludge and promising results have been obtained<sup>3-4,10</sup>.

Other S- and/or N- containing compounds have been studied. The inhibitory effect of the sulphur seems to be due to the poisoning properties of sulphur to metal catalysts and also due to the fact that the heavy metals are converted into stable metal sulphides at low temperatures<sup>14</sup>.

Samaras et al. (2000)<sup>14</sup> studied five different compounds for their PCDD/F inhibition effect: an amide (urea) as representative of nitrogen containing compounds, three S- and N- containing compounds, such as amidosulphonic acid (ASA), hydroxylamine-O-sulphonic acid (HOSA), and sulphamide (SA), and pure sulphur (S8). The group of compounds combining sulphur and amine/ammonium suppressants were proved as the most effective ones.

The same conclusion is drawn in other works. Pandelova et al. (2005)<sup>11</sup> obtained the highest efficiencies with N- and S- containing inhibitor (reductions higher than 92%), being the efficiencies of N- containing inhibitors and S-containing inhibitors between 68-94% and 71-90%, respectively. Differences in inhibitory effect were also observed between ammonium sulphate and urea (reduction for TEQ of 98% and 77%, respectively)<sup>7</sup>.

Table 1 shows a scheme of the main contributions.

**Table 1:** Recent studies of inhibition of PCDD/F formation in thermal processes.

Experimental description	Pollutants studied	Inhibitors studied	% of suppression of pollutant compounds	Ref.
Pilot-scale incinerator of municipal solid waste with a NH <sub>3</sub> -SCR reactor.	PCDD/Fs and NO <sub>x</sub>	NH <sub>3</sub>	The highest reductions were found at 300 °C (97.2% for PCDD/Fs and 90.3% for NO <sub>x</sub> )	18
Hazardous waste incinerator recirculating SO <sub>2</sub>	PCDD/Fs	SO <sub>2</sub> gas and pyrite	PCDD/F emission reduction of more than 90%	9
A laboratory scale fixed-bed reactor to study the influence of the injection of gaseous NH <sub>3</sub> (1000 ppm) or SO <sub>2</sub> (2000 ppm) on the PCDD/F formation on MWI flyash at the temperature of the post combustion zone.	PCDD/Fs	Gaseous NH <sub>3</sub> and SO <sub>2</sub>	NH <sub>3</sub> reduced the total I-TEQ of PCDD and PCDF by 42-75% and 24-57%, respectively. SO <sub>2</sub> reduced the total I-TEQ of PCDD and PCDF by 60-86% and 72-82%, respectively.	6
A lab-scale furnace where the sludge drying gases (SDG) pass through the model fly ash	PCDD/Fs	Sludge drying gases (SDG) that contains NH <sub>3</sub> , SO <sub>2</sub> and other N- and S-compounds.	Up to 97.6% of suppression of PCDD/Fs	3
A lab-scale furnace where the sludge drying gases (SDG) pass through the model fly ash	PCDD/Fs and HxCBz	Sludge drying gases (SDG) that contains NH <sub>3</sub> , SO <sub>2</sub> and other N- and S-compounds.	The reduction of HxCBz and PCDD/Fs was 92.1% and 78.7%, respectively, when the drying gas evolving from 2 g sludge flew through 2 g fly ash.	4
Pilot-scale experimental system in a 50-tonne/day hazardous waste rotary kiln incinerator	PCDD/Fs	Thiourea and sewage sludge decomposition gases	More than 80% of reduction.	10
A mixture of lignite coal, solid waste, and PVC in a laboratory-scale furnace at 400 °C	PCDD/Fs	<b>N-containing:</b> (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> ; N(CH <sub>2</sub> CH <sub>2</sub> OH) <sub>3</sub> ; and [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> P(O)	N(CH <sub>2</sub> CH <sub>2</sub> OH) <sub>3</sub> : 68.7 % ; [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> P(O): 81.4% ; (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> : 93.9% (% reduction for TEQ)	11
		<b>S-containing:</b> sulphur; phosphorus (V) sulphide; and sodium sulphide	Sulphur: 89.5 %; phosphorus (V) sulphide: 70.6%; sodium sulphide: 83.9 % (% reduction for TEQ)	
		<b>N- and S-containing:</b> H <sub>2</sub> NSO <sub>4</sub> H; H <sub>2</sub> NSO <sub>3</sub> H; sulfamide (H <sub>2</sub> NSO <sub>2</sub> NH <sub>2</sub> ); ammoniumthiosulfate ((NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ); urea + sulphur (1:1); and ammoniumsulfate	H <sub>2</sub> NSO <sub>4</sub> H: 93.1 %; H <sub>2</sub> NSO <sub>3</sub> H: 93.0 %; sulfamide: 92.0%; ammoniumthiosulfate: 98.6%; urea + sulphur (1:1): 97.8%; ammoniumsulfate: 97.9%	

Experimental description	Pollutants studied	Inhibitors studied	% of suppression of pollutant compounds	Ref.
		Pomace (olive oil residue)	21.9 % for TEQ	
Combustion of Refuse Derived Fuel with some inhibitor compounds in a laboratory scale horizontal reactor	PCDD/Fs	Urea; amidosulphonic acid; hydroxylamine-O-sulphonic acid; sulphamide and pure sulphur	A slight decrease of the PCDD/F emissions (28%) with urea. The addition of N- and S-containing compounds resulted in significant reduction of total PCDD/F concentration (higher than 98%).	14
Co-combustion of biomass with waste products from pulp and paper industry in a full-scale circulating fluidized-bed (CFB) boiler equipped with the ChlorOut technique	PCDD/Fs and PCBs	Ammonium sulphate	70 % reduction of the PCDD/F concentrations and 35% reduction of PCB concentrations.	13
Study of suppression of PCDD/F formation in the post-combustion zone of lab-scale reactor with a model-ash.	PCDD/Fs	Ammonium sulphate and urea	Ammonium sulphate: 98.0 % for TEQ. Urea: 77.2 % for TEQ	7
Inhibitors were added to the model fly ash in a laboratory scale system	PCDD/Fs	Ammonium thiosulphate, aminosulphonic acid, and thiourea	Between 87.4% and 99.8% for I-TEQ, where thiourea is the best inhibitor	5
Combustion of wood, hospital waste and ammonium sulphate in a domestic grid-stove	PCDD/Fs and PCBs	Ammonium sulphate	Reduction for PCDD/F and PCB emissions were determined between 50 - 66 %	15
Municipal solid waste incineration in a full-scale circulating fluidized bed (CFB)	PCDD/Fs and NOx	Thiourea	91.0% (81.8% for TEQ)	8
Combustion of modeled municipal solid waste in a laboratory scale tubular furnace	PCDD/Fs	Raw meal of a cement production process	The highest reduction (96% for PCDD/Fs) was achieved for a ratio of MSW to raw meal of 1:15	16
Combustion in tubular furnace of biomass pellets with limestone added with a molar ratio of Ca/S at 2, and with a 30 wt.% of coal tar residue (CTR)	NO, SO <sub>2</sub> , PAHs and PCDD/Fs	Limestone	Little effect on NO emissions. SO <sub>2</sub> emission: 55.6%-71%; PAH: 13.3%; and PCDD/F: 59.9%	12

Moreover, other inorganic additives have also been studied, such as alkaline sorbents, for instance: CaO, CaCO<sub>3</sub>, Ca(OH)<sub>2</sub>, CaSO<sub>4</sub>, KOH, NaHCO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, MgO, Mg(OH)<sub>2</sub>, MgSO<sub>4</sub> and so on<sup>12, 16, 21-22</sup>. These sorbents are used to control of acidic gas emissions (HCl, HBr, HF, etc) from combustion, and consequently PCDD/F formation is reduced in combustion processes.

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