

## Effect of urea on PCDD/F formation during combustion of coal and olive kernels in a pilot scale boiler

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### Introduction

Solid fuel combustion is a major source of Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) that are highly toxic compounds even in trace amounts. In addition, the complex conditions of the flue gases could favor, in some cases, PCDD/F formation. Thus, the presence of chlorine and metal catalysts (i.e. copper) in the flue gases, could lead, through heterogeneous reactions, to PCDD/F formation between 250 – 400°C. Three major theories have been established to elucidate the formation of PCDD/Fs in combustion systems: (i) PCDD/Fs are already present in the incoming feed and are incompletely destroyed or transformed during combustion (ii) PCDD/Fs can be formed during combustion and (iii) PCDD/Fs can be formed by de novo mechanism that is in the low-temperature post-combustion zone of incinerators through some heterogeneous catalytic reactions that occur in the flue gas-fly ash environment <sup>1,2,3</sup>. Post-combustion and pre-combustion techniques have been elaborated to minimize the PCDD/F emissions. Post combustion techniques utilize gas-cleaning devices to capture or destroy them after formation, while certain compounds could be added in the raw, prior the combustion zone, to inhibit PCDD/Fs formation <sup>4,5,6</sup> (pre-combustion measures). In his work the PCDD/F emissions during the combustion of lignite, olive kernel and blends were measured and the efficiency of urea to act as potential inhibitor in PCDD/F formation was investigated also.

### Materials and methods

Tests were performed in a commercial hot water boiler of 756 kW<sub>th</sub> (Figure 1) equipped with an automatic solid fuel burner. The combustion is controlled automatically by reducing or increasing the amount of air entering the chamber via a fan. The solid fuel is entering the burner by means of a screw-type feeder. Primary air is distributed through a duct around the fuel, while secondary air is fed just above the fuel supply. The raw gases passed through a cluster of tubes, surrounded from the cooling water, before entering the duct. A multi cyclone is used for flue gas dedusting. The combustion gases are removed by means of natural convection through an 8m high chimney. Samples for PCDD/F measurements were collected from the duct, isokinetically using the cooled probe method, according to VDI guideline 3499 (VDI, 1990). Analysis and quantification of PCDD/F were performed in the

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extracts by using a mixed silica column, an alumina column and a florisil column <sup>7</sup>. PCDD/F measurements were performed in a HRGC/HRMS system (HP5890/MAT 95 Finnigan). Greek lignite from Ptolemais reserve and olive kernels, a by-product olive treatment industry were used as raw fuels, while urea, a non-toxic, inexpensive and easy to handle compound, was used as potential additive <sup>9,10</sup>. Proximate, ultimate, ash analyses, as well as heavy metals content of the selected fuels are given in Table 1. Fuel ash contains compounds like copper that may catalyze the mechanism of PCDD/F formation, and it could be considered that fuel blends with large amounts of these elements, have higher potential for increased PCDD/F emissions <sup>11</sup>. Furthermore, although not generally accepted <sup>12</sup>, the chlorine content of the raw fuel is considered important for the formation of PCDD/F, particularly when it exceeds 1%. Aiming to increase the PCDD/F emissions, and, thus to obtain more reliable results and clearer evidence of the potential effect of additives, a standard portion of 3% PVC was added, as chlorine source, in all fuels and blends.

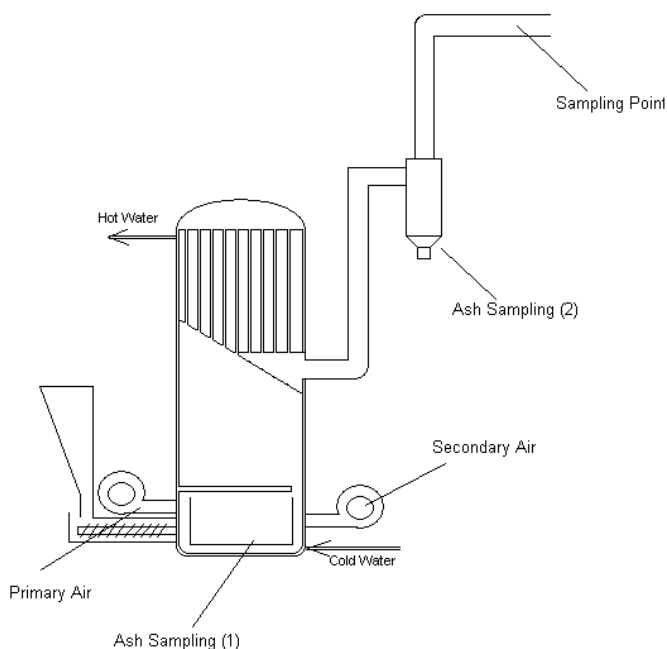


Figure 1. Flow diagram of the hot water boiler

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Table 1. Proximate, ultimate, ash and metal analysis of the raw fuels

Ultimate & Proximate Analysis			Ash chemical analysis			Metals in the ash		
Element (%w/w)	Lignite	Olive kernels	Element (%wt)	Lignite	Olive Kernels	Element (ppm)	Lignite	Olive Kernels
C	53.93	48.79	CaO	30.80	19.18	Zn	210±20	220±10
N	4.38	1.43	Al <sub>2</sub> O <sub>3</sub>	10.77	3.02	Cu	45±5	210±10
H	4.36	6.28	Fe <sub>2</sub> O <sub>3</sub>	6.44	3.58	Co	30±2	22±2
S	0.00	0.00	MgO	4.81	5.15	Cd	<10	<10
O	19.94	36.78	Na <sub>2</sub> O	0.36	0.64	Ni	490±20	525±30
Net HV (Kcal/Kg)	5699	5839	TiO <sub>2</sub>	0.36	0.17	Cr	400±30	597±40
Volatiles	44.80	71.66	Mn <sub>3</sub> O <sub>4</sub>	0.03	0.08	V	175±10	40±3
Fixed carbon	37.81	21.61	Rest(diff)	46.22	68.18	Ag	<75	<75
Combustibles	82.61	93.28				As	<75	<75
Ash	17.38	6.72				Pb	<75	<75
Cl (ppm db)	129	1059				Sn	<75	<75

### Results and Discussion

The fuel test matrix employed in this work for the measurement of PCDD/F emissions and the evaluation of the efficiency of urea and the corresponding total concentration and TEQ values of PCDD/F emitted during combustion tests are given in table 2.

Table 2. Fuel blends in co-combustion tests and corresponding emissions

Fuel / Blend	Fuel Code	Content (%w/w)	PCDD/F total conc. (ng/Nm <sup>3</sup> )	PCDD/F TEQ NATO (ng/Nm <sup>3</sup> )
Lignite	(a)	100	4	0.1
Lignite/PVC	(b)	97/3	65	0.9
Lignite /Urea/PVC	(c)	87.3/10/2.7	21	0.2
Lignite/Olive kernels/PVC	(d)	78/19/3	113	3.8
Lignite/Olive kernels/Urea/PVC	(e)	70.2/17.1/10/2.7	107	3.6
Olive kernels	(f)	100	28	0.4
Olive kernels/PVC	(g)	97/3	3716	74.7
Olive kernels/Urea/PVC	(h)	87.3/10/2.7	741	12.9

Operating conditions of the boiler varied in each co-combustion experiment. The feeding rate and the amount of the air supply depended on the heating value of the corresponding fuel mixture. Based on the fact that PCDD/Fs are mostly formed on the surface of the unburned carbon, efforts were taken to succeed conditions of incomplete burn in the boiler. The samples were collected after achieving steady state conditions in the chamber.

The PCDD/F emissions during combustion of lignite, olive kernels, and the co-combustion of them in portion 80/20 w/w, as well as with the corresponding emissions when a portion of 10% urea was added to the raw fuel, are shown in Figure 2. Comparing the PCDD/F emissions during combustion of the raw fuels with 3% PVC without adding urea, we can see that combustion of Olive kernels resulted in emissions up to 75 ng/Nm<sup>3</sup> almost two orders of magnitude higher than emissions during combustion of Lignite. This is probably because Olive kernels contain much more Copper, compound that acts as a catalyst in the PCDD/F formation mechanism. It seems that urea gave a considerable reduction in PCDD/F emissions, in all cases, although this effect is not stable. In the case of lignite and olive kernel co-combustion, the reduction was 6%, while much higher decrease was observed when urea was added to a Lignite/PVC (97/3) mixture (68%) and an Olive kernel/PVC (97/3) mixture (81%).

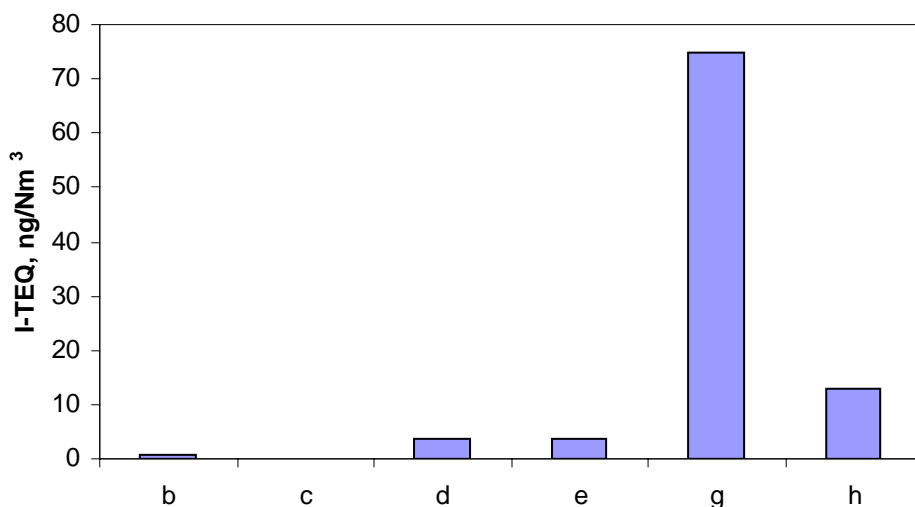


Figure 2. I-TEQ values of all fuel mixtures

The influence of PVC addition in the raw fuels is shown in Figures 3 and 4. It is clear that the addition of 3% of PVC leads to about 50 times higher PCDD/F emissions

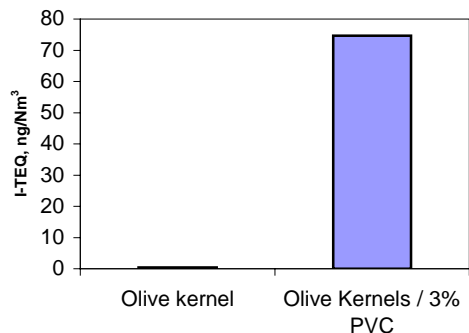


Figure 3. I-TEQ values for the lignite fuel, with and without PVC

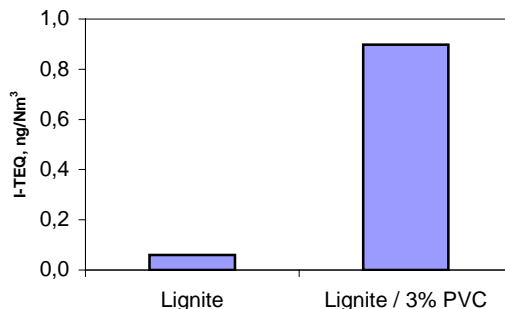


Figure 4. I-TEQ values for the olive kernel fuel, with and without PVC

As it is shown from the homologue pattern distributions of PCDD and PCDF for all the combustion experiments (Figures 5 and 6) the homologues allocation differs between dioxins and furans. These distribution profiles are similar to typical profiles from the combustion of municipal solid wastes<sup>13</sup>. Dioxins presented a more equal contribution between the homologues, with penta- and hexa-chlorinated being the higher ones. In the case of furans the lower chlorinated homologues prevailed over the higher ones. The addition of urea did not affect the homologue pattern indicating that the primary mechanism of dioxin and furan formation remained similar in all runs.

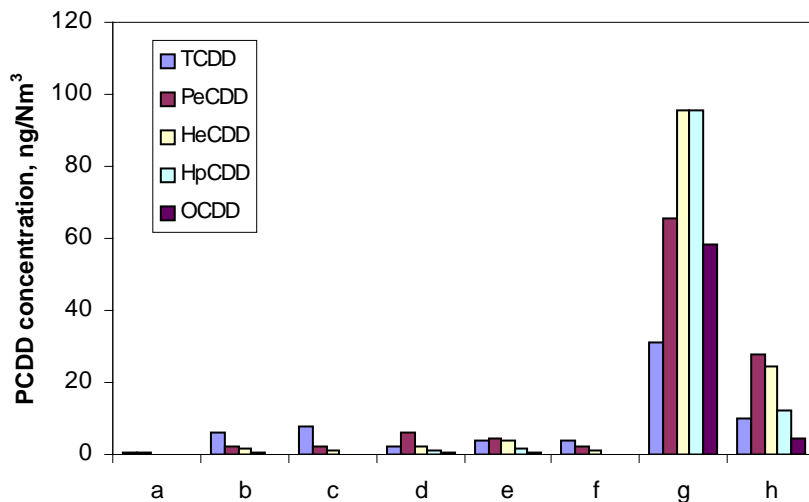


Figure 5. PCDD homologue pattern

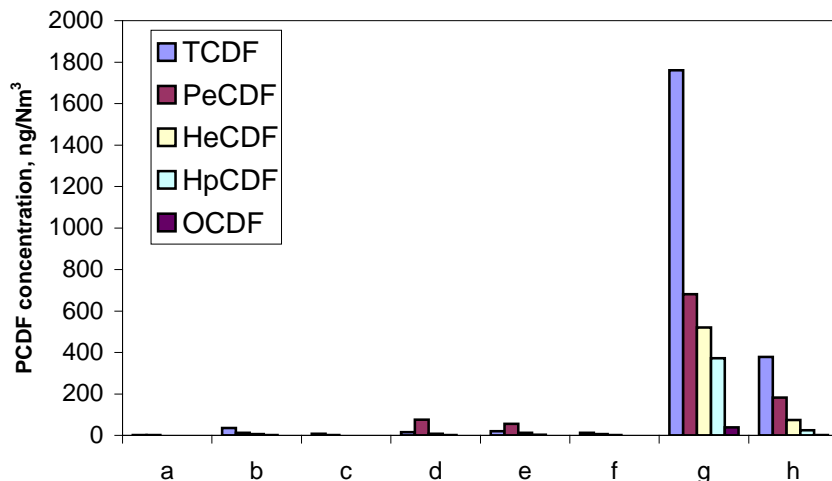


Figure 6. PCDF homologue pattern

The aim of this study was to measure the PCDD/F emissions at flue gases during combustion of certain raw fuels in a pilot scale boiler, and see the effect that urea has on these emissions, when it is added before the combustion in the fuel. The results showed a reduction of toxic emissions, although this behavior was unstable. Further testing of urea in different fuels is required, in order to study more in detail its inhibition ability, and substitutionally other potential inhibitors have to be examined.

#### Acknowledgement

Authors wish to thank European Union for the financial support of this work (contract No ECSC 7220-PR/108) and Institute of Ecological Chemistry at the GSF Research centre in Munich, for performing the analysis of the samples in HRGC/HRMS.

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