PCDD/F formation in the co-combustion with biomass and coal: the influence of chlorine, copper, calcium and sulphur

Ana Teresa Crujeira[(1)], Luís Moreira[(2,3)], Isabel Cabrita [(1,2)] & Ibrahim Gulyurtlu[(1)]

[(1)] *Laboratório Nacional de Energia e Geologia - LNEG, Estrada do Paço do Lumiar, n.º22, 1649-038 Lisboa.*
Tel:+351 210924600 E-mail: teresa.crujeira@lneg.pt
[(2)] *Instituto Superior de Educação e Ciências - ISEC, Alameda das Linhas de Torres, n.º179, 1750-142 Lisboa.*
[(3)] *Centro de Química e Bioquímica, CQB/DQB, Faculdade de Ciências, Universidade de Lisboa, Ed. C8, Campo Grande, 1749-016 Lisboa.*

1. Introduction - The reduction of CO_2 emissions is the primary goal of partially replacing coal with Renewable Energy Sources (RES) of biomass origin, accompanied with the reduction of emissions of other pollutants. At the same time, there are advantages in mixing this particular resource - solid biomass - with coal, due to positive synergies arising from the introduction of different amounts of volatile matter, ash, sulphur, calcium, chlorine, and heavy metals. The option for the co-combustion with biomass with coal using fluidised bed technology could contribute to the fulfilment of the EU objectives in terms of environmental protection and sustainable energy production.

Dioxins and furans are the general term used for a group of chemical compounds consisting of 75 polychlorinated dibenzo-*p*-dioxins (PCDD) and 135 polychlorinated dibenzofurans (PCDF), respectively. These compounds are structurally very similar, differing in the number and position of chlorine atoms (Figure 1), following international nomenclature. From these 210 compounds there are seventeen - 7 PCDD and 10 PCDF - which are recognized as persistent, toxic and bio-accumulative compounds, and classified as persistent organic pollutants (POP). Although their formation occurs in lower amounts, their toxicity for human health is much greater and serious; in fact, 2,3,7,8-TCDD is the most toxic known compound.

Dioxins and Furans may occur naturally in the environment, although the combustion of organic matter in the presence of chlorine and metals is widely recognized as a major source of dioxins to the environment. The most commonly accepted mechanisms for PCDD/F formation are [1]:

a) through various organic precursors, which may be formed in the gas phase during incomplete combustion and combine heterogeneously and catalytically with the fly ash surface, and; b) *de novo* synthesis from macromolecular carbon and the organic or inorganic chlorine present in the fly ashes. Both mechanisms are promoted by several catalysts, being the copper catalysts the most important.

Figure 1. Basic structure of (a) dibenzo-para-dioxin; (b) dibenzofuran.

Chlorine is an intermediate in the formation of chlorinated dioxin and furan compounds. It is recognized that the PCDD/F formation is related with the presence of Cl_2 instead of HCl [2]. If HCl is present, it can be converted to Cl_2 through the Deacon reaction. On the other hand, the Cl_2 content in the gaseous emissions is dependent on the simultaneous presence of sulphur and calcium. In fact, since sulphur is captured by calcium for molar ratios higher than 2.5 [3], the presence of calcium decreases the availability of sulphur in the gaseous phase, which drives the equilibrium to the formation of Cl_2, thus increasing PCDD/F formation.

The volatility of heavy metals is found to increase in the presence of chlorine by forming easily volatilized metal chlorides [4,5]. In the case of copper, its concentration in the fly ashes is enhanced in the presence of chlorine, thus increasing the PCDD/F formation.

Although, the emissions of some pollutants such as PCDD and PCDF could be considerable when fuels with high chlorine content are used, particularly in fluidized beds due to temperatures constraints, the partial substitution of coal with fuels of lower chlorine or other elements eventually contributing to reactions of pollutant formation may bring about positive synergies in decreasing pollutants like PCDD/F. The objective of this paper is to quantify a possible relation between chlorine, copper, calcium and sulphur contents in the feed material and the total emissions of PCDD/F.
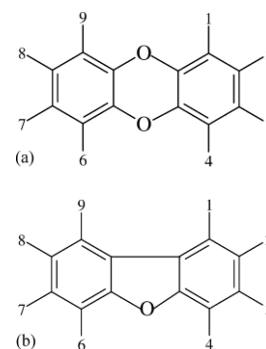
2. Experimental - The combustion studies were carried out in a pilot Fluidized Bed Combustor (FBC) of 75-100 kW$_{th}$. The fuels used were two different coals (CC-Colombian Coal and PC-Polish Coal), one type of waste material (MBM - Meat and Bone Meal) and two types of biomass, straw used in the form of pellets (SP) and rice husk (RH). The coals were selected in order to present the pretended contents of sulphur and chlorine when mixed with RES of biomass origin; the RES of biomass origin selected presented high levels of volatile matter, reaching more than 60% (wet basis) in the case of straw and rice husk. An extensive characterization of these fuels was carried out and the results are shown in Table I.

In terms of chlorine, Polish coal, straw pellets and MBM present similar contents. The Colombian coal contains 25% of that chlorine content whereas RH contains only 12.5%.

Sulphur present in the fuels range from 0.06% in the rice husk to 15 times higher in the case of the polish coal. However, it is more relevant to compare the S/Cl molar ratios of the fuels: the cerejon coal has the highest ratio whereas the straw presents the lower nS/nCl. As a consequence, higher levels of

Table I. Fuels Characterization

	SP	PC	CC	MBM	RH
Proximate Analysis (w.b., %)					
Moisture	9.1	4.7	9.3	3.2	9.2
Ash	6.3	10.5	11.4	37.3	13.4
Volatile Matter	68.5	31.5	33.6	54.1	62.4
Fixed Carbon	16.2	53.3	45.7	5.4	14.9
LHV (d.b., MJ/kg)	16.5	29.3	28.0	14.5	15.5
Elemental Analysis (d.b., %)					
C	41.7	69.5	66.4	32.2	38.1
H	6.2	5.0	4.7	5.0	5.8
N	0.7	1.3	1.4	8.2	0.4
S	0.13	0.5	0.95	0.4	0.06
Cl	0.24	0.26	0.07	0.28	0.03
Ca	0.30	0.45	0.23	13.4	0.09
Molar ratios (mol/mol)					
Ratio S/Cl	0.6	2.2	16.0	1.7	2.2
Ratio Ca/S	1.8	1.1	0.2	24.6	1.1
Ratio Ca/(S+Cl)	0.6	0.8	0.2	15.4	0.8
Heavy Metals (d.b.), mg/kg					
As	<10	<10	<10	<10	<10
Cd	<0.5	<0.5	<0.5	<5	<1
Cr	5.2	29.8	13.8	<10	<1
Cu	2.9	11.2	7.9	4.1	3
Hg	0.018	0.110	0.048	0.025	0.002
Mn	19.3	108	47.1	<10	101
Ni	4.5	30.9	8.5	<10	<1
Pb	<1.0	12.0	<1.0	<10	<1
Zn	6.5	27.2	25.5	97.5	16

PCDD/F are expected for the Straw test than for the Cerejon Coal test, although depending on the level of the calcium present. This is the case of MBM, where the Ca/S molar ratio is 24.6; for the other fuels the Ca/S ratios are lower than 2.5. Thus, it is expected that in these cases, calcium will not be effective in retaining the sulphur present in the combustion gases and may act as an inhibitor for PCDD/F formation.

Regarding the presence of the copper in the tested fuels, the Polish Coal has the higher content, being simultaneously the fuel with higher chlorine content. In this case, it is expected an extended volatilization of the copper due to the presence of chlorine, thus leading to higher PCDD/F formation.

Test runs included the mono-combustion of each fuel and the co-combustion of a mixture where 15% (w/w) of the coal was replaced by the same percentage of MBM or Straw. The operational conditions are presented in Table II. The combustion temperature was maintained at about 800-850ºC and the residence time of over 2 seconds was respected. In the co-combustion runs excess air level was maintained around 33 and 40%.

Table II. Operational conditions.

Fuel composition	RES fuels			Mixtures			Coals	
	100% MBM	100% SP	100% RH	15%MBM 85%CC	15%SP 85%CC	15%SP 85%PC	100% CC	100% PC
Feed rate (kg/h)	15.2	16.1	20.4	10.4	13.1	10.1	9.8	10.0
Energy Input (MJ/h)	212	238	288	244	310	260	246	277
Bed height (m)	0.20	0.16	0.50	0.18	0.50	0.18	0.16	0.17
Bed temperature (ºC)	759	688	819	774	823	830	836	816
Bed gas velocity@T$_{bed\_average}$ (m/s)	0.8	0.8	0.8	0.7	0.9	1.0	1.0	1.1
Freeboard velocity@T$_{freeboard\_average}$ (m/s)	1.5	1.5	1.3	1.2	1.1	1.2	1.1	1.3
Excess air (%)	83	41	40	43	45	31	39	36
Secondary air (%)	46	35	30	46	25	21	19	18

The combustion studies were carried out in two pilot installations of INETI - National Institute of Engineering, Technology and Innovation (restructured to LNEG – National Laboratory of Energy and

Geology). The smaller size installation has a nominal capacity of $70kW_{th}$; the larger installation has a nominal capacity of $100kW_{th}$.

Both installations have square cross sections and the combustor body were made of refractory steel and were externally insulated. Air staging was done in both installations between the bed and the freeboard to deal with high volatile fuels. Ashes are separated from the flue gases through two cyclones installed in series. The gases leaving the second cyclone are conducted to the stack where isokinetic sampling of the gases are performed. A detailed description of the installations is given elsewhere [6,7].

Dioxins and furans in the stack gases were sampled for 6 hours under isokinetic conditions in accordance with the European Standard EN 1948 - Parts 1,2,3. The method used was the filter/condensation system; XAD-2 resin is used, spiked with ^{13}C PCDD/F. The samples analyses were made by high resolution gas chromatography/ high resolution mass spectrometry (HRGC/HRMS).

3. Results and Discussion – The combustion efficiency for SP, MBM and RH monocombustion tests were found to be higher than 99.4%. For the coal tests significantly lower efficiencies were found 93.3% for Polish coal and 92.8% for Colombian coal; the co-combustion tests presented medium values, which are adequate for FBC systems. Another advantage of replacing coal with RES of biomass origin is the higher freeboard temperature, higher than the bed temperature, which could be due to the fact that the extent of volatile combustion was greater in the freeboard, as previously discussed by Gulyurtlu et al. [8]. The total emissions of PCDD/F in the different streams, i.e. 1st Cyclone, 2nd Cyclone and stack gas, were correlated with different parameters/descriptors. The sum of the toxic PCDF and PCDD will hereafter be referred as D+F. Table III presents the molar fractions of total formed PCDD/F (y_{D+F}) and the molar fraction of the selected elements (x_i), in terms of the total fuel moles.

To establish a possible relationship between the molar fraction of the formed PCDD/F (y_{D+F}) and the molar fraction of the several analyzed elements (x_i), we performed standard multiple linear regressions (MLR), using the Data Analysis add-in, available in Microsoft Excel and a statistical validation test to ensure the reliability of the model. Since the y_D quantities ranged over three orders of magnitude, the regressions are performed on a log-log basis.

Table III. Molar fractions of selected parameters.

Test runs	y_{D+F} (10^{15} mol/mol)	x_{Cu} (10^6 mol/mol)	x_{Ca} (10^3 mol/mol)	x_S (10^3 mol/mol)	x_{Cl} (10^3 mol/mol)
100%RH	**66120**	**0.61**	**0.24**	**0.21**	**0.10**
100%CC	**108**	**1.24**	**0.57**	**2.97**	**0.19**
15%MBM/85%CC	**73**	**1.20**	**6.00**	**2.83**	**0.30**
100%MBM	**1474**	**0.88**	**45.20**	**1.84**	**1.10**
100%PC	**3298**	**1.84**	**1.17**	**1.69**	**0.77**
15%SP/85%PC	**3016**	**1.62**	**1.10**	**1.50**	**0.76**
100%SP	**22938**	**0.44**	**0.73**	**0.41**	**0.72**
15%SP/85%CC	7465	1.12	0.60	2.57	0.27

Our first procedure was to test all four uniparametric regressions possible to compute with each descriptor ($\log y_{D+F} = a_0 + a_1 \log x_i$). The attained results were quite modest, with calculated regression coefficients (r^2) of 0.20 (Ca), 0.28 (Cu), <0.01 (Cl) and 0.66 (S). Noticeably, a systematic inspection of the sulphur's results indicated the existence of a point which considerably deviated from the predicted linear trend. The exclusion of the 15%SP/85%CC value substantially improved the results and, considering only the data for the first seven points (bold values in Table III) the determination coefficient for the uniparametric model obtained with $\log x_S$ was higher than the threshold value of 0.80, usually considered an acceptable result. The other three uniparametric models didn't show any significant improvement. Despite this result and since there were 7 experimental points available, we have tested all possible six biparametric relations. Table IV shows that the independency of the chosen descriptors is guaranteed since it is small the r^2 for each pair of descriptors.

From the tested biparametric relations only the model equations which included $\log x_S$ descriptor showed a determination coefficient (R^2) value higher than 0.80. However, the biparametric models which included also $\log x_{Cu}$ or $\log x_{Ca}$ presented a low significance level (SL) for these two descriptors and usually SL > 95% is a common statistical requirement. Bearing in mind these restrains only the two following models were

Table IV. Correlation coefficients between descriptors.

r^2	Cu	Cl	S
Ca	0.02	0.34	0.28
Cu		0.04	0.56
Cl			0.10

considered statistically appropriate (Eqs. I and II). The standard deviation of the fit, s_{fit}, and Fisher's F value were also computed and analysed.

$$\log y_{D+F} = -18.42_{\pm 1.29} - 2.30_{\pm 0.44} \log x_S \quad \log y_{D+F} = -18.42_{\pm 1.29} - 2.30_{\pm 0.44} \log x_S \quad \text{(Eq. I)}$$

$$\quad (SL > 99\%) \qquad\qquad (> 99\%) \qquad\qquad\qquad (s_{fit} = 0.470, \ R^2 = 0.847, \ N = 7, \ F = 28)$$

$$\text{(Eq. II)}$$
$$\log y_{D+F} = -16.11_{\pm 1.34} - 2.55_{\pm 0.33} \log x_S + 0.90_{\pm 0.38} \log x_{Cl}$$

$$\quad (SL > 99\%) \qquad\qquad (> 99\%) \qquad\qquad (92\%) \quad (s_{fit} = 0.337, \ R^2 = 0.937, \ N = 7, \ F = 30)$$

The results show, as expected, that the presence of sulphur inhibits the formation of PCDD/F and the presence of chlorine promotes its formation. Since the tested descriptors were orthogonal, the tested models do not seem to indicate the statistical relevance of calcium or copper's content on PCDD/F formation. Since the equations were computed on a log-log basis, our results are consistent with the empirical model $y_{D+F} \propto x_{Cl} / x_S^{2.5}$. This relation was further tested (again on a log-log basis) and the outcomes were quite satisfactory (Eq. III).

$$\log y_D = -15.70_{\pm 0.49} + 1.02_{\pm 0.12} \log(x_{cl}/x_S^{2.5}) \qquad\qquad \text{(Eq. III)}$$

$$\quad (SL > 99\%) \qquad\qquad (> 99\%) \qquad\qquad (s_{fit} = 0.306, \ R^2 = 0.935, \ N = 7, \ F = 72)$$

Internal validation strategies were used to test the attained model and Q^2, a cross-validated *leave-one-out* correlation coefficient, was calculated, exhibiting a high value (0.939) and fully ensuring the robustness of the model [9,10]. Figure 2 illustrates unambiguously the goodness-of-fit.

4. Conclusions – It was found a strong correlation between PCDD/F formation and the sulphur and chlorine content. Our results point to an interesting empirical model which should be further tested with more experimental data and that is partly in accordance with the work of Thomas and McCreight [11].

Additionally, the attained mathematical model can be used to adjust fuel mixtures with appropriate sulphur and chlorine input in order to maintain PCDD/F emissions below the legal limits.

Figure 2. Predicted vs. Experimental log y_{D+F} ($\diamond$ - data for 15%SP/85%CC).

6. References
[1] Tuppurainen K, Halonen I, Ruokojärvi P. *Chemosphere,* **36(7)**, (1998), p. 1493.
[2] Xie W, Liu K, Pan, W-P, Riley J., *Fuel*, **78**, (1999), p. 1425.
[3] Xie Y, Xie W, Liu K, Dicken L, Pan W-P, Riley JT. *Energy and Fuels*, **14 (3)**, (2000), p. 597.
[4] Liu, K., Pan, W.-P., Riley, J.T. Fuel, **79**, (2000), p. 1115.
[5] Crujeira, T., Lopes, H., Abelha P., Sargaço, C., Gonçalves, R., Freire, M., Cabrita, I., Gulyurtlu, I. *Environmental Engineering Science*, **22(2)**, (2005) p. 241.
[6] Gulyurtlu I, Boavida D, Abelha P, Lopes MH, Cabrita I., *Fuel*, **84**, (2005), p. 2137.
[7] H. Lopes, I. Gulyurtlu, P. Abelha, T. Crujeira, D. Salema, M. Freire, R. Pereira and I. Cabrita, *Fuel*, **88**, (2009), p. 2373.
[8] I. Gulyurtlu, A.T. Crujeira, P. Abelha, and I. Cabrita, *Fuel*, **86**, (2007), p. 2090.
[9] A. Golbraikh and A. Tropsha, *Journal of Molecular Graphics and Modelling*, **20**, (2002) p. 269.
[10] A. Tropsha, P. Gramatica and V. Gombar, *QSAR Comb. Sci*., **22**, (2003) p. 69.
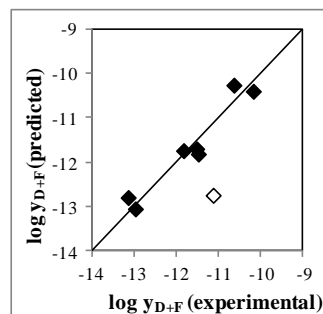[11] V.M. Thomas and C.M. McCreight, *Journal of Hazardous Materials,* **151,** (2008) p. 164.