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Kinetics of the formation and destruction of PCDD/Fs in a laboratory tubular furnace

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## 24 1. Introduction.

25 Since the beginning of the 21st century the European Union (EU) has undoubtedly  
26 supported the valorisation of municipal solid waste (MSW), encouraging the  
27 implementation of management systems where the incineration of this waste should be  
28 a priority rather than landfilling (European Parliament and of the Council, 2008). In  
29 order to accomplish this goal most countries in the EU promoted the construction of  
30 municipal solid waste incineration facilities (European Commission, 2016). These waste  
31 to energy strategies are considered as a powerful tool to achieve the objective of a  
32 circular economy (European Commission, 2017). The incineration of MSW is considered  
33 partially as a renewable energy resource (Cheng and Hu, 2010; U.S. Environmental  
34 Protection Agency, 2014) since all energy obtained through the combustion of the  
35 biogenic content in the MSW is considered as renewable energy (Glover and Mattingly,  
36 2009; U.S. Department of Energy, 2007). Although the carbon footprint of MSW  
37 incinerators is less demanding for the environment than landfilling, other  
38 environmental issues, like polychlorinated dibenzo-*p*-dioxins and dibenzofuran  
39 (PCDD/F) emissions during combustion processes (McKay, 2002; Shaub and Tsang,  
40 1983) should be taken into consideration.

41 Although two major dioxins formation mechanisms have been considered, *de novo*  
42 synthesis and precursor-based reactions (Stanmore, 2004; Zhang et al., 2017), up to four  
43 different mechanistic pathways to PCDD/F formation can be differentiated with a  
44 more detailed review: gas-phase reactions, uncatalyzed surface reactions, catalytic  
45 precursors and *de novo* synthesis reactions (Environment Australia, 1999). It is  
46 believed that the *de novo synthesis* route is the major contributor to the total formation  
47 of dioxins during MSW incineration since the EU legislation determines that the  
48 incineration process shall be produced at least at 850°C during at least 2 seconds

49 (European Parliament and of the Council, 2010). There, the source of the carbon used is  
50 obtained from the solid carbon matrix of the fly ash of incinerated MSW, being able to  
51 produce complete aromatic rings in lack of oxygen (Huang and Buekens, 1996). It is  
52 also believed that chlorine is transferred from the ash surface to the carbon rings  
53 producing PCDD/Fs (Stieglitz and Vogg, 1987). The influence of catalysts and selected  
54 additions on these pathways have also been studied (Wielgosiński et al., 2016). Model  
55 fly ash is used in several publications to determine the influence of PCDD/F  
56 precursors (Mubeen et al., 2017), catalysts such as copper (Masaki et al., 2008; Zhang et  
57 al., 2021), chrome (Zhang et al., 2020) or other metals (Verhulst et al., 2014), oxygen  
58 concentration (Yang et al., 2015), and other process parameters like temperature on  
59 their formation pathways.

60 Trying to determine a kinetic model of the formation of PCDDF/s, following any of the  
61 routes described before, also assumes a reduction of all the variables involved in the  
62 process. Many simplifications have been considered during the attempts of modelling.  
63 One of the first kinetic models considered four steps during PCDD/F formation:  
64 reaction, desorption, dechlorination and decomposition. The model was consistent  
65 only in long timescales (Altwicker et al., 1990). Other investigations modelled the  
66 formation of PCDD/Fs, for both *de novo* synthesis and precursor-based routes, as a  
67 two-stage process. There, the formation of a graphitic initial structure was needed,  
68 which was transformed into many aromatic compounds (Huang and Buekens, 1995).  
69 Another empirical model for *de novo* formation of PCDD/Fs in medical waste  
70 incinerators was published using data from a pilot scale incinerator, and was  
71 dependant on the cooling regime of the incinerator from combustion to ambient  
72 temperature (Stanmore and Clunies-Ross, 2000). This model suggested that the  
73 gas-phase adsorption process was the limiting one in the formation process. Thus, the

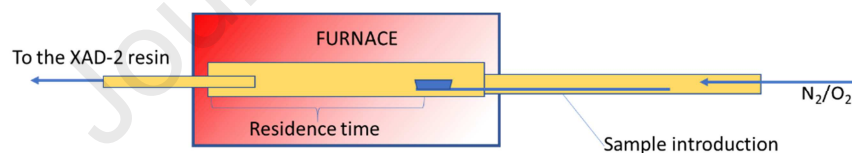
74 diffusion and the amount of HCl molecules adsorbed on the fly ash played a key role  
75 in the model. Other kinetic models considered three reaction steps: the global PCDD/F  
76 formation (including the carbon source gasification), the desorption of the PCDD/Fs  
77 formed to the gas phase, and their possible degradation to other products. This kinetic  
78 model also used as parameters the carbon content in the fly ash, the partial pressure of  
79 oxygen and the temperature. The model was verified with laboratory data with a good  
80 agreement (Huang and Buekens, 2001). The precursor mechanism of formation has  
81 also been modelled, involving other parameters like chlorobenzene and chlorophenol  
82 concentration in the gas phase (Stanmore, 2002).

83 With this in mind, the aim of the present study is to propose a kinetic model for the  
84 formation and destruction of different PCDD/F congeners that only considers process  
85 parameters, and to determine the kinetic parameters involved. The experimental data  
86 used to fit the parameters correspond to data from the decomposition of different  
87 wastes in our laboratory from previously published articles. This kinetic study  
88 pretends to be simple in order to be used in a future simulation process, where the  
89 operational parameters will be selected for simulating total PCDD/F emissions. In  
90 order to simplify the kinetics, a correlation between the formation of the PCDD/F  
91 congeners previously published will also be taken into consideration (Palmer et al.,  
92 2019, 2018).

## 93 2. Experimental data.

### 94 2.1. Thermal decomposition runs carried out at the UA laboratory.

95 During the last 15 years a great amount of work has been done at the University of  
96 Alicante (UA) laboratory of waste studies, where thermal decomposition of a great  
97 variety of wastes has been done under different conditions. Through the years,  
98 different ovens and systems for the thermal treatment of wastes were used, but  
99 following a general scheme, shown in **Error! Reference source not found.** In such  
100 systems, the waste sample is introduced at a controlled speed into an oven with a  
101 programmed temperature. The nominal temperature of the runs was varied between  
102 500 and 1000 °C. The residence time of the volatiles evolved is determined, and the  
103 pollutants evolved are sampled in a XAD-2 resin, that is later extracted with solvents  
104 for the analysis of the different species. In the present work, only PCDD/Fs will be  
105 considered. A blank without sample, using the laboratory scale reactor in the same  
106 conditions as the runs, was done before the combustion experiments.



107  
108 Figure 1. Schematic figure of the batch laboratory scale tubular reactor.

109 The analytical procedure comprises the extraction with toluene, change of solvent to  
110 hexane, acid treatment with sulphuric acid (when needed) and clean-up using the  
111 Power Prep™ system (FMS Inc., MA, USA) with three different columns: silica,  
112 alumina and activated carbon (FMS Inc. Boston, USA). <sup>13</sup>C-labelled compounds  
113 included in the EPA 1613 method were used as internal standards. The PCDD/F  
114 analysis was carried out by high resolution gas chromatography coupled to a high-  
115 resolution mass spectrometer (HRGC/HRMS). For HRGC, an Agilent HP5890 gas

116 chromatograph equipped with a PTV inlet with septumless head was used. For HRMS,  
117 a Micromass Autospec Ultima NT mass spectrometer (Micromass, Waters, UK) with a  
118 positive electron impact (EI+) source was employed.

119 As a result of this work, a complete and interesting set of data was collected,  
120 combining different wastes and conditions of thermal decomposition (temperature,  
121 residence time, oxygen presence). Specifically, data from the following previous papers  
122 was used in the present work (classified by the waste used in the study):

- 123 • Meat and bone meal (Conesa et al., 2005)
- 124 • Polyvinyl chloride (PVC) (Aracil et al., 2005)
- 125 • Cotton and polyester fabrics (Molto et al., 2006, 2005)
- 126 • Sewage sludges (Conesa et al., 2011a, 2007; Galvez et al., 2007)
- 127 • Paper wastes (Conesa et al., 2008)
- 128 • Electronic waste (including materials from mobile phones and electric wires)  
129 (Conesa et al., 2013; Moltó et al., 2011, 2009)
- 130 • Polychloroprene (Aracil et al., 2010)
- 131 • Solid Recovered Fuel (SRF) (Conesa et al., 2011b)
- 132 • Waste mattress (viscoelastic and polyurethane foams) (Garrido et al., 2017;  
133 Garrido and Font, 2015)
- 134 • Furniture wood waste (Moreno et al., 2017)
- 135 • Automotive Shredder Residue (ASR) (Rey et al., 2016)
- 136 • Pine cones and needles (Moltó et al., 2010)

137 In the previous papers, a study of the evolution of the emissions of PCDD/Fs is done,  
138 as a function of the conditions in the decomposition zone. Apart from temperature and  
139 residence time of the gas in the hot zone, the presence of oxygen is controlled by using



140 a constant flow of air and modulating the rate of introduction of the waste. In order to  
 141 quantify the air excess (or defect), an oxygen ratio is used in all previous works,  
 142 defined as:

$$\lambda = \frac{(m_{O_2})_{actual}}{(m_{O_2})_{stoic}} = \frac{m_{air} \cdot 23}{\frac{m_{sample} v}{L} \left( \frac{\%C}{12} + \frac{\%H}{4} + \frac{\%S}{32} - \frac{\%O}{32} \right) \cdot 32} \quad [Equation 1]$$

143 where:

144 %O, %H, %S, %C = weight percentage of oxygen, hydrogen, sulphur and carbon in the  
 145 waste sample,  $m_{air}$  = air flow rate (kg/s),  $m_{sample}$  = weight of the waste (kg), L = length of  
 146 tube occupied by the residue (m), v = linear velocity of introduction of the tube (m/s).

147 That ratio compares the oxygen mass flow introduced in the furnace,  $(m_{O_2})_{actual}$ , and  
 148 the oxygen mass flow that is stoichiometrically needed to produce a complete  
 149 combustion,  $(m_{O_2})_{stoic}$  (Aracil et al., 2010). Using this definition, a value of  $\lambda$  lower  
 150 than unity involves combustion in sub-stoichiometric conditions while values of  $\lambda$   
 151 higher than unity represent excess air.

152 Previous work show that the presence of small amounts oxygen in the gas can promote  
 153 the formation of PCDD/Fs, and that the emission under pyrolysis conditions is not  
 154 zero (Conesa et al., 2007; Rey et al., 2016). The oxygen needed for that formation is  
 155 obviously present in the waste. With the aim to introduce the oxygen ratio data in a  
 156 kinetic model, a change in the definition of the oxygen ratio is needed, bearing in mind  
 157 the presence of oxygen in the waste samples themselves. In this sense, the following  
 158 corrected oxygen ratio ( $\lambda_c$ ) is defined:

$$\lambda_c = \frac{(m_{O_2})_{actual}}{(m_{O_2})_{stoic}} = \frac{m_{air} \cdot 23 + \frac{(\%O)m_{sample} \cdot v}{L}}{\frac{m_{sample} v}{L} \left( \frac{\%C}{12} + \frac{\%H}{4} + \frac{\%S}{32} \right) \cdot 32} \quad [Equation 2]$$

159 Note that all the data used in this study were previously published based on the  
160 definition given in Equation 1. Thus, the corrected oxygen ratio ( $\lambda_c$ ) has been  
161 recalculated for all runs before using them for kinetic modelling. Table SM1 of the  
162 supplementary material shows all data used in the present work, with mention to the  
163 specific conditions and PCDD/F emissions.

## 164 **2.2. Correlation between congener emissions in thermal decomposition systems.**

165 Previous work at the Universitat Ramon Llull (URL) (Palmer et al., 2019, 2018) showed  
166 a dependence on the dioxin and furan emissions from thermal decomposition of  
167 different products. This work established three linear regression models that were able  
168 to estimate properly the total amount and toxicity of a sample considering only the  
169 amount of 1,2,3,6,7,8-HxCDD, OCDF and 2,3,7,8-TCDF in the sample. A kinetic  
170 modelling for only these three congeners will be presented since it has been  
171 demonstrated that these three are enough to estimate the total amount and toxicity of  
172 an emission.

## 173 **2.3. Mathematical treatment of the data.**

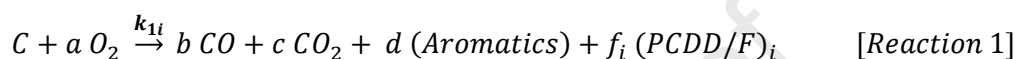
174 For the kinetic modelling of the experimental data, an optimization of the kinetic  
175 constants has been done using MATLAB® software. The experimental data on the  
176 emissions of the three considered congeners was transformed by using decimal  
177 logarithm, as the emission factors at the different runs were clearly of many different  
178 orders of magnitude. In that situation, the logarithm of the experimental data and  
179 those calculated by the model were compared using the following objective function:

$$180 \quad O.F. = \sum_{i=1,2,3}^{three\ cong.} (\log(PCDD/F)_{i, expe.} - \log(PCDD/F)_{i, calc.})^2 \quad [Equation\ 3]$$

181 In the previous equation,  $(PCDD/F)_i$  represents the measured emission of all three  
 182 congeners of dioxins and furans considered (in pg/g).

### 183 3. Kinetic model.

184 A mechanistic scheme for the synthesis and destruction of the three considered  
 185 congeners was to be proposed and tested. For that purpose, the following reaction  
 186 steps were considered:



187 In the scheme, 'C' represents a carbonaceous part of the wastes to be decomposed, and  
 188 the subindex 'i' refers to each one of the congeners considered (i=1, 2, 3). The values of  
 189 'a', 'b', 'c', 'd' and 'f' represent the yield coefficients of each species (g of species/g of  
 190 waste decomposed). Parameter 'f<sub>i</sub>' represents the PCDD/F yield from the  
 191 carbonaceous material and should be different for each congener. Once the different  
 192 species are formed, they can react with the oxygen present in the surrounding  
 193 atmosphere, following the second reaction shown in the previous scheme.

194 It is important to note that the proposed model considers the decomposition of each  
 195 congener by its reaction with oxygen. As a first approach, the kinetic constant for this  
 196 reaction of decomposition is considered the same for the three congeners.

197 Formation of the chlorinated dioxins and furans (Reaction 1) is clearly influenced by  
 198 the presence of metals and chlorine (Verhulst et al., 2014). Literature shows that the  
 199 presence of a small amount of metals or chlorine increases dramatically the formation  
 200 of PCDD/Fs. On the other hand, an excess of these species would not increase the  
 201 PCDD/F production rate above a certain point. For modelling such behaviour, it is

202 proposed to use a parameter in the kinetic equation that accounts for the 'saturation' of  
 203 the chlorine and metal effects, being

204 Chlorine effect =  $[Cl]_{\text{in the sample}} / ([Cl]_{\text{in the sample}} + K_{Cl})$  and

205 Metal effect =  $[Fe + Cu]_{\text{in the sample}} / ([Fe + Cu]_{\text{in the sample}} + K_{Me})$ .

206 The values of  $K_{Cl}$  and  $K_{Me}$  are constants to be optimized, and they represent half of the  
 207 concentration that would 'saturate' the corresponding effect of its presence. This means  
 208 that a waste containing an amount of chlorine higher than two times the  $K_{Cl}$  value  
 209 would present the maximum effect of this reactant in the reaction rate, and a higher  
 210 amount would present the same effect. The same mathematic structure is proposed for  
 211 the metal presence, with its corresponding value  $K_{Me}$ .

212 A dependence of the kinetics on the presence of oxygen is necessary to account for the  
 213 experimental evidences, for both reactions. As a first approximation, a first-order  
 214 dependence on the corrected value of the oxygen ratio ( $\lambda_c$ ) is considered.

215 With these considerations, the differential rate equations for the above set of reactions  
 216 are:

$$-\frac{dC}{dt} = k_{1,i} \cdot C \cdot \lambda_c \cdot (Chl.E.) \cdot (Me.E.) \quad [Equation 4]$$

$$\frac{d(PCDD/F)_i}{dt} = f_i \cdot k_{1,i} \cdot C \cdot \lambda_c \cdot (Chl.E.) \cdot (Me.E.) - k_2 \cdot (PCDD/F)_i \cdot \lambda_c \quad [Equation 5]$$

217 In this sense, a high presence of oxygen (high value of  $\lambda_c$ ) would produce a high  
 218 amount of dioxins through Reaction 1 (in Equation 4) but also an important amount of  
 219 this product would react following Reaction 2 (in Equation 5). Note that under  
 220 pyrolysis conditions ( $\lambda_c$  values close to 0) the amount of oxygen within the sample is  
 221 enough to produce a certain amount of PCDD/Fs. On the other hand, if  $\lambda_c$  is high, the

222 Reaction 2 would be predominant and the amount of PCDD/Fs that survive would be  
223 scarce.

224 The initial condition of Equation 5 is  $(\text{PCDD}/\text{F})_i=0$  at the initial position of the sample  
225 (residence time  $t=0$ ). Equation 5 will be integrated by numerical methods (Euler  
226 method) until the corresponding residence time of the experiment, assuming that the  
227 reactor is isotherm at the temperature of the run. During the integration, it is not  
228 possible to distinguish between  $f_i$  and  $k_{1,i}$ , so a value of  $k'_{1,i}=(f_i \cdot k_{1,i})$  would be  
229 considered. Besides, the variation of 'C' species is negligible (much smaller than the  
230 variation of dioxin and furan yields), and a constant value is expected. In this way, a  
231 value of  $k'_{1,i}=(f_i \cdot k_{1,i} \cdot C)$  will be considered. Note that the presence of chlorine and metals  
232 does not affect the rate of the second reaction, as it would be produced in the gas  
233 phase, where the different volatile species react with the oxygen present.

234 The variation of the kinetic constants with temperature follows the Arrhenius equation:

$$k'_{1,i} = k'_{10,i} \cdot \exp\left(-\frac{E_{1,i}}{RT}\right) \quad [\text{Equation 6}]$$

$$k_2 = k_{20} \cdot \exp\left(-\frac{E_2}{RT}\right) \quad [\text{Equation 7}]$$

235 For the sake of simplicity, the activation energies for the formation of all three  
236 congeners will be considered identical ( $E_{1,1}=E_{1,2}=E_{1,3}=E_1$ ).

237 The parameters of the model are then:  $k'_{10,1}$ ,  $k'_{10,2}$ ,  $k'_{10,3}$ ,  $E_1$ ,  $k_{20}$ ,  $E_2$ ,  $K_{\text{Cl}}$  and  $K_{\text{Me}}$  (8  
238 parameters for a total of 64 runs). It is known that a great interrelation exists between  
239 the pre-exponential factor, the activation energy and the reaction order, so with the aim  
240 of reducing it, the constants at a defined temperature ( $k_{993\text{K}}$ ) were optimized instead of  
241 the pre-exponential factor, that is easily calculated from the following equations:

$$k_{0i} = k_{993K} \cdot \exp\left(\frac{E_i}{R \cdot 993}\right) \quad [\text{Equation 8}]$$

$$k_i = k_{993K} \cdot \exp\left(\frac{E_i}{R \cdot 993} - \frac{E_i}{R \cdot T}\right) \quad [\text{Equation 9}]$$

242 Other more complicated models have been tested for the fitting of the experimental  
243 data, but no significant improvements were found. The modifications considered  
244 include the variation of the reaction order for the effect of oxygen in both reactions,  
245 and the consideration of three different activation energies for Reaction 1.

#### 246 4. Results and discussion.

247 For the optimization of the kinetic constants, first of all, data from wastes where  
248 chlorine and metal content is not too high are considered. Table SM1 of the  
249 supplementary material shows all data used in the present work (Congener 1 = 2,3,7,8-  
250 TCDF, Congener 2 = OCDF, Congener 3 = 1,2,3,6,7,8-HxCDD), but in a first  
251 approximation only 46 runs (those presenting chlorine and metal content of the waste  
252 smaller than 0,04 g/g waste) were considered.

253 The optimization of the O.F. defined before (Equation 3) was done by using a  
254 multidimensional unconstrained nonlinear minimization (Nelder-Mead) by using the  
255 function 'fminsearch' of the Matlab® language.

256 Table 1 (third column) shows the values of the optimized parameters. Figure 2 shows  
257 the fitting of these 46 runs, presenting the calculated vs. experimental values of the  
258 yields of each congener. A satisfactory correlation has been obtained (O.F.=180.1), with  
259 a good ordering of the runs in all three cases. It can be verified that the activation  
260 energies obtained in the fitting are quite low, in the order of 15-45 kJ/mol. Similar  
261 values were obtained previously by other authors for a unique reaction that modelled  
262 the formation of all dioxins as a single congener, with an activation energy of 71  
263 kJ/mol as a result (Huang and Buekens, 2001).

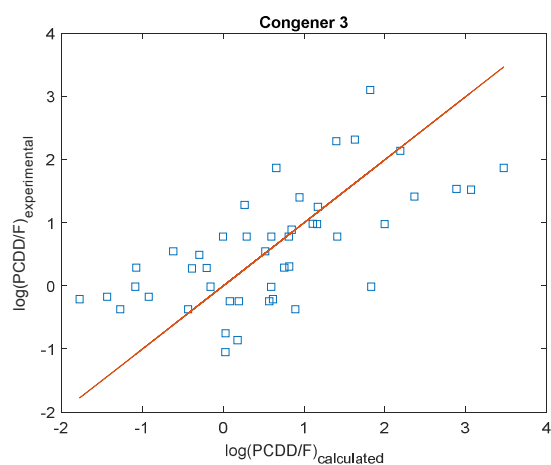
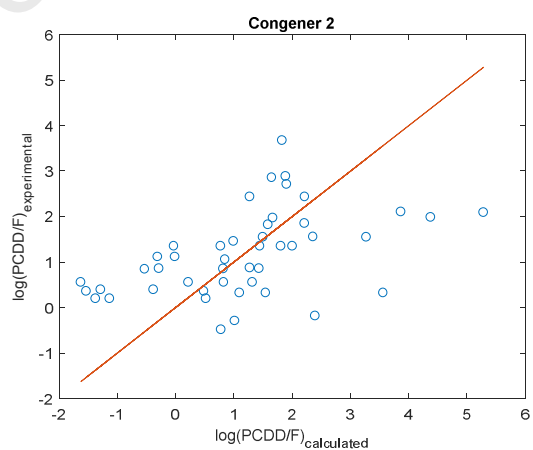
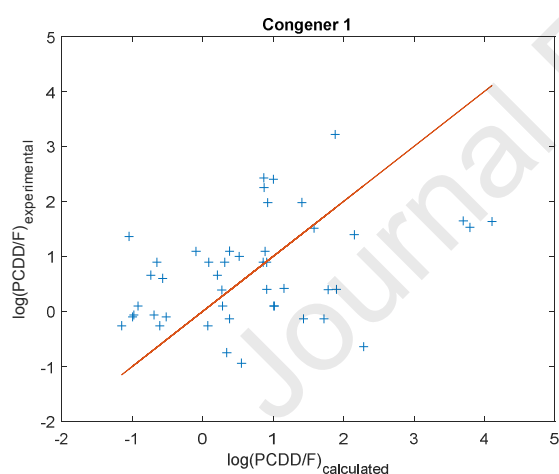
264 The values of the preexponential factors (Table 1) indicate that the formation of  
265 congener 2 is favoured with respect to the other congeners, as the value of  $k'_{10,2}$  is one  
266 order of magnitude higher than the other two.

267 Regarding the optimized value for  $K_{Cl}$ , as mentioned before, it would indicate that a  
268 concentration of chlorine higher than twice 0.0509 g/g, i.e., 10.18 wt. % of chlorine,  
269 would not produce a further increase in the formation rate of PCDD/Fs. In a similar

270 way,  $K_{Me}$  is ca. 0.25 wt. %, i.e., a very small amount of metals is needed to get the  
 271 maximum PCDD/F formation rate.

272 Table 1. Parameters of the kinetic model and optimized values.

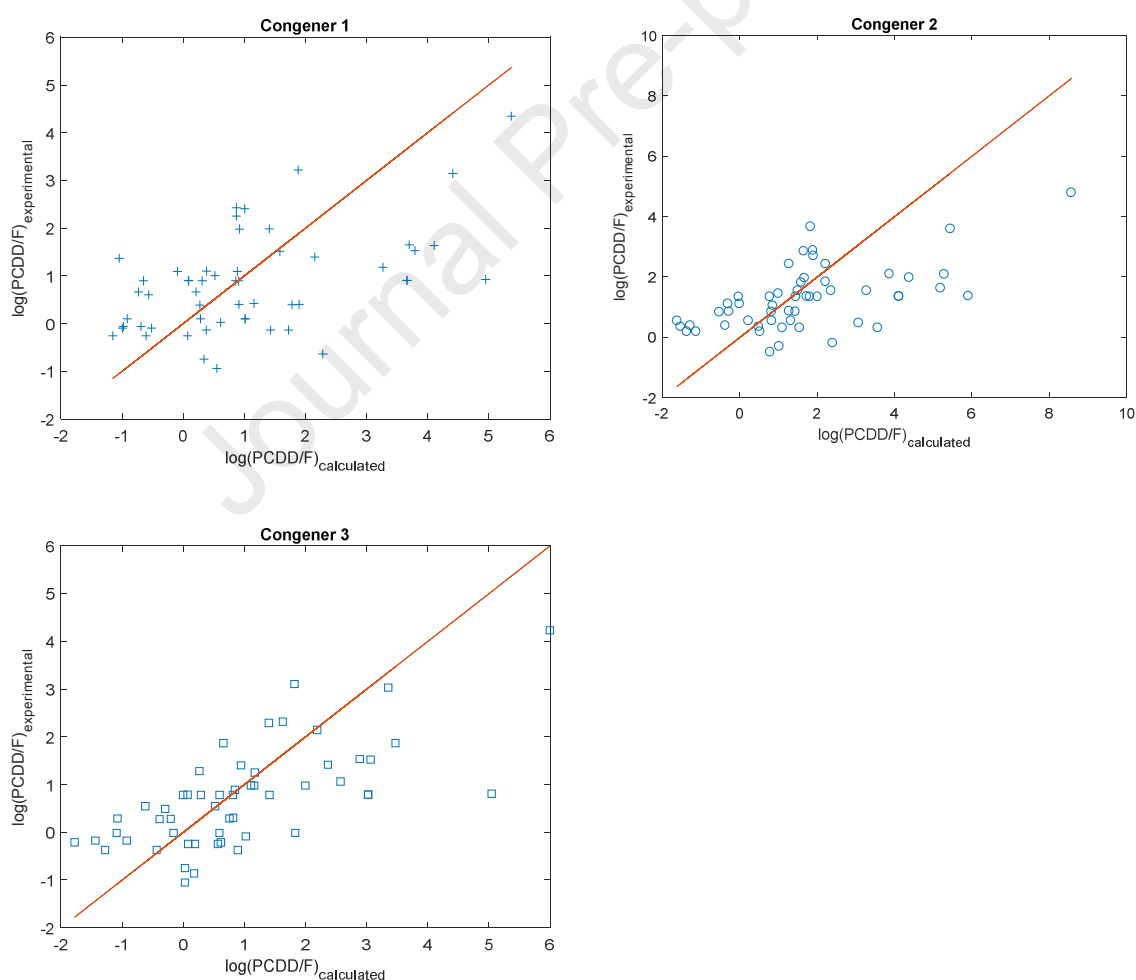
Parameter	Units	Optimized	Optimized
		value (n=46)	value (n=64)
		O.F.=180.1	O.F.=338.0
$k'_{10,1}$	pg PCDD/Fs / (g waste · s)	$5.73 \cdot 10^5$	$2.10 \cdot 10^4$
$k'_{10,2}$	pg PCDD/Fs / (g waste · s)	$1.73 \cdot 10^6$	$8.47 \cdot 10^4$
$k'_{10,3}$	pg PCDD/Fs / (g waste · s)	$5.03 \cdot 10^5$	$6.18 \cdot 10^4$
$E_1$	kJ/mol	16.79	12.16
$k_{20}$	$s^{-1}$	$2.23 \cdot 10^2$	$2.15 \cdot 10^4$
$E_2$	kJ/mol	44.56	54.36
$K_{Cl}$	g Cl/g waste	0.0509	0.0450
$K_{Me}$	g (Fe+Cu)/g waste	0.00259	0.0175





273 Figure 2. Results of the fitting using optimized values of the model adjusted using 46  
274 runs for 2,3,7,8-TCDF (Congener 1), OCDF (Congener 2) and 1,2,3,6,7,8-HxCDD  
275 (Congener 3).

276 Using the optimized values of the kinetic constants, it is possible to predict the  
277 emission of the rest of experiments carried out. In this way, a simulation of all other  
278 runs, without regarding the content of chlorine or metal in the waste, has been done  
279 using the kinetic constants optimized with n=46 runs, shown in Table 1. Figure 3  
280 shows the results of the fitting/simulation of n=64 runs. As it can be seen, the  
281 simulated values of the emissions are satisfactory.



282 Figure 3. Results of the fitting using optimized values of the model adjusted using 64  
283 runs for 2,3,7,8-TCDF (Congener 1), OCDF (Congener 2) and 1,2,3,6,7,8-HxCDD  
284 (Congener 3).

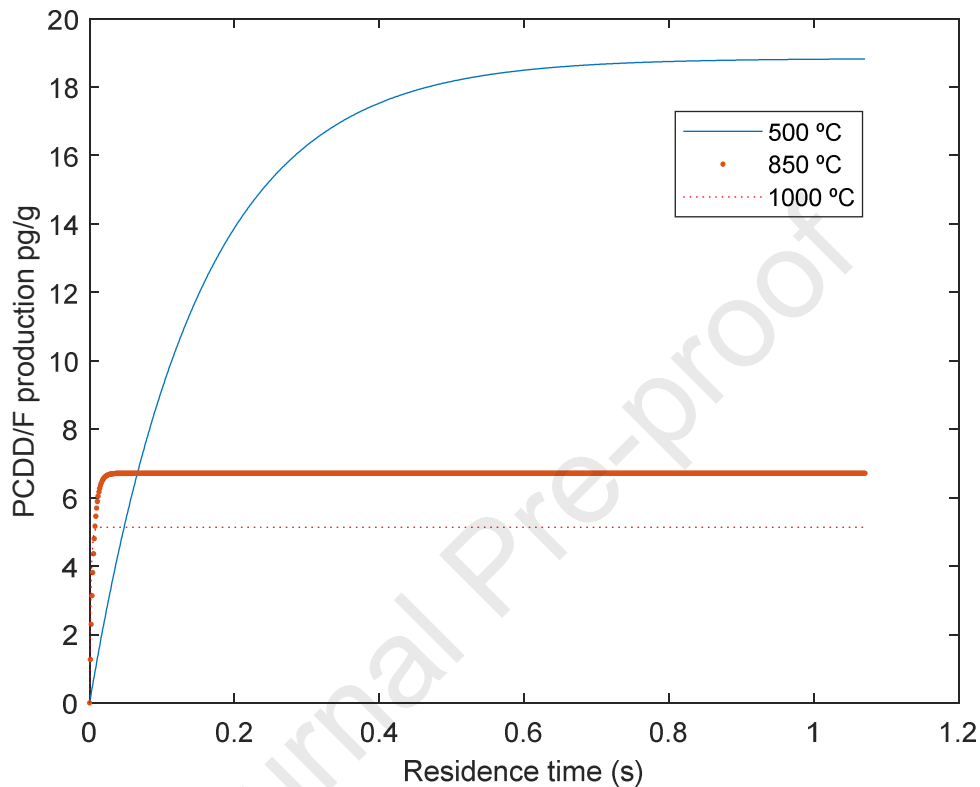
285 Also, an optimization of the kinetic constants was done using all 64 runs presented in  
286 Table SM1. The optimized values are also shown in Table 1 (last column). As can be  
287 seen, the values of the activation energies found considering all runs are a little bit  
288 higher, but still very low, now in the range 10-55 kJ/mol. The value of  $k'_{10,2}$  is the  
289 highest one, compared to the values for the other two congeners, as was obtained  
290 when considering less runs. A study on estimation of the industrial emissions of this  
291 dataset was also performed and published (Conesa et al., 2020). After that study it can  
292 be ensured that all of the PCDD/F amounts in this dataset would cause atmospheric  
293 emission values clearly above 0.1 ng I-TEQ/Nm<sup>3</sup>, which is a typical limit emission  
294 value. Thus, no risk of underestimation is committed when using the proposed kinetic  
295 model.

#### 296 4.1. Simulation of the PCDD/F evolution.

297 The proposed model with the optimized kinetic constants has been used for the  
298 simulation of the formation and destruction of the selected PCDD/F congeners in  
299 different situations. For doing this, values of temperature, ratio of oxygen, chlorine and  
300 metal content in the sample were selected, and the model was used to calculate the  
301 variation of the concentration of the dioxin congeners with residence time.

302 In a first simulation, the following values were used:  $\lambda_c = 0.57$ ; metal  
303 content=0.0003182 g metal/g waste; chlorine content = 0.001804 g chlorine/g waste.  
304 Figure 4 shows the evolution of the concentration of Congener 1 with the residence  
305 time at different temperatures (500, 850 and 1000 °C). As it is shown, a low temperature

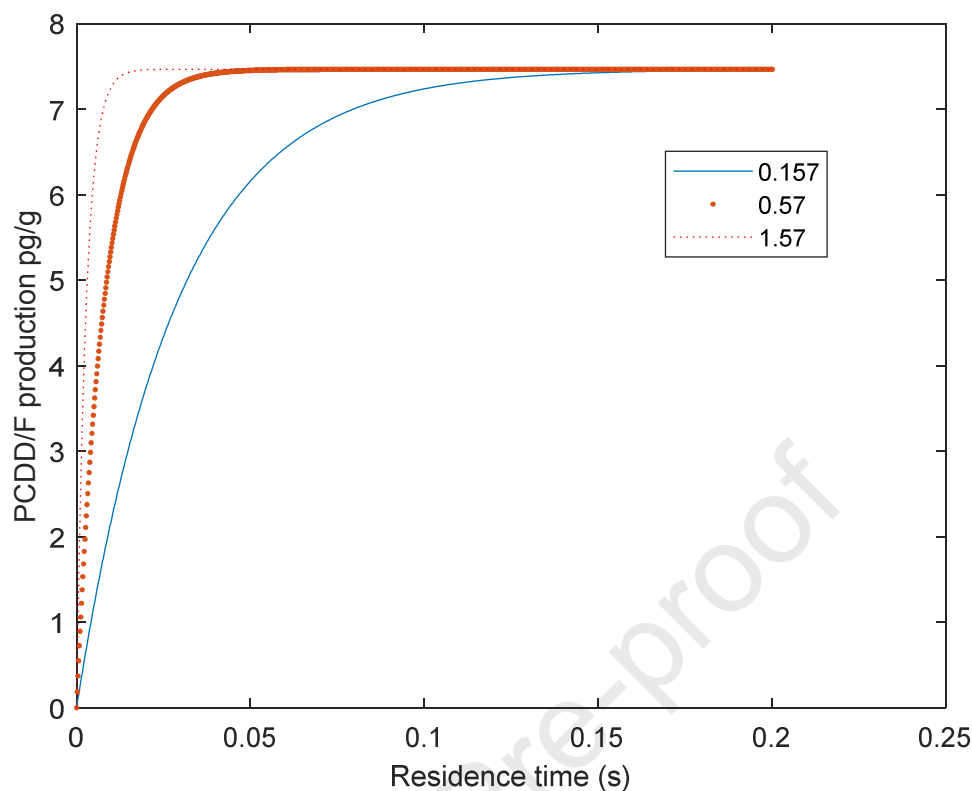
306 increased the amount of dioxin produced, mainly because Reaction 2 does produce a  
 307 consumption of this species. In this way, at 1000 °C the destruction of such pollutants is  
 308 much higher than at lower temperatures.



309

310 Figure 4. Evolution of the production of PCDD/Fs (Congener 1) with residence time at  
 311 different temperatures (500, 850 and 1000 °C).

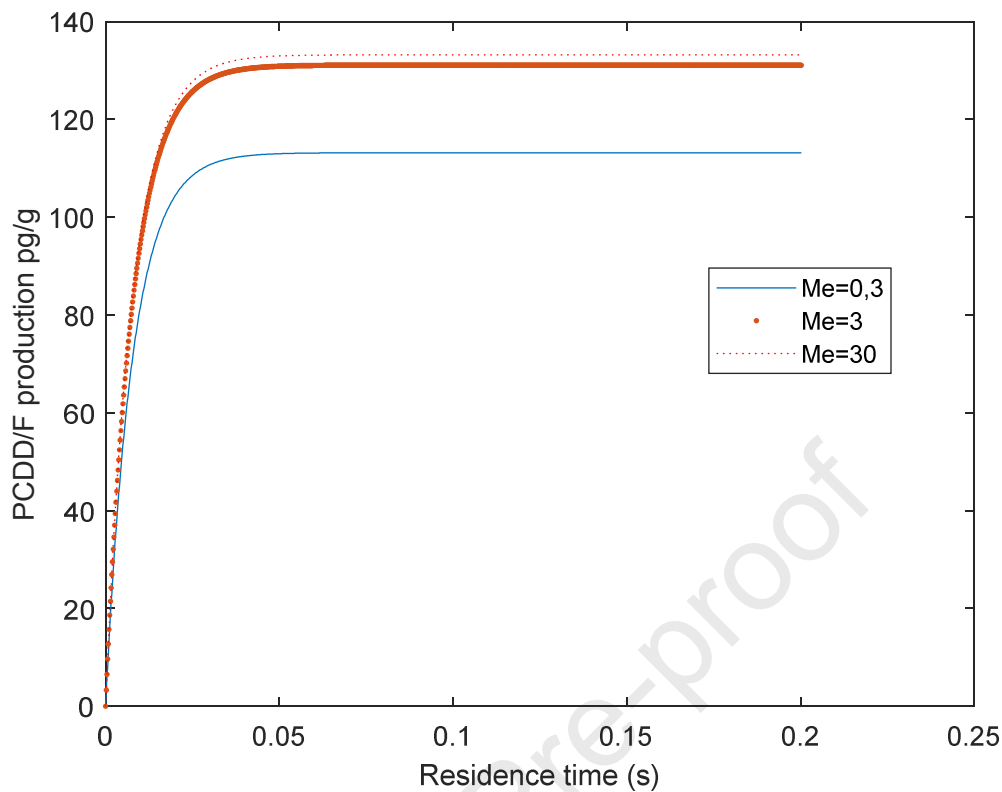
312 A second simulation was done, in this case maintaining the temperature at 850 °C and  
 313 varying the value of  $\lambda_c$ . Figure 5 shows the results using the same values of the rest of  
 314 variables presented before and using three different values of  $\lambda_c$ . As it can be seen, a  
 315 higher destruction of PCDD/Fs is logically found at the higher value of  $\lambda_c$ , related to  
 316 the presence of oxygen.



317

318 Figure 5. Evolution of the production of PCDD/Fs (Congener 1) with the amount of  
319 oxygen in the atmosphere ( $\lambda_c$  values of 0.157, 0.57 and 1.57).

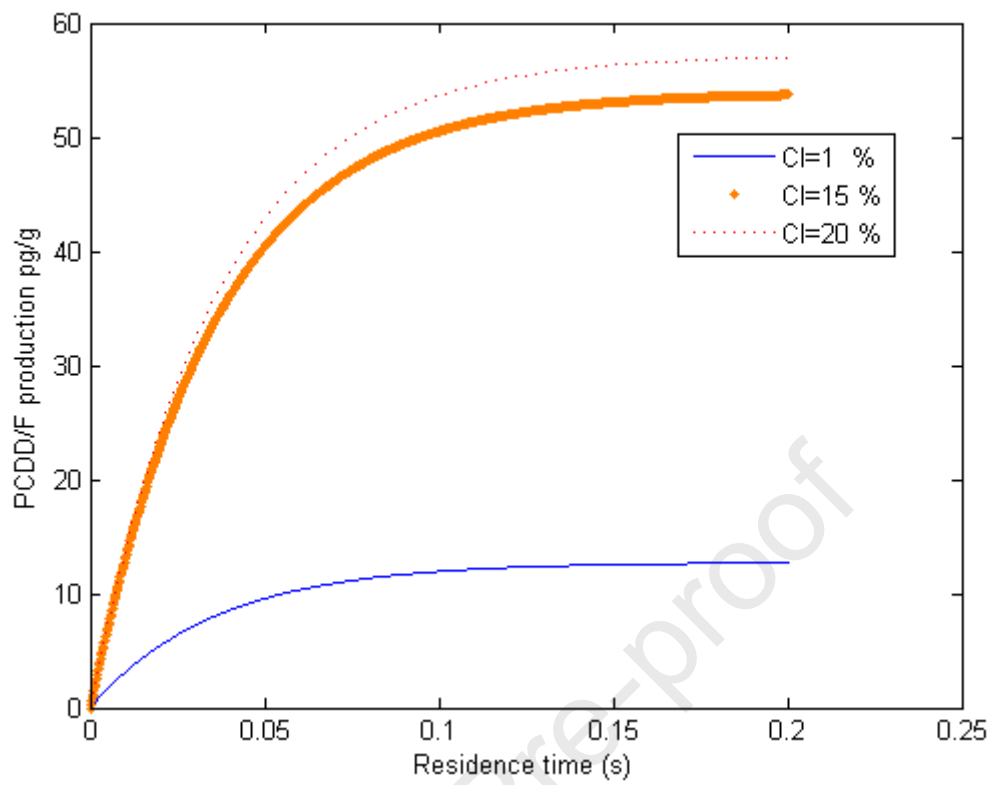
320 A third simulation was done in order to see the effect of the metals in the waste  
321 (mathematically equivalent to the presence of chlorine in the presented model). Figure  
322 6 shows the results for this simulation, where temperature and other variables are  
323 maintained invariant for all three values of metal content used (0.3, 3 and 30 %). As  
324 expected, a sharp increase in PCDD/F production is observed when increasing the  
325 metal content from 0.3 % to 3 %, but the increase is not so important when the metal  
326 content is increased up to 30 %.



327

328 Figure 6. Evolution of the production of PCDD/Fs (Congener 1) with the amount of  
 329 metals in the waste (metal content, Me = 0.3, 3 and 30 %).

330 One last simulation was done to show the effect of chlorine content in the waste in  
 331 PCDD/F production. Figure 7 shows the result for this simulation where temperature,  
 332 oxygen ratio and metal content are maintained invariant for all three values of chlorine  
 333 content used (1, 15 and 20 %). As it was expected, a similar behaviour with metal  
 334 content is produced, since both saturation effects have been simulated using  
 335 mathematically equivalent expressions. As it can be seen, another sharp increase in  
 336 PCDD/F production is observed when increasing the chlorine content from 1 % to 15  
 337 %, but the increase is not so important when the metal content is increased up to 20 %.



338

339 Figure 7. Evolution of the production of PCDD/Fs (Congener 1) with the amount of  
340 chlorine in the waste (chlorine, Cl = 1, 15 and 20 %).

## 341 5. Conclusions and future work.

342 In this study, a model that represents the kinetics of the formation and destruction of  
343 PCDD/Fs has been developed, that only depends on process parameters. This model  
344 follows two major reactions: the *de novo synthesis* formation of PCDD/Fs from the  
345 carbonaceous part of the combusted wastes, and its destruction by its reaction with  
346 oxygen. Going into more details, it also considers a saturation effect for the presence of  
347 chlorine and metals, where the saturation constants result to be around 10% for  
348 chlorine and 3.5% for metals. The model has been integrated using 64 laboratory runs  
349 from a laboratory scale tubular reactor using many different wastes, being able to  
350 correctly predict the formation of three different PCDD/F congeners, considered  
351 independents. This model has also been tested simulating variations on its main  
352 parameters to estimate the effects of the oxygen ratio, the temperature, and the chlorine  
353 and metals content, showing the utility of the present model, with results in  
354 concordance with the experiences and feedback that we have received from the  
355 industry sector.

356 The comparison of this kinetic model with the previously published ones is difficult to  
357 perform, since neither the equations nor the parameters are the same. Only the  
358 Reaction 1 was also considered in a previously published model where PCDD/F  
359 formation was considered by means of a unique reaction for all congeners, with an  
360 activation energy of 71 kJ/mol as a result (Huang and Buekens, 2001). Our results,  
361 shown in the third column of Table 1, are in the same range, in the order of 15-45  
362 kJ/mol.

363 As a main singularity, this model represents the formation of PCDD/Fs considering  
364 only process parameters such as temperature, oxygen ratio and chlorine/metal  
365 presence, regardless of the nature of the combusted waste. As a future work, this

366 kinetic model of formation is intended to be used integrated with a process simulation  
367 model of a municipal solid waste incinerator, which will calculate the process  
368 parameters needed. The complete model will predict the emissions of PCDD/F from  
369 process parameters only. This model could be used for solving plenty of problems that  
370 the incineration facilities have to overcome in order to reduce toxic emissions, such as  
371 improving the control processes, optimizing the temperature ratios in the gas-cleaning  
372 system and estimating the emissions due to special scenarios such as emergency stop  
373 and set-up.



374 **6. References.**

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518

Journal Pre-proof

- Description of a new model for PCDD/F formation
- Data taken from combustion and pyrolysis of several wastes
- The dependence between PCDD/F congeners reduces the parameters needed by the model
- The model considers process variables such as temperature,  $O_2$ , Cl and metal ratios

Journal Pre-proof



**Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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