

## De novo synthesis of brominated dioxins and furans

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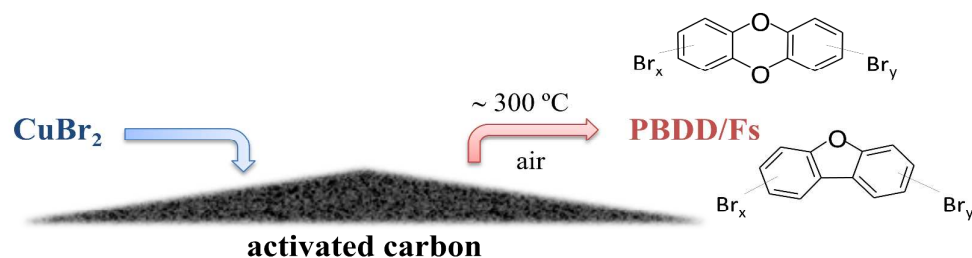


1 DE NOVO SYNTHESIS OF BROMINATED  
2 DIOXINS AND FURANS

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6 TOC/ABSTRACT ART



7

8 ABSTRACT

9 Based on laboratory experiments with model mixtures (active carbon +  $\text{CuBr}_2$  at different  
10 loads), this work studies the formation of polybrominated dibenzo-*p*-dioxins and  
11 dibenzofurans (PBDD/Fs) by de novo synthesis. For the different samples, the temperature  
12 of the maximum carbon oxidation rate was determined by thermogravimetric analysis, and

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13 a kinetic model was proposed for the degradation of the materials in an oxidizing  
14 atmosphere (synthetic air). The effect of the addition of different amounts of  $\text{CuBr}_2$  was  
15 studied, finding that its presence accelerates the degradation of the carbonaceous structure  
16 in the presence of oxygen. The thermal degradation of the samples in air is satisfactorily  
17 described by a first-order single-reaction model. In addition, combustion runs of one of the  
18 mixtures (consisting of activated carbon + 50 wt. %  $\text{CuBr}_2$ , pyrolyzed at 700 °C) were  
19 performed in a quartz horizontal laboratory furnace. The analysis of the emissions and the  
20 solid residue proved the formation of brominated dioxins and furans at 300, 400 and  
21 500 °C, with maximum yield at 300 °C (91.7 ng/g of total PBDD/Fs) and a higher  
22 bromination degree with increasing temperature.

## 23 INTRODUCTION

24 A prevalent pathway for the emission of chlorinated organic pollutants, including  
25 polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), has been recognized to  
26 be the synthesis of halogenated organic compounds in fly ash from combustion processes  
27 (e.g. sintering processes or municipal waste incinerators). Organic residual carbon and high  
28 molecular weight compounds from incomplete combustion have been found to be the  
29 precursor material for de novo synthesis, in the presence of chlorine and oxygen<sup>1-10</sup>.

30 As reported by Stieglitz et al.<sup>1</sup>, copper(II) ions were found to catalyze reactions on the  
31 surface of the particulate carbon in oxygen presence, promoting the oxidation of the carbon  
32 to  $\text{CO}_2$ , as well as the formation of aromatic chlorinated/brominated compounds.

33 The formation of brominated organic compounds was also observed in the low  
34 temperature oxidation of carbonaceous materials, but the de novo synthesis of brominated  
35 (PBDD/Fs) and mixed chlorinated–brominated (PXDD/Fs) analogues in the presence of  
36 bromide has not been that extensively studied. In such a way, Heinbuch and Stieglitz<sup>11</sup>  
37 substituted chloride by bromide in a fly ash, without changing its composition (especially

38 the copper content, an essential catalyst in the de novo synthesis) and found formation of  
39 many different aromatic brominated compounds (benzenes, biphenyls, thiophenes,  
40 naphthalenes, benzonitriles and furans) during the thermal treatment of the ash. The  
41 formation of these compounds started at 250 °C, with a maximum production at 350 °C,  
42 during a very long time (up to 120 min) and increasing with the amount of added bromide.

43 Weber et al.<sup>12</sup> reported on the formation of chlorinated–brominated dioxins and furans  
44 via de novo synthesis from experiments with model fly ash in the presence of chlorine and  
45 bromine. The resulting bromine/chlorine substitution ratio was studied in the range 250 -  
46 350 °C, being the bromine substitution less active at higher temperature and/or higher  
47 residence time. The authors suggested similar substitution mechanisms for bromine and  
48 chlorine during de novo synthesis, based on the similar isomer patterns found for  
49 chlorinated, brominated–chlorinated and brominated dioxins<sup>12, 13</sup>. Stieglitz et al.<sup>1</sup> also  
50 found that, in the presence of chlorine and bromine (molar ratio Cl:Br of 10:1), mixed  
51 chlorinated-brominated dioxins and furans were formed.

52 Examining the pattern of the dibromobenzenes, which showed a preference for the  
53 ortho-position, Heinbuch and Stieglitz<sup>11</sup> suggested two steps in the bromination of the  
54 residual carbon on the fly ash surface. First, the bromination of the carbon surface, yielding  
55 side by side orientation, followed by the oxidative decomposition of the carbon, separating  
56 side by side substituted species.

57 In a pilot incineration plant, Schüler and Jager<sup>14</sup> studied the formation of chlorinated  
58 and brominated dioxins and other halogenated organic compounds. Results showed that  
59 PBDD/F formation could also be explained by the reaction of brominated and mixed  
60 halogenated phenols. As is the case in other studies<sup>15-17</sup>, Schüler and Jager<sup>14</sup> showed that  
61 the efficiency of the post-combustion is more important than other parameters (i.e.  
62 moisture, halogen proportions, temperature, air feed, dust or structure of the fuel).

63 Du et al.<sup>18</sup> suggested that the emissions of PBDD/Fs in stack gas emissions from  
64 industrial thermal processes is due to both de novo formation and also reactions of  
65 precursors, mainly brominated flame retardants as polybrominated diphenyl ethers  
66 (PBDEs) present in wastes from commercial products (e.g. electronic equipment, foams,  
67 textiles,...), which can be used as alternative fuels in such processes.

68 Weber and Kuch<sup>13</sup> also highlighted the fact that in waste incineration, the source of  
69 chlorine are mainly inorganic compounds, minimizing the possible formation of PCDD/Fs  
70 by the precursor pathway. However, the formation of PBDD/Fs by precursor reactions  
71 could prevail over the de novo synthesis, due to the presence of PBDEs, brominated  
72 phenols and other brominated flame retardants as common sources of bromine in wastes.  
73 Under efficient combustion conditions, these brominated precursors can be decomposed,  
74 giving preference to the de novo synthesis in the formation of new PBDD/Fs, as is the case  
75 of PCDD/Fs in municipal waste incinerators<sup>13</sup>.

76 Xiao et al.<sup>19</sup> reported that the destruction of organobrominated compounds contained in  
77 the electronic wastes could be very much effective, forming a mix HBr/Br<sub>2</sub> that reaches  
78 thermodynamic equilibrium, and that is later a reagent for the formation of PBDD/Fs on  
79 the fly ash catalyzed de novo synthesis.

80 In a previous paper by Conesa et al.<sup>10</sup>, the de novo formation of PCDD/Fs was studied  
81 both in a thermobalance and in a horizontal laboratory furnace, using model mixtures. In a  
82 similar way, the present paper investigates the de novo synthesis of PBDD/Fs, considering  
83 the following aspects:

- 84 1. Effect of CuBr<sub>2</sub> in the combustion of activated carbon, at different loads.
- 85 2. Thermogravimetric kinetic study of the oxidation of activated carbon and different  
86 model mixtures.

87 3. Analysis of PBDD/Fs in the emissions from the combustion of a model mixture at  
88 different temperatures (300 – 500 °C) to confirm the formation of such compounds  
89 by de novo synthesis, and analysis of the influence of temperature.

## 90 EXPERIMENTAL

### 91 **Materials**

92 For preparing the mixtures, an activated carbon (100-200 mesh) made by Euroglas  
93 Analytical Instruments was used, as in the previous study<sup>10</sup>. This material is used for the  
94 analysis of AOX (adsorbable organic halides), hence it has very low halide content. An  
95 ultimate analysis of the sample was obtained with a Carlo Erba Instrument, model  
96 CHNS-O EA110 and the results were 80.8 wt. % C, 0.65 wt. % H, 2.0 wt. % S and  
97 0.24 wt. % N. An analysis of chlorine (0.02 wt. %) was carried out in an ECS 1600  
98 Euroglas AOX analyzer and a confirmation was obtained by X-ray fluorescence<sup>10</sup>.

99 CuBr<sub>2</sub> (99 %, Alfa Aesar) was mixed in different proportions and conditions with the  
100 activated carbon. A total of five samples were studied:

- 101 - Activated carbon (Sample C).
- 102 - Activated carbon + very little amount of CuBr<sub>2</sub> (approx. 0.15 wt. %), with no further  
103 treatment (Sample C+traceB).
- 104 - Activated carbon + 1 wt. % CuBr<sub>2</sub>, with no further treatment (Sample C+1B).
- 105 - Activated carbon + 50 wt. % CuBr<sub>2</sub>, with no further treatment (Sample C+50B).
- 106 - Activated carbon + 50 wt. % CuBr<sub>2</sub>, later pyrolyzed at 700 °C for 17 min (1000 s) in  
107 a quartz horizontal laboratory furnace, and washed for removal of CuBr<sub>2</sub> excess  
108 (Sample py+wash(C+50B)).

109 In this last case, the mixture was first pyrolyzed and then washed with an acidified  
110 nitrate solution (0.01 mol/L NaNO<sub>3</sub> acidified with HNO<sub>3</sub>), which causes competitive  
111 desorption of inorganic halide species, removing the CuBr<sub>2</sub> excess. In this way, the sample

112 maintains the organically bound brominated compounds inside the carbonaceous structure,  
113 but the subsequent combustion in the thermobalance is not affected by  $\text{CuBr}_2$   
114 decomposition. An X-ray fluorescence analysis was carried out on the final sample, which  
115 contained 4.2 wt. % Br and 0.8 wt. % Cu.

116 Pure  $\text{CuBr}_2$  was also decomposed in the thermobalance for comparing the different  
117 behaviors.

118 All solvents for organic trace analysis were purchased from Merck (Germany) and the  
119 unlabeled/ $^{13}\text{C}_{12}$ -labeled standards for PBDD/F analysis (EDF-5407, EDF-5408, EDF-5409  
120 and EF-5410) were obtained from Cambridge Isotope Laboratories (Andover, USA).

### 121 **Thermogravimetric analysis**

122 The TG study was performed in a Mettler Toledo thermobalance (model  
123 TGA/SDTA851e/LF/1600) with a horizontal furnace and a parallel-guided balance. The  
124 sample temperature was measured with a thermocouple directly at the crucible, i.e., next to  
125 the sample. Runs were performed at different heating rates (5, 10 and 20 K/min), using  
126 sample amounts close to 8 mg and a flow rate of synthetic air of 100 mL/min (STP). A  
127 total of twelve duplicated runs were carried out for the present study.

128 According to the recommendations in specialized literature, runs were correlated  
129 simultaneously in order to obtain one single set of parameters for each sample.

### 130 **Experiments in laboratory reactor**

131 Using a quartz horizontal laboratory furnace, previously described elsewhere<sup>20</sup>,  
132 combustion runs were performed on the sample prepared by pyrolysis and subsequent  
133 washing (sample 'py+wash(C+50B)'). The runs were carried out at 300, 400 and 500 °C in  
134 synthetic air, in order to check the formation of brominated dioxins and furans by the de  
135 novo pathway at low temperatures. The volatiles evolved from the combustion runs were

136 collected with a sorbent resin (polyaromatic Amberlite<sup>®</sup> XAD-2, Supelco, Bellefonte,  
137 USA) placed at the outlet of the reactor during the entire run (60 min).

138 For each experiment, the resin and the residue (solid fraction remaining after the  
139 combustion) were extracted separately with dichloromethane by Accelerated Solvent  
140 Extraction in a DIONEX ASE<sup>®</sup> 100. Prior to extraction, samples were spiked with a <sup>13</sup>C<sub>12</sub>-  
141 labeled PBDD/F internal standard solution (EDF-5408). All extracts were concentrated  
142 down to 1 mL by rotary evaporation. After addition of a <sup>13</sup>C<sub>12</sub>-labeled PBDD/F cleanup  
143 standard solution (EF-5410), the extracts were purified using an automated cleanup system  
144 (Power Prep, FMS Inc., Boston, MA) with silica gel and alumina pre-packed columns. The  
145 extracts were concentrated in a rotary evaporator and with a gentle stream of nitrogen for  
146 analysis by gas chromatography coupled to high resolution mass spectrometry  
147 (HRGC-HRMS).

148 The HRGC-HRMS analyses were performed on an Autospec Ultima NT mass  
149 spectrometer (Micromass, UK) with a positive electron impact (EI+) source, provided with  
150 an Agilent/HP 6890 Plus gas chromatograph (Palo Alto, CA, USA) with Programmed  
151 Temperature Vaporization (PTV) and split/splitless injectors. The GC was equipped with a  
152 TRB-Meta X5 Restek chromatographic column (15 m x 0.25 mm x 0.25 μm) and the oven  
153 temperature was programmed from 130 to 320 °C at 10 °C/min (15 min hold), with a  
154 carrier gas (helium) flow rate of 1 mL/min. The HRMS was operated in an electron impact  
155 mode (35 eV and 650 μA current) selective ion recording (SIR) mode at resolution  
156 > 10 000 (10 % valley) and 290 °C as the temperature of the ion source.

157 The isotope dilution methodology was used to quantify the samples, using the relative  
158 response factors previously obtained from the calibration standard solutions (EDF-5407-  
159 CS1 to CS5). Recoveries of the spiked labeled standards were calculated using a labeled  
160 recovery standard solution (EDF-5409) that was added to the samples prior to the injection



161 on the gas chromatograph, obtaining the following recoveries: 31 - 129 % for tetra- to  
162 hepta-substituted congeners and 21 - 122 % for octabrominated ones. A laboratory blank  
163 was also prepared and analyzed together with the samples, as well as the activated carbon  
164 itself, where no PBDD/Fs were detected.

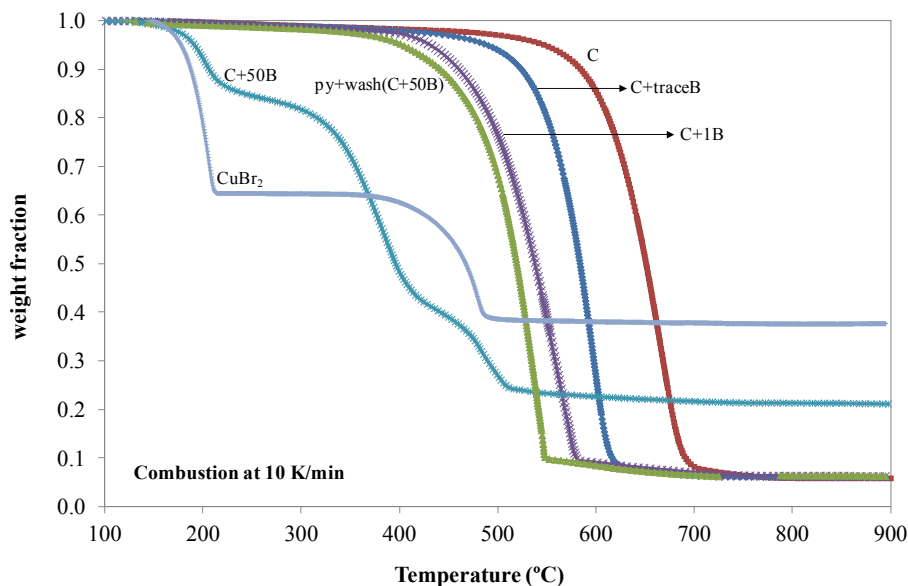
165 Along all the experimental process, restrictive measures were adopted to avoid sunlight  
166 exposure (using amber quartz or covering the laboratory material with aluminum foil) in  
167 order to minimize brominated compounds degradation.

## 168 RESULTS AND DISCUSSION

### 169 **Effect of CuBr<sub>2</sub> on combustion**

170 **Figure 1** presents the decomposition of all the samples heated in synthetic air (N<sub>2</sub>:O<sub>2</sub>=  
171 4:1) at 10 K/min. Similar residues are obtained with activated carbon 'C', mixtures with a  
172 very low CuBr<sub>2</sub> content 'C+traceB' and 'C+1B', and the pyrolyzed sample  
173 'py+wash(C+50B)' (approx. 5 wt. %, which corresponds to the ash content of the carbon),  
174 whereas it is 22 wt. % for sample 'C+50B', and 32 wt. % in the case of CuBr<sub>2</sub>. The  
175 mixture of carbon and CuBr<sub>2</sub> in sample 'C+50B' leads to a final residue that is comprised  
176 between that from active carbon and pure CuBr<sub>2</sub>.

177 As can be seen, pure CuBr<sub>2</sub> presents two weight loss steps, corresponding to the  
178 following reactions<sup>21</sup>: when heated at more than 150 °C, CuBr<sub>2</sub> loses Br<sub>2</sub> to give CuBr,  
179 which in air gives CuO at a temperature above 400 °C. These reactions are also observed in  
180 sample 'C+50B' (at temperatures slightly higher, due to the mixture with active carbon),  
181 while the oxidation of the carbon occurs at an intermediate step (beginning at about  
182 265 °C).



183

184 **Figure 1.** Combustion runs ( $N_2:O_2 = 4:1$ ) at 10 K/min with the following samples:  
 185 activated carbon 'C', activated carbon with trace amounts of  $CuBr_2$  'C+traceB', activated  
 186 carbon with 1 wt. %  $CuBr_2$  'C+1B', activated carbon with 50 wt. %  $CuBr_2$  'C+50B',  
 187 activated carbon + 50 wt. %  $CuBr_2$  pyrolyzed and washed 'py+wash(C+50B)' and  
 188 copper(II) bromide ( $CuBr_2$ ).

189 **Table 1** presents the temperatures of maximum weight loss rate ( $T_{max}$ ) at 10 K/min for  
 190 the different samples, as well as those obtained in the previous work<sup>10</sup> when studying  
 191 chlorinated dioxins production by addition of  $CuCl_2$  or  $CuO$ . Note that the maximum  
 192 oxidation rate refers to the oxidative breakdown of the carbonaceous species without  
 193 considering the thermal decomposition of  $CuCl_2$  or  $CuBr_2$ , as can be verified in **Figure 1**,  
 194 by comparing the decomposition in air of each sample prepared with that of metal halides.

195

196

197

198 **Table 1.** Comparison between temperatures of maximum oxidative decomposition rate  
 199 ( $T_{\max}$ ) of activated carbon in the presence of different copper halides (some data from  
 200 Conesa et al.<sup>10</sup>).

Combustion runs performed at 10 K/min			
Sample	Material	$T_{\max}$ (°C)	$\Delta T_{\max}$
C	Activated carbon (C)	655	-
**	C + 50 wt. % CuCl <sub>2</sub> pyrolyzed* and washed	485	-170
**	C + 0.15 wt. % CuCl <sub>2</sub>	604	-51
C+50B	C + 50 wt. % CuBr <sub>2</sub>	371	-284
py+wash(C+50B)	C + 50 wt. % CuBr <sub>2</sub> pyrolyzed* and washed	508	-147
C+1B	C + 1 wt. % CuBr <sub>2</sub>	535	-120
C+traceB	C + 0.15 wt. % CuBr <sub>2</sub>	577	-78

\*pyrolyzed in nitrogen at 700 °C for 17 min

\*\*From Conesa et al.<sup>10</sup>

201 First of all, it is clear that the presence of CuBr<sub>2</sub> accelerates the oxidative breakdown of  
 202 the carbonaceous structure, as well as CuCl<sub>2</sub> does. A decrease in the temperature of  
 203 maximum carbon oxidation rate of almost 290 °C has been observed in the sample  
 204 consisting of carbon in the presence of 50 wt. % CuBr<sub>2</sub>. For the oxidation of the pyrolyzed  
 205 sample a decrease of 147 °C is observed, whereas in the presence of metal chloride the  
 206 decrease was of 170 °C. If samples with presence of trace amounts of metal halides are  
 207 compared, it is observed that sample with bromine (temperature decrease of 78 °C) is  
 208 slightly more reactive than sample with chlorine (temperature decrease of 51 °C).

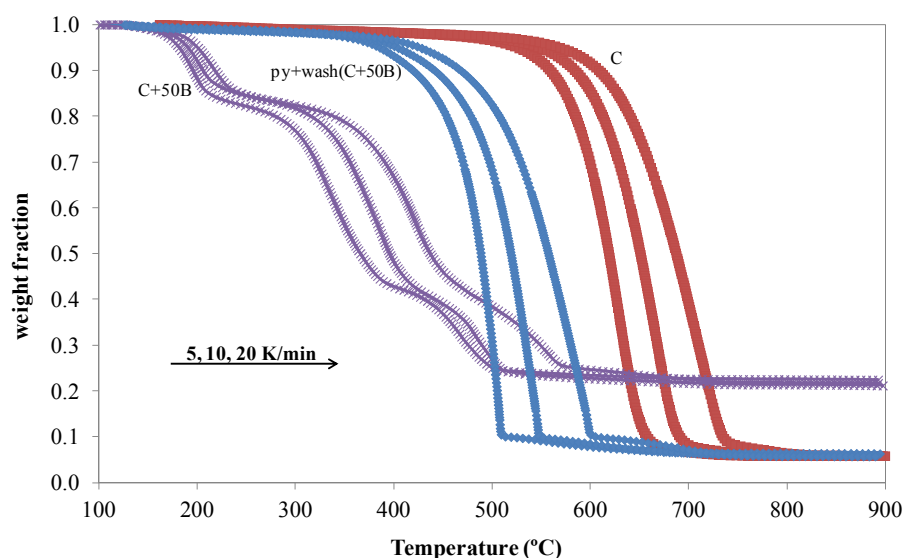
209 Some authors<sup>1, 3, 22</sup> already reported on the catalytic effect of copper chlorides,  
 210 accelerating the oxidative degradation process of carbon particles. Schwarz and Stieglitz<sup>4</sup>  
 211 indicated that, without catalyst, the oxidation of carbon to yield CO<sub>2</sub> occurs at 700 °C, but  
 212 it showed a peak temperature of 345 °C in presence of copper (in a sample of fly ash from  
 213 a municipal waste incinerator). In a model mixture with charcoal and KBr, the oxidation

214 rate presented a maximum at 335 °C, which is similar to the value observed for sample  
215 'C+50B' in this study.

216 Comparing in **Figure 1** the curves obtained in the oxidation of the sample prepared by  
217 mixing the carbon with CuBr<sub>2</sub> in excess (sample 'C+50B'), with those for the material  
218 pyrolyzed and washed (sample 'py+wash(C+50B)'), it is concluded that the presence of a  
219 high amount of available bromine intensively accelerates the oxidative degradation. In the  
220 sample washed to eliminate the excess, some copper and bromine remains bonded to the  
221 carbonaceous structure provoking an acceleration of the carbon oxidation process, but not  
222 as intense as in the case of the sample 'C+50B'. Previous work<sup>10</sup> indicated that copper(II)  
223 ion is not the only responsible for the change in the reactivity of the carbon, but also the  
224 presence of a halogen is necessary to accelerate the oxidative breakdown.

### 225 Kinetic study

226 A kinetic study was performed on the combustion of three of the previous samples: 'C',  
227 'C+50B' and 'py+wash(C+50B)'. As already commented, for sample 'py+wash(C+50B)',  
228 the pyrolytic step used for the preparation of the sample was carried out before the  
229 combustion runs in the thermobalance.



230

231 **Figure 2.** Combustion runs performed at 5, 10 and 20 K/min with samples ‘C’, ‘C+50B’  
232 and ‘py+wash(C+50B)’.

233 **Figure 2** presents the combustion runs performed at three different heating rates in  
234 order to obtain a detailed kinetic analysis<sup>23-25</sup>. As suggested in a previous study<sup>24</sup>, the  
235 simplified kinetic equation for the chosen first-order single-reaction model can be written  
236 as follows:

$$237 \quad \frac{dw}{dt} = k_0 \exp\left(-\frac{E}{RT}\right)(w - w_\infty)$$

238 where  $w$  is the weight fraction (weight of the solid at any time divided by the initial  
239 weight),  $k_0$  is the pre-exponential factor ( $s^{-1}$ ),  $E$  is the activation energy (kJ/mol),  $R$  is the  
240 gas constant (kJ/mol·K),  $T$  is the temperature (K) and  $w_\infty$  is the weight fraction at time  
241 infinity, which corresponds to the final residue of the experimental runs.

242 The objective function (O.F.) to minimize was the sum of the square differences  
243 between experimental and calculated weight derivatives, as proposed in previous studies<sup>24</sup>.  
244 In order to check the model validity, a previously reported<sup>10</sup> variation coefficient (V.C.)  
245 was calculated, which takes into account the number of experimental points correlated in  
246 each model and the number of parameters to be fitted.

247 The Runge-Kutta fourth-order method was used to integrate the differential kinetic  
248 equation, and the optimization was done using Solver<sup>®</sup> tool in a MS Excel<sup>®</sup> spreadsheet.  
249 **Table 2** shows the kinetics parameters obtained in the optimization. The values of the  
250 variation coefficients are presented, which are quite low in all cases, bearing in mind that  
251 the three curves obtained at different heating rates are considered.

252

253

254

255 **Table 2.** Kinetic parameters for the combustion models and V.C. values.

Sample	$k_0$ ( $s^{-1}$ )	E (kJ/mol)	V.C. (%)
C	$3.31 \cdot 10^6$	158.4	1.1
C+50B	$8.90 \cdot 10^3$	78.7	1.0
py+wash(C+50B)	$2.49 \cdot 10^5$	118.9	1.9

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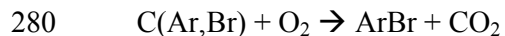
257 For the fitting of the curves obtained with sample ‘C+50B’ (i.e. activated carbon with a  
 258 50 wt. % of  $CuBr_2$ ), only the oxidative degradation of the activated carbon is considered  
 259 (temperature range 265 - 440 °C), by comparison with the curves obtained for  $CuBr_2$  alone  
 260 (see **Figure 1**).

261 In previous work<sup>10</sup> analyzing the effect of  $CuCl_2$  we found similar pre-exponential  
 262 factors (in the order of  $10^6 s^{-1}$ ), as is the case of sample ‘C’ and ‘py+wash(C+50B)’. The  
 263 value of this parameter can be related to the number of active sites in the surface of the  
 264 carbon<sup>26, 27</sup>.

265 The values of the activation energy, that can be related to the strength of the bonds  
 266 formed<sup>26, 27</sup>, correlate well with the observations from the samples, indicating that the C-H  
 267 bond (sample ‘C’) is quite stronger than the C-Br bond (sample ‘C+50B’). The effect of  
 268 the pyrolysis and washing of ‘C+50B’ sample is to eliminate some bromine excess and  
 269 then to reduce the amount of C-Br bonds; in this way, an intermediate value of activation  
 270 energy is found. In the case of C+ $CuCl_2$  or C+ $CuO$ +HCl mixtures, higher activation  
 271 energies were found ( $> 120$  kJ/mol in all cases), what suggests that the C-Br bond is  
 272 weaker than C-Cl. These observations agree with the values of bond energies found in  
 273 literature<sup>28</sup>.

274 The decomposition (in the presence of oxygen) of samples ‘C+50B’ and  
 275 ‘py+wash(C+50B)’ would produce different but small amounts of brominated aromatic  
 276 structures and a high amount of carbon oxides. In sample ‘C+50B’ the amount of bromine

277 is so high that a lot of C-Br bonds can be formed during the decomposition, and so a high  
278 amount of brominated species is expected. Actually the reaction producing brominated  
279 species and carbon oxides is the same, and can be represented by:



281 where  $C(\text{Ar},\text{Br})$  represents macromolecular carbon with bromine and aromatic compounds.  
282 This is the rate-controlling step and, as mentioned, a first-order kinetic law was used to  
283 correlate the experimental data, where different activation energies for samples with  
284 low/high amount of bromine are found.

### 285 **Polybrominated dioxins and furan analysis and evolution with temperature**

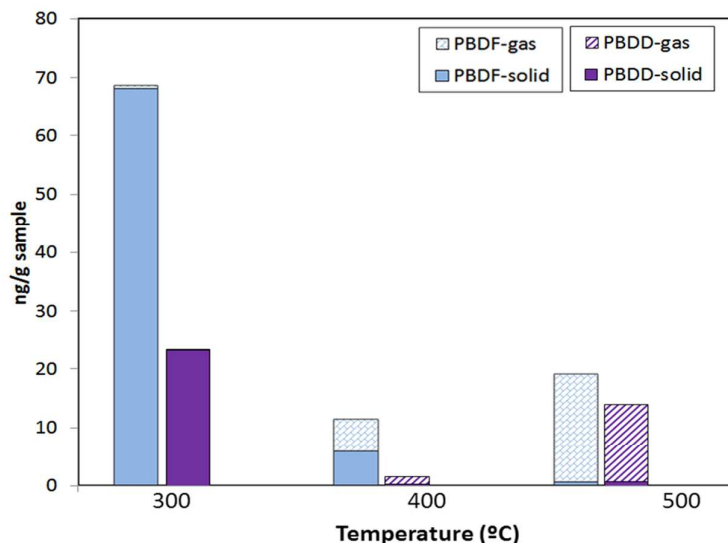
286 The PBDD/F analysis carried out comprised the quantitative determination of 13  
287 different 2,3,7,8-substituted tetra- to octabrominated congeners (equivalent to the toxic  
288 congeners of PCDD/Fs) and the corresponding total homologues.

289 As indicated above, sample 'py+wash(C+50B)' was treated at 300, 400 and 500 °C in  
290 presence of air for 60 minutes in a horizontal laboratory reactor, obtaining a solid residue  
291 of 81.7 wt. %, 49.7 wt. % and 4.7 wt. %, respectively.

292 Both the resin containing the volatiles evolved and the residual solid were analyzed for  
293 PBDD/Fs, as described in the Experimental section, and the values of total yields at the  
294 different temperatures are shown in **Figure 3**. Maximum yield is found at 300 °C, with the  
295 emission of 91.7 ng/g of total PBDD/Fs, while at 400 and 500 °C the emissions are reduced  
296 down to 12.7 and 32.8 ng/g, respectively. The results are in accordance with the  
297 phenomena observed by Heinbuch and Stieglitz<sup>11</sup> who found a maximum production at ca.  
298 350 °C, and in contrast with the maximum production of PCDD/Fs found at 400 °C in  
299 different studies<sup>3, 5, 10</sup>.

300 **Figure 3** also presents the distribution of the produced PBDD/Fs between solid residue  
301 (lower part of the bar) and gas phase (upper part of the bar) at the different temperatures.

302 As expected, at low temperature the higher amounts are found in the solid residue, but as  
 303 temperature increases, emission in the gas phase is more and more important, while the  
 304 amount remaining in the solid phase decreases.



305  
 306 **Figure 3.** Evolution of total brominated dioxins (PBDDs) and furans (PBDFs) at the  
 307 different temperatures. Partitioning of the evolved PBDDs and PBDFs between gas phase  
 308 and solid residue is shown.

309 Comparing the results with those found for de novo formation of chlorinated species in  
 310 similar conditions by Conesa et al.<sup>10</sup>, the amount of D/Fs structures formed is  
 311 approximately 10 times lower in the present study. Schöler and Jäger<sup>14</sup> found formation  
 312 rates of PBDD/Fs 4 to 20 times higher than those of their chlorinated analogues in a pilot  
 313 incineration plant, but only mono- to tetrabrominated congeners were analyzed and, as in  
 314 the present study, furans were more abundant than dioxins. This later observation is in  
 315 accordance with a dioxin/furan ratio < 1, characteristic of de novo synthesis<sup>6</sup>.

316 **Table 3** shows the yields of the analyzed 2,3,7,8-substituted PBDD/Fs and the total  
 317 yields for each homologue group found in the experiments at 300, 400 and 500 °C.

318 **Table 3.** Formation of PBDD/Fs (ng/g sample) by de novo synthesis at different  
 319 temperatures.



Temperature	300 °C	400 °C	500 °C
<b>Congeners</b>			
2,3,7,8-TBDF	2.48	0.38	0.73
1,2,3,7,8-PeBDF	nd	nd	0.002
2,3,4,7,8-PeBDF	0.34	0.06	0.14
1,2,3,4,7,8-HxBDF	0.17	0.07	0.78
1,2,3,4,6,7,8-HpBDF	0.85	1.42	5.02
OBDF	nd	nd	0.99
2,3,7,8-TBDD	0.48	0.06	0.10
1,2,3,7,8-PeBDD	nd	nd	0.13
1,2,3,4,7,8+1,2,3,6,7,8-HxBDD	0.35	nd	0.25
1,2,3,7,8,9-HxBDD	nd	nd	0.07
1,2,3,4,6,7,8-HpBDD	0.59	0.20	0.58
OBDD	nd	nd	0.49
Total 2,3,7,8-PBDFs	3.84	1.92	7.66
Total 2,3,7,8-PBDDs	1.43	0.25	1.63
Total 2,3,7,8-PBDD/Fs	5.27	2.17	9.29
<b>Homologues</b>			
Total TBDF	52.0	4.85	4.78
Total PeBDF	7.56	1.47	3.87
Total HxBDF	4.07	2.56	3.93
Total HpBDF	4.73	2.33	5.41
OBDF	nd	nd	0.99
Total TBDD	16.9	1.30	8.35
Total PeBDD	3.93	nd	2.61
Total HxBDD	1.93	nd	1.82
Total HpBDD	0.59	0.20	0.58
OBDD	nd	nd	0.49
Total PBDFs	68.4	11.2	19.0
Total PBDDs	23.3	1.49	13.9
Total PBDD/Fs	91.7	12.7	32.8

nd: not detected

320

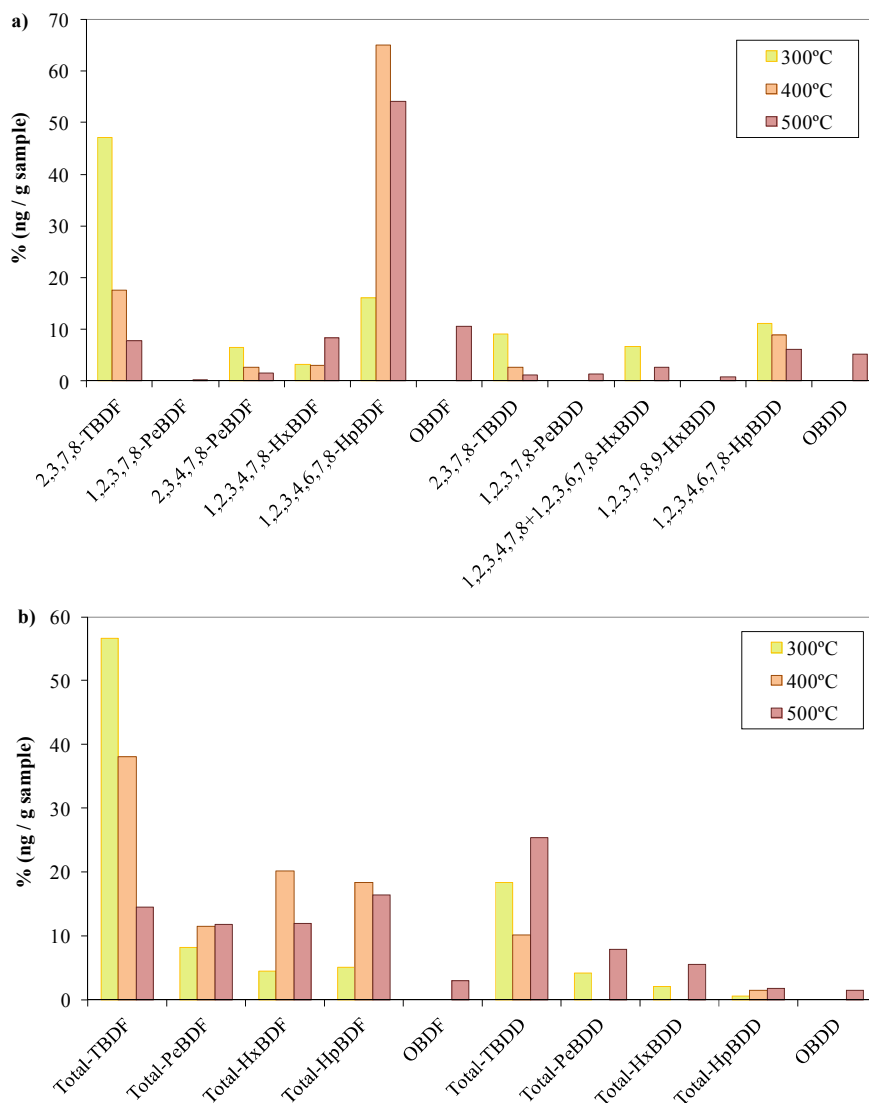
321 **Figure 4** shows the relative contribution of the different 2,3,7,8-bromosubstituted  
 322 congeners (equivalent to the toxic congeners of chlorinated dioxins) and the total  
 323 homologues. Regarding furans, tetrabrominated homologues are the most abundant at  
 324 300 °C, with formation of 2.48 ng/g of 2,3,7,8-TeBDF, if we look at the 2,3,7,8-congeners.  
 325 At 400 °C, tetrafurans are also predominant, but a shift in the bromination degree is  
 326 observed toward hexa- and heptabrominted homologues, with 1.42 ng/g of 1,2,3,4,6,7,8-  
 327 HpBDF being the most abundant toxic isomer. The increase in the bromination degree is  
 328 more pronounced at 500 °C, with heptafurans as the most abundant homologues and

329 5.02 ng/g of 1,2,3,4,6,7,8-HpBDF; also a slight formation of OBDF is observed, which had  
330 not been detected at lower temperatures.

331 As for dioxins, the profiles do not show that marked effect of temperature. Important  
332 amounts of tetra- and heptabrominated congeners are found at 300 °C, with 0.48 ng/g of  
333 2,3,7,8-TeBDD and 0.59 ng/g of 1,2,3,4,6,7,8-HpBDD within the 2,3,7,8-substituted  
334 congeners. Tetrabrominated dioxins are also dominant at 400 and 500 °C, whereas  
335 1,2,3,4,6,7,8-HpBDD predominates in the toxic congeners (0.20 and 0.58 ng/g  
336 respectively). As in furans, OBDD is only found at 500 °C.

337 Other authors have also observed a higher degree of halogenation with increasing  
338 temperature in the formation of dioxins and furans by de novo synthesis<sup>3-5</sup>. Luijk et al.<sup>5</sup>  
339 linked that fact to the higher thermal energy needed for the formation of the compounds  
340 with a higher halogenation degree.

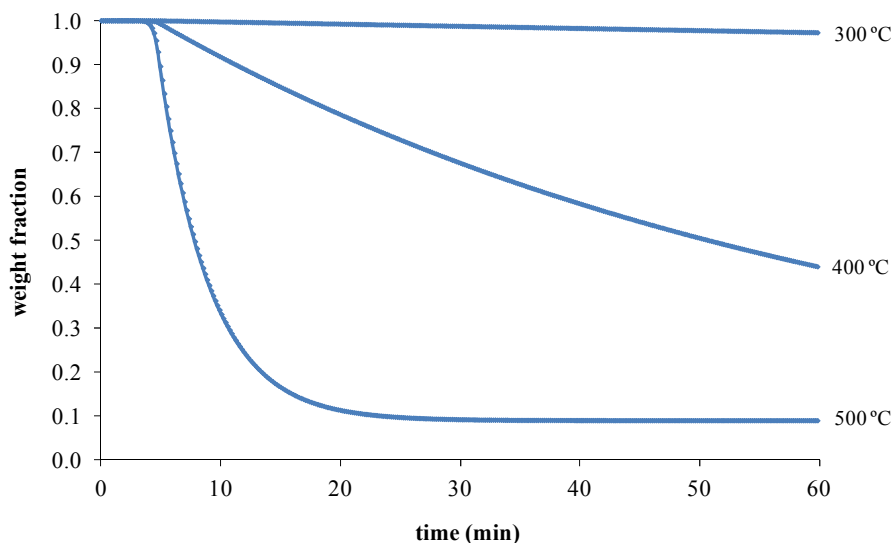
341 In comparing the profiles with the ones obtained for PCDD/Fs in our previous work<sup>10</sup>,  
342 the degree of halogenation at a set temperature is always lower in the case of bromine,  
343 since the activation energy barrier for bromination is higher than for chlorination, as  
344 indicated by Luijk et al.<sup>29</sup>. In addition, the formation of PBDFs of high bromination degree  
345 is more difficult than the low brominated ones, and compared to the chlorinated ones, due  
346 to steric hindrance in the molecule<sup>13</sup>.



347 **Figure 4.** De novo synthesis of PBDD/Fs at different temperatures: a) Isomer profile of  
 348 2,3,7,8-brominated congeners and b) Total homologue profiles.

349 A simulation of the isothermal runs has been carried out using the optimal kinetic  
 350 parameters obtained in the previous section (**Table 2**). The resulting curves, using an  
 351 estimated heating rate of 100 K/min in the laboratory furnace until the final temperature is  
 352 reached<sup>30</sup>, is shown in **Figure 5**. The predicted final weight fraction for each run  
 353 corresponds reasonably well with the remaining solid fraction measured after 60 min in the  
 354 laboratory reactor combustion experiments, which were 0.82, 0.50 and 0.05, at 300, 400  
 355 and 500 °C, respectively.

356 Comparing with the simulation of the oxidation of an analogous sample (with  $\text{CuCl}_2$   
357 instead of  $\text{CuBr}_2$ ) presented by Conesa et al.<sup>10</sup>, as in the previous study, a quite low  
358 degradation is observed at 300 °C, whereas an intermediate weight loss is found at 400 °C  
359 and almost complete at 500 °C. The behavior and weight fraction of the sample prepared  
360 with  $\text{CuBr}_2$  is similar to the one with  $\text{CuCl}_2$ , but slightly lower at any time.



361  
362 **Figure 5.** Simulated isothermal runs for the samples of activated carbon mixed with 50 wt.  
363 % of  $\text{CuBr}_2$  (sample 'py+wash(C+50B)').

364 Considering the yields of brominated dioxins and furans formed by de novo pathway in  
365 the present study, with a maximum at 300 °C, it seems that this mechanism is favored at  
366 low oxidative breakdown levels, i.e. when the carbonaceous surface begins to react with  
367 oxygen but still has a definite structure. At increasing temperatures, when the oxidation of  
368 the carbon is faster, formation of new PBDD/Fs decreases.

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