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De Novo Synthesis of PCDD/F by Thermogravimetry

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On the basis of laboratory experiments with model mixtures, the steps in the de novo synthesis of halogenated compounds were studied. The study was performed using a thermobalance to evaluate the temperature of the maximum rate and the kinetics of the decomposition of the materials in the presence of air. The effect of the presence of CuCl_2 and CuO with an atmosphere of HCl was studied. Analysis of the volatiles and solids after combustion in a horizontal furnace confirms the presence of organochloride compounds (including PCDD/F) at various temperatures. With the procedure that we followed, combustion is separated from pyrolysis, and it is possible to analyze the essential factors involved in the combustion process.

Introduction

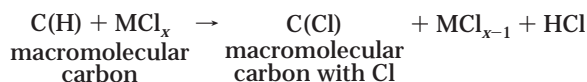
The formation of organohalogen compounds from the fly ash of municipal waste incinerators and sintering processes has been recognized as an important pathway for the release of polychlorinated dibenzodioxins (PCDD), furans (PCDF), and some other chlorinated compounds (1–14).

In combustion processes, two important steps are present in the solid phase (15): (i) a pyrolysis stage, in which the solid fed undergoes devolatilization reactions to yield volatiles (gases and tars) and a solid fraction (char); (ii) a combustion stage, in which the char undergoes heterogeneous reactions to yield gaseous products and an inert residue (ash). Pyrolysis and combustion stages may be sequential or contemporary, depending on the feature of the process considered (15, 16).

Several authors found that the residual carbon and high molecular weight compounds from incomplete combustion are the precursor materials for this so-called de novo synthesis. The formation of PCDD/Fs in the low-temperature region of incinerators could be regarded as an isothermal de novo synthesis from carbon and inorganic chloride in the fly ash.

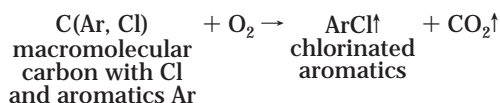
On the basis of laboratory experiments, two basic reactions were postulated to occur (3, 6):

(a) The metal ion-catalyzed transfer of chloride (halide) to the macromolecular structure of the carbon with the formation of carbon–halide bonds, in symbols:



It is important to note that only one chloride from the CuCl_2 is used in this stage and added to the macromolecular structure of the carbon.

(b) The oxidative degradation of these structures in the presence of oxygen and metal ions (Cu^{2+}) as catalyst to form carbon dioxide (as the main product) and volatile chlorinated aromatic compounds (as byproducts, originated in a non-complete oxidation):



Stieglitz et al. (2, 3) found that the degradation of carbon in the presence of such compounds can be described by a combination of two first-order reactions. These reactions and the change of the organic chloride content correlated with the de novo synthesis of organic chlorocompounds.

In a recent paper (17), we found that the reaction between metal chlorides and volatiles probably does not take place in the decomposition. Instead, it was suggested that all the CuCl_2 present reacts with the carbonaceous material in a first stage, being later degraded to form dioxins and furans structures. In this same paper (17), the effect of the surface area of the carbonaceous material is studied, confirming that the more surface area that has carbon, the more easily it is to decompose it, although some degenerated graphitic structure is needed for the de novo synthesis (3, 8, 9), as was pointed out earlier.

In the present paper, the de novo synthesis of PCDD/F is investigated using model mixtures. The following aspects were considered:

(i) Effect of CuCl_2 and also of CuO in the presence (or absence) of hydrogen chloride in the combustion of carbon.

(ii) Detailed thermogravimetric kinetic study of such processes. Special interest has been taken in the reproducibility of the runs and on the fitting of the runs performed at various conditions at the same time, as suggested in the specialized literature (15, 18, 19).

(iii) Confirmation of the de novo process by combustion of the materials at different temperatures: analysis of PCDD/F and comparison with the literature data reported and analysis of the temperature dependence using the kinetic parameters calculated in the thermogravimetric runs.

Experimental Section

The material employed was an activated carbon made by EUROGLAS with a very low chloride content; this activated carbon is used for the analysis of AOX (adsorbable organic halides), so it is expected to have a small amount of chloride. Table 1 presents the ultimate analysis of the sample performed in Carlo Erba Instrument model CHNS-O EA110.

Figure 1 presents a schematic of the treatment performed on the carbon. For some runs, the activated carbon was mixed with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in a proportion similar to that found in fly ash materials from municipal solid waste incinerators (7, 9). The exact amount of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ added was 1 g/g of sample. The selection of the proportion was also based on the previous work of Stieglitz (5), who studied the effect of several halides in different proportions. Other runs were performed with

TABLE 1. Ultimate Analysis of the Activated Carbon (wt %)

C	H	S	N	Cl ^a
80.8	0.65	2.0	0.24	0.02

^a Measured in an ECS 1600 Euroglas AOX analyzer, confirmed by X-ray fluorescence.

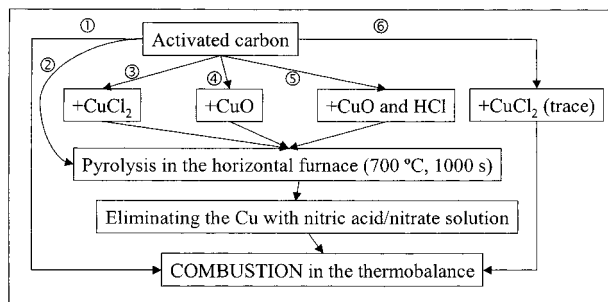


FIGURE 1. Scheme of the treatment processes.

the activated carbon mixed with CuO, maintaining the proportion C:Cu of the sample with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$.

These mixtures were pyrolyzed in a horizontal furnace (in a nitrogen atmosphere). The horizontal furnace has already been described (21, 22) and operated at 700 °C for 17 min (1000 s). The residence time estimated is 5–7 s inside the central part of the furnace (21). In the run performed using 38 ppm wt/vol of HCl in the atmosphere, the nitrogen bubbled into a solution of HCl 35%. The amount of HCl in the gas phase was measured by titration with a known amount of NaOH (measuring pH of the solution, flow rate, and time to be consumed of this basic compound). The final result indicates that an atmosphere of ca. 37.8 mg of HCl/L of gas was flowing (i.e., approximately 38 ppm wt/vol).

The solid samples obtained at the previous pyrolytic step were washed with an acid solution of nitric acid/nitrate until there was no detection of Cu in the washing fluid, before the combustion step, which is performed in a thermobalance. The objective of this washing step is to eliminate the excess of metal chloride to obtain a TG-curve with no interferences from the decomposition of the metal chloride. The washing is performed, introducing the sample in a quartz column; the washing solution flows through the vessel at a flow rate close to 2 mL/min. The operation is stopped when no Cu^{2+} is detected in the washing solution.

To confirm the formation of chloro compounds at low temperature, a series of combustion experiments were performed at 300, 400, and 500 °C in the horizontal furnace and in the presence of air. The volatiles were collected in a XAD-2 resin that was extracted with dichloromethane for 18 h. The solution was concentrated by evaporation with N_2 for MS analysis. The yields of solid residue at the three different temperatures (300, 400, and 500 °C) were 0.736, 0.167, and 0.078 for the runs performed with the material prepared in the presence of CuCl_2 and 0.982, 0.551, and 0.107 in the case of $\text{CuO} + \text{HCl}$. This solid fraction remaining after the decomposition was also extracted, and the fraction obtained was concentrated and analyzed. The analysis routine has been explained in another paper (21). The formation of PCDDs and PCDFs in incineration processes shows a typical congener distribution pattern including almost all 210 possible congeners (24). This study deals with tetra- to octachlorinated dioxins and furans. The results are given as the sum of different isomer groups (tetrachlorinated, pentachlorinated, ...). The HRGC–HRMS analyses were performed on a Finnigan MAT 95 apparatus, provided with a Hewlett-Packard GC. The spectrometer was operated in the electron impact ionization at 10000 resolving power. For PCDD/F analysis, ^{13}C -labeled PCDD/F standards (Wellington Labs, Canada) were used. Quantitative determination was performed by the isotope dilution method based on the relative response factors previously obtained from three standard solutions (EPA1613-CS1, -CS2, and -CS3).

The thermogravimetric study was performed in a thermobalance, at various heating rates (5, 10, and 20 K/min) and using sample amounts close to 8 mg. Twelve duplicated

TABLE 2. Scheme of Combustion Runs Performed at 10 K/min and Temperatures of the Maximum Rate of Decomposition

sample	runs performed (10 K/min) and T_{max} (°C)	
	material	T_{max}
1	activated carbon (C)	663
2	C pyrolyzed ^a and washed	650
3	C + 50% CuCl_2 pyrolyzed ^a and washed	485
4	C + 31.8% CuO pyrolyzed ^a and washed	659
5	C + 31.8% CuO in HCl atm pyrolyzed ^a and washed	555
6	C + 0.15% CuCl_2	604

^a Prepared in an horizontal furnace at 700 °C for 17 min in N_2 atmosphere.

runs have been performed in this equipment for the present study.

Runs were performed in a Netzsch thermobalance, model TG 209, controlled by a PC system operating under the Windows 3.11 operating system. The atmosphere used was synthetic air. Gas flowed at 20 $\text{cm}^3 \text{min}^{-1}$ (STP), according to the specifications of the equipment. The sample temperature was measured with a thermocouple directly at the crucible, i.e., next to the sample. Because a water-cooled microfurnace was used, the temperature could be rapidly lowered. The reproducibility of the experiments was very good (temperature deviations <0.1%) and acceptable, and the experimental data presented in this paper corresponding to the different conditions are the mean values of the runs carried out.

Discussion

Effect of Copper and Chloride on Combustion. Table 2 and Figure 2 present an outline of the combustion runs performed at 10 K/min. Furthermore, some samples were treated at three heating rates to perform a detailed kinetic analysis (15, 18, 19). Figure 3 presents these combustion runs at three different rates. The residue formed in each run performed is almost the same (approximately 8.8%, which would be the ash content of the carbon).

The maximum weight loss rate, commonly used in the literature to characterize char reactivity, occurs at different temperatures for the different samples. Table 2 also presents the temperatures of the maximum decomposition rate (T_{max}) for the different samples.

First of all, the differences between the curves obtained with activated carbon and the curves obtained with activated carbon pyrolyzed and washed are quite small (T_{max} at 663 and 650 °C), so the differences could be caused by the partial volatilization that occurred in the pyrolytic step. The curve corresponding to the activated carbon mixed with CuO, pyrolyzed and washed (T_{max} at 659 °C), is quite similar to that corresponding to the carbon, but the form of curve is different, especially in the last parts. Various papers in the literature (25–27) analyze the effect of CuO on the decomposition of activated carbon and/or fly ashes. The authors conclude that, to act as a catalyst, copper has to be present in an ionic form and not bound as in CuO. Nevertheless, small differences such as those presented in the present work have been pointed out between combustion of activated carbon in the presence and in the absence of CuO.

When CuCl_2 is added to the material, the process is highly accelerated. For sample 6, with a very low concentration of 0.05% Cu, the T_{max} is equal to 604 °C. The presence of traces of copper and other metals has been pointed out to catalyze the decomposition of such as materials (1, 5, 12) using metalchlorides as catalysts. In this way, we cannot separate the effect of the copper and that of the chloride. But, is the

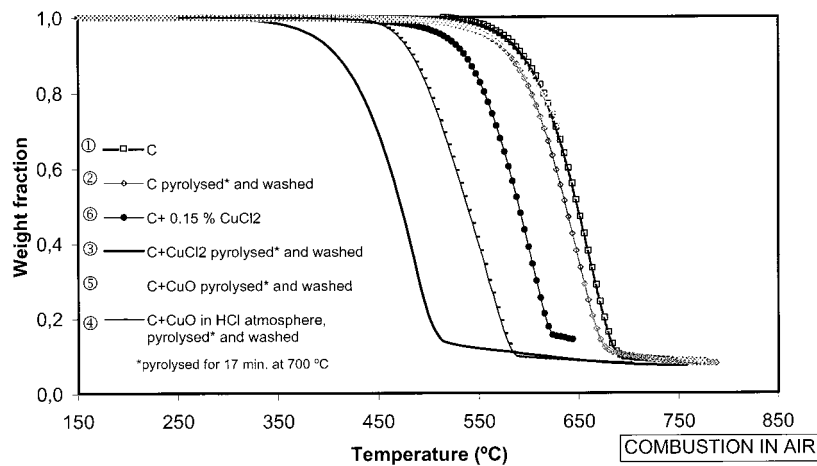


FIGURE 2. Combustion of different model mixtures at 10 K/min.

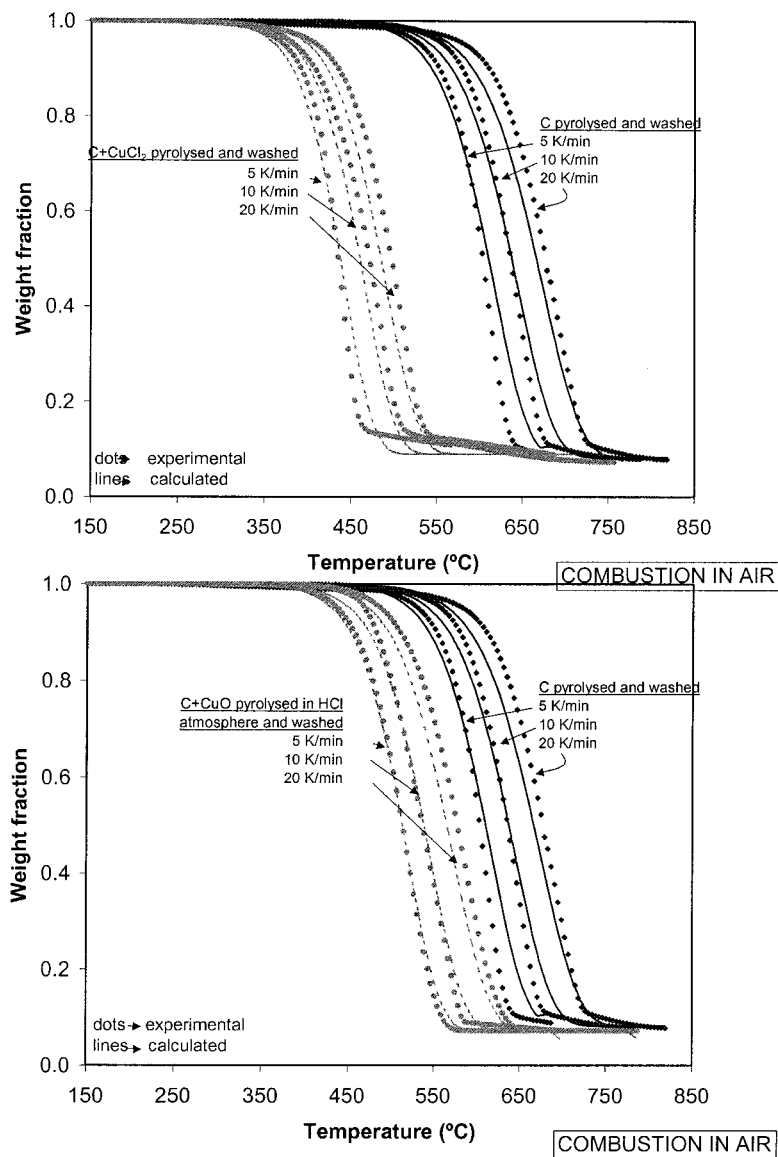
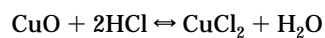


FIGURE 3. Combustion of three mixtures at three different heating rates. Activated carbon pyrolyzed alone and in the presence of (a) CuCl_2 and (b) $\text{CuO} + \text{HCl}$.

presence of copper or the presence of chloride responsible for the catalytic process?

With respect to the experiment performed with CuO in HCl atmosphere, probably the catalytic effect (see Figure 2)

is due to the formation of copper chloride through the following reaction (11, 28):



If the standard free energy change (ΔG°) of this reaction is calculated, and using the data of Yaw's handbook (28), it can be concluded that the former reaction is spontaneous at temperatures between 25 and 1200 °C. The correlation with the temperature would be as follows: ΔG° (J/mol) = 65.5 T (K) - 126 140.1. This indicates that the reaction is more spontaneous at low temperature than at high temperature. The ΔG° for the reaction between metal oxides and chlorine to form metal chloride and oxygen has been proposed as a measure of the efficiency of metal chloride volatilization (27). Similarly, in the case of the copper, it would be said that the efficiency of the formation of metal chloride is high at low temperature.

Comparing the curves in Figure 2 obtained by mixing the carbon with CuO, in the presence and in the absence of HCl, it is clear that the values of T_{\max} are quite different, 558 and 659 °C, respectively. Consequently, it seems that the Cu^{2+} ion is not uniquely responsible for the change in the temperature of the combustion, and it is necessary as a source of Cl^- to promote the decomposition. From Figure 2, it could be observed that if only a very small amount of CuCl_2 is added to the carbon (0.15 wt %), the combustion process is very much accelerated (T_{\max} at 604 vs 650 °C for the activated carbon alone). Schwartz and Stieglitz (6) indicated that the reaction $\text{C} + \text{O}_2$ to give carbon dioxide takes place at 700 °C without catalyst and at 345 °C if trace amounts of Cu^{2+} are present but always using chlorinated metals. Tuppurainen et al. (11) indicated that the highest PCDD/F formation rates occur in the presence of HCl and trace amounts of CuCl_2 . In addition, some research has been done about the effect of the chlorination of activated carbons on the reactivity vs the oxygen (29, 30). In these papers, it is concluded that the pretreatment of the surfaces with diatomic chlorine stabilizes the material, increasing the stabilization effect with the pretreatment temperature.

Kinetic Study. As pointed out previously, a kinetic study of the combustion of the different model mixtures prepared was performed. Following the scheme of Figure 1, the samples were washed with an acid solution in order to eliminate the excess of CuCl_2 before the thermogravimetric analysis. Note that the previous pyrolytic decomposition took place separated from the combustion considered in this section.

Figure 3 presents the combustion runs performed at three different heating rates. The kinetic model chosen for analysis was a single reaction of first order, with a simplified kinetic equation written as (18)

$$\frac{dw}{dt} = k_0 \exp\left(-\frac{E}{RT}\right)(w - w_\infty) \quad (1)$$

where w is the weight fraction (actual weight/initial weight), k_0 is the preexponential factor (s^{-1}), E is the activation energy (kJ/mol), R is the gas constant (kJ/mol·K), T is the temperature (K), and w_∞ is the weight fraction at time infinity, which accounts for the final residue of the process.

For the kinetic analysis, the following objective function (OF) has been selected:

$$\text{OF} = \sum_{j=1}^3 \sum_{m=1}^M \left[\left(\frac{d(w_{m,j})}{dt} \right)_{\text{exp}} - \left(\frac{d(w_{m,j})}{dt} \right)_{\text{cal}} \right]^2 \quad (2)$$

where m represents the experimental data at temperature T_m and time t_m of the experiment at heating rate j , and M is the number of experimental points. This OF has been used in various studies and has given satisfactory results (18, 19, 31).

TABLE 3. Values of Kinetic Parameters from TG Curves and VC Obtained

sample	allowing to vary k_0 and E			same k_0 for three materials		
	k_0 (s^{-1})	E (kJ/mol)	VC (%)	k_0 (s^{-1})	E (kJ/mol)	VC (%)
C	3.78×10^6	158.0	1.5	3.91×10^6	157.4	4.4
C + CuCl_2	1.71×10^6	121.4	3.0		126.6	3.1
C + CuO + HCl	1.96×10^6	135.0	1.5		140.9	3.0

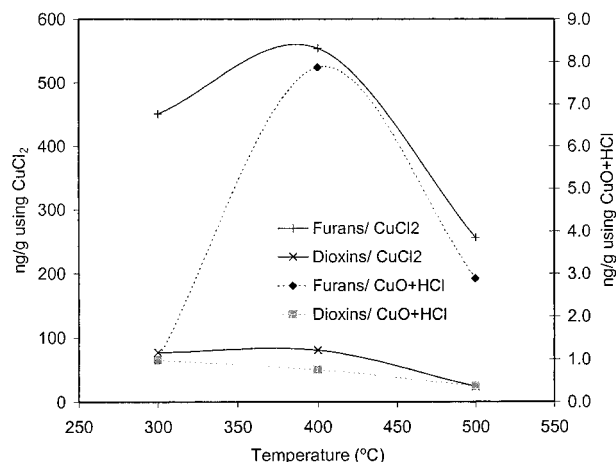


FIGURE 4. Total yield of dioxins and furans at three different temperatures.

To compare the different kinetic models, a variation coefficient (VC) is introduced:

$$\text{VC} (\%) = \frac{100 \times \frac{\sqrt{\text{OF}}}{M - P}}{\left(\frac{dw}{dt} \right)_{\text{exp}}} \quad (3)$$

where P is the number of parameters to be fitted. The integration of the differential eq 1 was performed using the fourth-order Runge-Kutta method, and the optimization has been done with the Flexible Simplex Method.

The results of the optimization are presented in Table 3. The first part of this table represents the better fit obtained for first-order reactions. In Table 3, the values of the variation coefficients are presented. Figure 3 presents also the calculated curves. Better fits are obtained when allowing varying the order of the reaction, having a minimum in the OF for an order close to 0.9.

The values of k_0 and E , although correlation parameters, could be related, respectively, to the amount of active sites in the activated carbon and to the energy of the bond formed (32, 33). The values of the preexponential factor are similar for the three samples analyzed, but the activation energy clearly indicates that the C-H bond (first sample) is quite stronger than the C-Cl bond (second sample). This is in accordance to the values of bond energy found in the literature (34). In the same way, the values of activation energy for $\text{CuO} + \text{HCl}$ treatment (third sample) would indicate that some C-H bonds are present and some others would indicate that C-Cl bonds are present.

Because of the similarity of the values of preexponential factors, the curves have been also fitted considering the same value of k_0 for the three materials. The results of the fit are presented in the second part of Table 3. It could be seen that the values of the activation energies follow the same trend

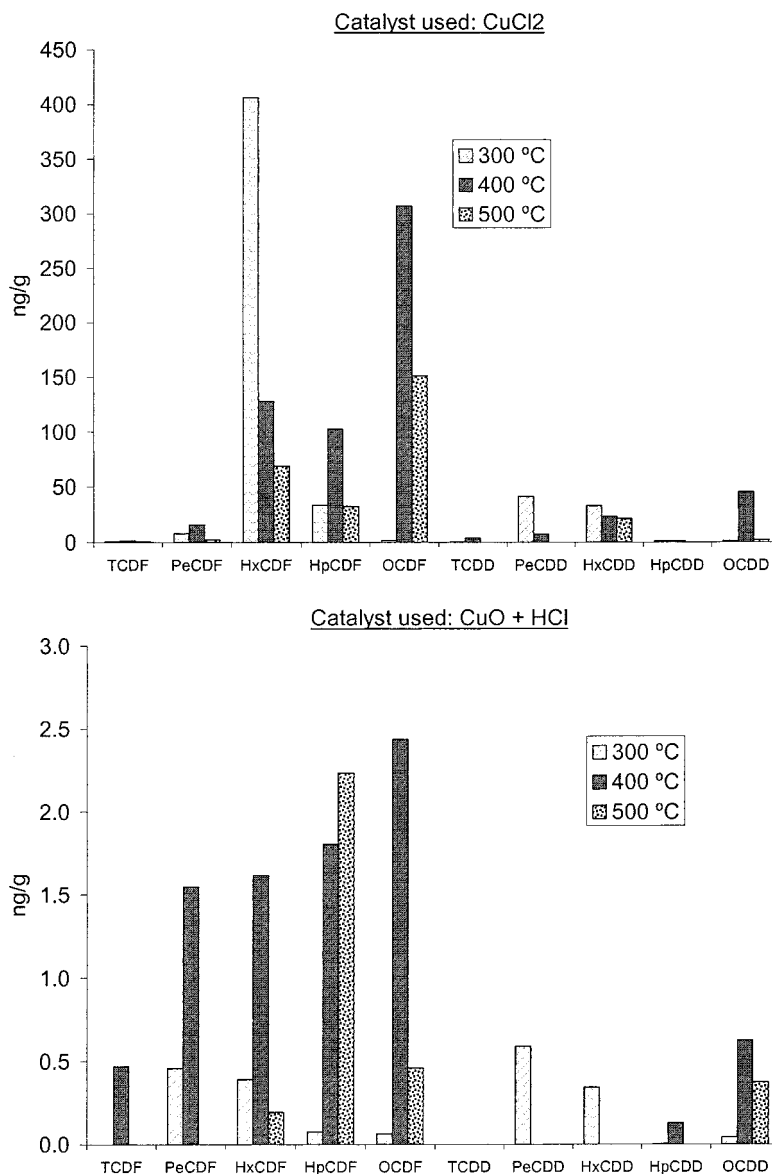


FIGURE 5. Yields of the different species analyzed. Combustion runs of the material pyrolyzed in the presence of (a) CuCl₂ and (b) CuO + HCl.

as that presented above, so although eq 1 is an approximate equation, it is remarkable that the activation energies very probably are in the following order: activated carbon > sample treated with CuO/HCl > sample treated with CuCl₂.

PCDD/F Analysis and Evolution with Temperature.

Some of the mixtures prepared by pyrolysis in the horizontal furnace and washed with acid as described before (second and third samples) were also decomposed in the presence of air at 300, 400, and 500 °C for 60 min in the same furnace. The volatiles evolved were extracted and analyzed, and also the residual solid was extracted and analyzed as described previously. Figure 4 presents the total yield of dioxins and furans obtained for the material prepared in the presence of CuCl₂ (second sample) and in the presence of CuO + HCl (third sample). In the same way, Figure 5a,b shows the contribution of each species to the total yield at the different temperatures.

Several aspects could be highlighted:

(i) The material prepared in the presence of CuCl₂ produces almost 100 times more PCDD/F than the material prepared in the presence of CuO + HCl (maxima around 550 and 8 ng/g, respectively).

(ii) Both materials present the higher yield of furans at 400 °C. In the case of dioxins, the maximum is not so clear, moving to 300 °C for the material prepared in the presence of CuO + HCl.

(iii) With respect to the yields of the different species, furans are more abundant than dioxins; furthermore, the ratio of furans/dioxins increases with temperature. In the furans series, hexachloro compounds are the most abundant at 300 °C, but at higher temperatures, the chlorination seems to be more pronounced. Something similar occurs with the dioxins, with the penta-substituted congeners being the most abundant at 300 °C. Both materials tested present similar behaviors.

Comparing these results with the previous literature, the total yield of dioxins and furans is similar to those found by other researchers (7, 12), and the typical "fingerprint" of the de novo process is obtained (7–9, 12). Nevertheless, the higher PCDD/F yield is usually found at 300 °C instead of at 400 °C as found in the present paper. Nevertheless, from the data presented it could not be concluded that the maxima is situated at 400 °C. It could be situated in some place

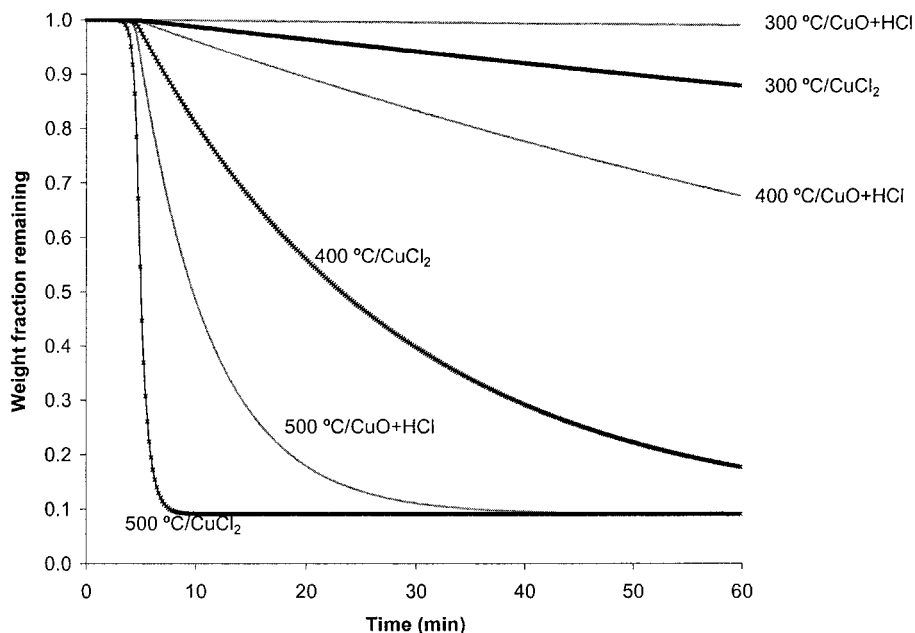


FIGURE 6. Mathematical simulation of the isothermal runs.

between approximately 350 and 450 °C; two maxima are even possible.

Xhrouet et al. (7) found two maxima in the production, at approximately 325 and 400 °C, using fly ash from a sintering process. The same authors indicated that the differential scanning calorimetry of the oxidation reaction showed that there were two different processes at the temperatures indicated (in dynamic runs at a heating rate of 1 °C/min) and proposed that actually two de novo syntheses took place. Before these researchers, Stieglitz et al. (4, 5) also found two processes in the combustion (at 5 °C/min) and talked about two maxima in the PCDD/F production (at 300 and 470 °C) (6). Nevertheless, the authors did not take into account that they analyzed the PCDD/F in isothermal runs and not in dynamic ones. The maximum rate of a process (indicated by the differential scanning measurements) in dynamic runs does not correspond to the maximum in isothermal runs. The maximum rate in the dynamic regime could be, for example, at 325 °C, but obviously in isothermal runs an increase of the temperature is accompanied by an increase in the rate of decomposition and probably in the amount of more volatiles produced.

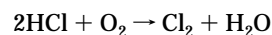
In the present work, a unique process in the decomposition is presented in the thermogravimetric study, with the process focus at ≈400 °C (at a heating rate of 5 °C/min). With the kinetic parameters calculated in the preceding study, the isothermal runs can be simulated subsequently. Figure 6 shows the result of the simulation. The heating rate until the final temperature has been estimated to be 100 °C/min (35).

The weight fraction remaining after 60 min of each run predicted in Figure 6 coincides quite well with the experimental ones obtained in the laboratory furnace (differences between 1.0 and 16.8%). In Figure 6, it could be noted that the weight loss in the experiments performed at 300 °C is quite low, being intermediate at 400 °C and total at 500 °C. It could be seen that, as expected, an increase in the temperature produces an increase in the volatiles released and in the rate of devolatilization. Taking into account that in the present work a maximum in the yield of de novo products at 400 °C is found, it is proposed that the de novo products are formed at intermediate levels of decomposition preferably, i.e., when the surface of the carbon has lost the most volatile products but still has a definite structure and

a high amount of volatiles. If the heating is too fast (as it is at 500 °C), the de novo synthesis is reduced. Another important fact that could be drawn from Figure 6 is that the total amount of volatiles produced from the material treated with CuO + HCl is quite low and is not only PCDD/Fs.

The difference of the results presented with the usually accepted 300 °C for the maximum in de novo synthesis may be due to the differences in the materials used and to the washing treatment that is performed to the sample used in this work, eliminating the excess of CuCl₂ that could be present.

Another important conclusion from the present study is that the presence of chlorine is not necessary for the formation of PCDD/F at yields similar to that of literature. This is in accordance with previous literature (14). Bearing in mind the procedure for the preparation of the different materials, it follows that there is no contact between the air in the combustion step and the HCl in the pyrolysis step. In this way the Deacon reaction



could not occur, and no elemental chlorine is present. Some authors, however, explain the effect of the copper on the formation of polychlorinated compounds by a Deacon reaction such as that presented with an intermediate formation of elemental chlorine (1, 36, 37).

Acknowledgments

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Literature Cited

- (1) Stieglitz, L.; Zwick, G.; Beck, J.; Bautz, H.; Roth, W. *Chemosphere* **1989**, *19*, 283–290.
- (2) Stieglitz, L.; Eichberger, M.; Bautz, H.; Roth, W.; Romer, J.; Schild, D. *Organohalogen Compd.* **1994**, *20*, 391–396.
- (3) Stieglitz, L.; Beck, J.; Zwick, G.; Roth, W.; Vogt, H. *Chemosphere* **1989**, *18*, 1219–1226.
- (4) Stieglitz, L.; Eichberger, M.; Scheihauf, J.; Beck, J.; Zwick, G.; Will, R. *Chemosphere* **1993**, *27*, 343–350.
- (5) Stieglitz, L. *Environ. Eng. Sci.* **1998**, *15*, 5–18.
- (6) Schwartz, G.; Stieglitz, L. *Chemosphere* **1992**, *25*, 277–282.
- (7) Xhrouet, C.; Pirard, C.; DePauw, E. *Environ. Sci. Technol.* **2001**, *35*, 1616–1623.

- (8) Huang, H.; Buekens, A. *Sci. Total Environ.* **1996**, *193*, 121–141.
- (9) Huang, H.; Buekens, A. *Chemosphere* **1995**, *31*, 4099–4117.
- (10) Baker, J. I.; Hites, R. A. *Environ. Sci. Technol.* **2000**, *34*, 2879–2886.
- (11) Tuppurainen, K.; Halonnen, I.; Ruokojarvi, P.; Tarhanen, J.; Ruuskanen, J. *Chemosphere* **1998**, *36*, 1493–1511.
- (12) Luijk, R.; Akkerman, D. M.; Slot, P.; Olie, K.; Kapteijn, F. *Environ. Sci. Technol.* **1994**, *28*, 312–321.
- (13) Vogg, H.; Stieglitz, L. *Chemosphere* **1986**, *15*, 1373–1378.
- (14) Stieglitz, L.; Vogg, H.; Zwick, G.; Beck, J.; Bautz, H. *Chemosphere* **1991**, *23*, 1255–1264.
- (15) Conesa, J. A.; Font, R.; Fullana, A.; Caballero, J. A. *Fuel* **1998**, *77*, 1469–1475.
- (16) Font, R.; Fullana, A.; Conesa, J. A. *J. Anal. Appl. Pyrol.* **2001**, *58–59*, 931–945.
- (17) Conesa, J. A.; Fullana, A.; Font, R. *J. Anal. Appl. Pyrol.* **2001**, *58–59*, 555–570.
- (18) Conesa, J. A.; Font, R.; Caballero, J. A.; Marcilla, A. *J. Anal. Appl. Pyrol.* **2001**, *58–59*, 619–635.
- (19) Caballero, J. A.; Font, R.; Conesa, J. A.; Marcilla, A. *Ind. Eng. Chem. Res.* **1995**, *34*, 806–812.
- (20) Weber, P.; Dinjus, E.; Stieglitz, L. *Chemosphere* **2001**, *42*, 579–582.
- (21) Fullana, A.; Font, R.; Conesa, J. A.; Blasco, P. *Environ. Sci. Technol.* **2000**, *34*, 2092–2099.
- (22) Conesa, J. A.; Fullana, A.; Font, R. *Energy Fuels* **2000**, *14*, 409–418.
- (23) Yasuhara, A.; Hiroyasu, I.; Morita, M. *Environ. Sci. Technol.* **1987**, *21*, 971–979.
- (24) Gullet, B. K.; Bruce, K. R.; Beach, L. O. *Chemosphere* **1990**, *20*, 1945–1952.
- (25) Fermo, P.; Cariati, F.; Santacesaria, S.; Bruni, S.; Lasagni, M.; Tettamanti, M.; Collina, E.; Pitea, D. *Environ. Sci. Technol.* **2000**, *34*, 4370–4375.
- (26) Froese, K. L.; Hutzinger, O. *Chemosphere* **1994**, *28* (11), 1977–1987.
- (27) Chan, C. C. Y.; Kirk, D. W. *J. Hazard. Mater.* **1999**, *B64*, 75–89.
- (28) Yaws, C. L. *Chemical Properties Handbook*; McGraw-Hill: New York, 1999.
- (29) McKee, D. W.; Spiro, C. L. *Carbon* **1985**, *23*, 437–444.
- (30) Evans, M. J. B.; Halliop, E.; Liang, S.; MacDonald, J. A. F. *Carbon* **1998**, *36*, 1677–1682.
- (31) Conesa, J. A.; Marcilla, A.; Font, R.; Caballero, J. A. *J. Anal. Appl. Pyrol.* **1996**, *36*, 1–15.
- (32) Font, R.; García, A. N. *J. Anal. Appl. Pyrol.* **1995**, *35*, 249–258.
- (33) Dellinger, B.; Taylor, P. H. *Cent. Eur. J. Public Health* **1988**, *6* (2), 79–87.
- (34) Lide, D. R.; Frederikse, H. P. R., Eds. *Handbook of Chemistry and Physics*, 74th ed.; CRC Press: Boca Raton, FL, 1993.
- (35) Fullana, A. Estudio de Contaminantes en Pyrolysis y Combustión de Neumáticos. M.S. Thesis, University of Alicante, 2000.
- (36) Gullet, B. K.; Bruce, K. R.; Beach, L. O. *Proceedings of the International Conference on Municipal Waste Combustion*, April 11–14, 1989, Hollywood, CA.
- (37) Hagenmaier, H.; Kraft, H. M.; Brunner, H.; Haag, R. *Environ. Sci. Technol.* **1987**, *21*, 1080.

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