Study of the memory effect of PCDD/F during the combustion of several biomasses in a moving grate boiler

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Abstract
The objective of this work was to study the influence of temperature on the PCDD/Fs behavior stored in biomass ashes issued from an automatic pilot-scale wood boiler. A mixture of these ashes with a dioxin mass ratio dry based of 5.9 μg kg⁻¹ was used for thermal treatment at temperatures ranging between 200 and 500°C. First tests were carried out in a macro thermo-gravimetric analysis instrument while a couple of other tests were carried out in a quartz-lined crossed fixed-bed reactor. These treated ashes were afterwards analyzed and their dioxin mass ratio was determined. Results obtained from these both experiments are radically different: ashes treated in macro-TGA contain 18 times more PCDD/Fs than the initial non-treated ashes while those from the reactor have 84% less of PCDD/Fs. Ninety-one percent of stored PCDD/Fs in the initial ashes were eliminated after 1h at 400°C in crossed fixed-bed reactor. Macro-TGA experiments are a representation of what happens during the shutdown and cooling phase of the boiler, some areas reaching temperatures for which the formation of PCDD/Fs is optimal. Without cleaning the boiler, a memory effect on further tests is observed.

Keywords PCDD/Fs · Emission · Combustion · Biomasses · Energy · Memory effect

Introduction
The necessity to reduce greenhouse gas emissions and to increase sustainable energy production has led to the promotion of renewable energy, such as biomass energy. According to International Energy Agency (IEA), the share of biomass in the total energy supply is about 9% in 2018, the highest among all other renewable energy sources (International Energy Agency 2020). According to the same source, the share of biomass and waste in the total primary energy consumption is relatively stable at around 10%. In France, biomass energy is the main source of renewable energy: it represents more than 55% of final energy production in 2020 and therefore contributes significantly to reduce fossil fuels consumption (Ministry of ecological transition 2020). Wood combustion energy represents the majority of the biomass energy, with 35.8% (114 TWh) in primary renewable energy production in 2019 in France (Phan and Plouhinec 2020). Currently, wood combustion is used to produce heat and/or electricity in plants with capacities ranging from a few kWth to more than 500 MWth (Nussbaumer 2010).

Nevertheless, the use of this source of energy may accord the forest preservation policy and the quality of the ambient air standards. At the European level, directives 2004/107/EC and 2008/50/EC set sanitary standards which involves the obligation to monitor air quality, to inform the population about air quality, and to implement action plans (The european parliament and the council of the european union 2004, 2008). Therefore, expanding the wood resource could be very challenging since not only natural wood is used. Indeed, wood waste, coated and treated wood, and even wood mixed with other waste will be increasingly used (Cesprini et al. 2020).

The literature on the subject of wood waste combustion is well developed. The most used fuels are wood collected from waste disposal sites, industrial by-products, and those
emerging from construction and demolition activities. These types of fuels have very different compositions and could contain high levels of pollutants, which both promotes harmful emissions such as “emissions of dioxins” (Martti 1996; Nussbaumer and Hasler 1997; Conesa et al. 2009; Weidemann et al. 2016; Moreno et al. 2016). PCDD/Fs refer to a large family of 210 members called “congeners.” This family of compounds includes 75 polychlorinated dibenzo-p-dioxins (PCDD) congeners and 135 polychlorinated dibenzofurans (PCDF) congeners. These compounds are oxygenated heterocyclic aromatic molecules. They are considered among persistent organic pollutants (POPs) (CITEPA / Format SECTEN 2017). PCDD/Fs are very chemically stable, not biodegradable, and persisting in the environment and in the living organisms in which they accumulate. The half-life of these pollutants is about 7 years in the human body (CITEPA / Format SECTEN 2017). PCDD/Fs emissions are expressed as international toxic factors or I-TEFs. On the basis on human and animal epidemiological data information, the International Agency for Research on Cancer (IARC) has classified PCDD/Fs as “carcinogenic to humans” (CITEPA / Format SECTEN 2019). Seventeen of these isomers have been considered extremely toxic, mutagenic, and linked to the suppression of the human immune system (Alexander et al. 2017). Nowadays, these compounds are certainly among the most problematic as pollutants.

It is currently evident that PCDD/Fs can be formed under appropriate combustion conditions when carbon, hydrogen, oxygen, and chlorine are present. Formation can occur in two ways: in vapor phase (i.e., through a homogeneous reaction at a range of temperatures between 500 and 800°C) or on solid surfaces such as soot or ash particles (i.e., through heterogeneous reactions at a range of temperatures between 200 and 400°C) (Stanmore 2004). These both temperature ranges are crossed during the operating of a biomass combustion facilities, along with the combustion processes and while passing through the heat exchanger and the flue gas treatment system.

While many investigations have been performed to study the emissions of PCDD/Fs from municipal waste incinerators as well as hazardous waste incinerators (Fångmark et al. 1994; Huang and Buekens 1995; McKay 2002; Zhang et al. 2014, 2018a; Block et al. 2015; Li et al. 2019), there are fewer reports on dioxin emissions from wood combustions and especially from wood waste combustion and wood co-combustion with other biomass fuels (Schatowitz et al. 1994; Samaras et al. 2001; Lavric et al. 2004; Smotka-Danielowska and Jabłońska 2021). These studies showed that the combustion of natural wood (oak, beech, pine) and uncoated chipboard (in stoves and in boilers) involves low PCDD/Fs emissions as long as the combustion is well controlled (adequate air supply and well-functioning of flue gas treatment devices in case of boilers). This is most likely due to the fact that these type of fuels do not contain high levels of pollutants such as chlorine and copper (Liao et al. 2016; Zhang et al. 2017).

It is common in biomass heating plants that the quality of the fuel changes over time and within supplies. It is known in the literature that chlorine has a crucial role in the formation of PCDD/Fs as one of the main parameters (Stanmore 2004; Zhang et al. 2017). This can lead to variable and insufficiently controlled emission levels: for instance, after burning a waste biomass fuel with characteristics that allow the formation of PCDD/Fs, the use of a clean biomass (natural forest chips) in the facility afterwards will lead to release these molecules again in the flue gases for next combustion tests. This phenomenon is called “memory effect” and needs to be understood. It was already observed in waste treatment plants (Li et al. 2011). It consists of an enrichment of PCDD/Fs in the fly ashes during the cooling of the gases and the removal of dust, followed by a partial flight (Buekens and Huang 1998; Zhang et al. 2017).

Several studies have investigated the thermal treatment of fly ashes from municipal solid waste (MSW) incinerators, in order to understand the phenomena occurring during the cooling phase of flue gas in the plant. Abe et al. showed that dioxin concentration in flue gas resulting from fly ashes melting furnace increased from 0.13 ng/Nm³ (at 12% of O₂) at the inlet of the cooler to 0.54 ng/Nm³ at the outlet (Abe et al. 1996). Another study by Takasuka et al. showed that an electrostatic precipitator ashes collected from a municipal solid waste incinerator can regenerate PCDD/Fs when heated in a rotary kiln at 300°C for 2 h (Takasuka 1995). Another study conducted by Cunliffe et al. showed a significant increase of PCDD/Fs concentration in waste incineration fly ashes when treated in a bench scale reactor at a range of temperature between 200 and 400°C (Cunliffe and Williams 2009). The highest concentration was measured in fly ashes treated at 250°C (3478 μg/kg of ash) which is the equivalent of 12 times the initial amount of PCDD/Fs measured in the non-treated fly ashes (Cunliffe and Williams 2009). In this study, emissions were also analyzed; the highest level of PCDD/PCDFs emission (11,715 μg/kg of ash, which represents the equivalent of 42 times the initial amount of PCDD/Fs measured in the non-treated fly ashes (Cunliffe and Williams 2009). Another study by Yokohama et al. has revealed that PCDD/Fs (contained in ashes collected from a cooling system of a municipal waste incinerator) start to gasify at 350°C by thermal treatment performed using gas chromatograph (GC-12A) column oven (Yokohama et al. 2008). It was shown that dioxin gasification behavior in fly ashes depends on
Various conditions such as flow rate, ashes weight, heating period, and temperature of treatment (Yokohama et al. 2008).

In this context, the present paper aims to study ashes behavior resulting from biomass combustion and to investigate if the same PCDD/Fs re-release phenomenon would act from this type of ashes. This was done by simulating what happens in the facility and what ashes undergoes when being exposed to different temperature levels during cooling and stops of thermal plant. These experiments will allow a better understanding of what happens during the combustion test particularly the memory effect and therefore allow to avoid and/or reduce as much as possible the formation of dioxins and their emissions.

**Materials and methods**

**Presentation of the fuel**

In order to better understand the mechanisms of formation of PCDD/Fs, the properties of the studied fuel must be perfectly known. The fuel is a mixture between natural wood chips and a wood waste coming from disposal plants. The proportion of the mixture was chosen to be 50/50 in order to get chlorine content close to 0.2%. Table 1 gives proximate/ultimate characteristics of the fuel. The elemental analysis was carried out by external accredited (COFRAC) laboratory “SOCOR.”

This fuel was a mixture of two different types of biomasses. It was prepared by mixing natural wood chips with a contaminated biomass which is waste wood collected from waste disposal centers (containing a higher level of chlorine compared to wood chips). The chosen ratio of these two components yielded a chlorine amount of 0.172 % (mass ratio). Nitrogen was also included in this analysis since it can lead to nitrogen oxide (NOX) emissions that are concerned by European standards. Compared to natural biomass compositions, this fuel contains high level of nitrogen. In natural biomass as wood chips, the proportion of nitrogen is close to 0.06 to 0.3% (Martti 1996; Archan et al. 2021). Moisture contents of woody fuels commonly used in biomass boilers is significantly higher than the one used in this combustion test (13.2%). In general, moisture content can range between 25 and 40% (on raw basis) for very wet fuels in thermal facilities for heat production and between 5 and 20% for less wet fuels (Rules of the Art Grenelle Environnement 2015). The average ash content varies also depending on the used fuel. A high ash content does not promote a good combustion and can lead to technical problems such as the formation of slag ash and the clogging of the exchanger surfaces (Rules of the Art Grenelle Environnement 2015). The measurement of the ash content was carried out according to NF EN ISO 1171.

| Fuel                  | Average ash (dry basis %) | Moisture (raw basis %) | C (%) | H (%) | O (%) | Cl (%) | S (%) | N (%) | Cu (mg kg⁻¹) | LHVb (dry basis kJ kg⁻¹) |
|-----------------------|---------------------------|------------------------|-------|-------|-------|--------|-------|-------|-------------|--------------------------|
| Biomass mixture       | 6.1                       | 13.2                   | 50.7  | 6.3   | 41.3  | 0.1    | 0.1   | 1.4   | 228         | 21,100                   |

The oxygen was calculated by difference; b) Lower heating value.
18122 (AFNOR 2015a, p. 18122) using a Nabertherm muffle furnace. The moisture measurement is performed according to NF EN ISO 18134-2 (AFNOR 2017, pp. 18134–2) and is repeated three times per sample. The calorific value measurements are performed on anhydrous samples. This analysis is carried out in accordance with the NF EN 14918 standard (AFNOR 2018, p. 14918) and using the 6100 Calorimeter from Parr.

The elemental analysis was conducted by a certified laboratory “SOCOR.” Carbon, hydrogen, and nitrogen were measured by a microanalyzer in accordance with the standard NF EN ISO 16948 (AFNOR 2015b, p. 16948).

Carbon, hydrogen, oxygen, and nitrogen content varies and depends on the biomass type (Smolka-Danielowska and Jabłońska 2021).

Chlorine and sulfur were measured using ion chromatography according to the internal method PA 334. According to the bibliography, copper has an important role by acting as a catalyst during the formation of PCDD/Fs, whether in the homogeneous pathway (in the gas phase), heterogeneous pathway (via the precursor pathway by catalyzing the condensation and chlorination of aromatic compounds, on solid surfaces), or during the “De novo” synthesis (Huang and Buekens 1995; Stanmore 2004). Therefore, this metal was added to the list of elements to be analyzed. It was analyzed following the standard NF EN ISO 16968 (AFNOR 2015c, p. 16968).

**Presentation of the thermal facility**

A biomass combustion test was carried out in an automatic 200 kW wood boiler (about 50 kg per hour) with a moving grate firing (Fig. 1). The removal of particles present in the exhaust gas was carried out with a cyclone and a fabric filter. Gaseous emissions were also measured. Emissions were analyzed with gas analyzers TESTO 350XL and PG 350 (HORIBA, KYOTO, JAPAN). The TESTO 350XL analyzes the composition of the flue gas (O₂, CO, NOₓ, SOₓ) by means of photochemical cells. CO₂ was not directly measured, but calculated from the O₂ value. While the second measuring device; the PG350 applied several quantification methods depending on the gases to be analyzed; paramagnetic detector for O₂, detector based on the chemiluminescence principle for NO and non-dispersive infrared for CO, CO₂ and SO₂. In addition, all deposited ashes were collected separately at the end of the test and after the required cooling time. The combustion test was carried out for about 8 h of run in order to obtain a sufficient quantity of ashes.

Combustion test was carried out with primary and secondary air supplies optimized to maintain adequate O₂ levels and to minimize CO emission. During combustion, the boiler was operated with a power of approximately 200 kW. Main gaseous and particulate emissions are presented in Supplementary Materials in Table S1.

Preliminary tests were performed with the by-pass of the bag filter in order to quantify the efficiency of the dedusting in terms of PCDD/Fs. The presence of the bag filter allows a reduction of the total amount of PCDD/Fs of 70%.

**Ash sampling protocol**

**Collected ashes in the facility**

The collect ashes at different sampling points in a thermal facility during biomass combustion are not common in the published literature. The results often represent the analysis of total deposited ashes in the boiler (bottom ash) and the analysis of total collected ashes from the heat exchanger and...
investigating critical aspects of biomass ashes has presented some biomass combustions ashes. It was shown that bottom ashes have a distinct chemical composition from that of the fly ashes. Excluding C, H and N, most elements of the biomass fuel are partially or completely remained in ashes (Freire et al. 2015).

**PCDD/Fs amounts**

Table S4 in Supplementary Materials shows PCDD/Fs amounts in collected ashes from each sampling point and their temperatures during the combustion test. Temperatures are measured in each collecting point during the combustion test by means of thermocouple type K fitted all along the plant. The total amount of PCDD/Fs measured is the sum of the amounts measured in each type of ashes. This total amount was 69,000 I-TEQ ng per kg of dry ashes (381,000 ng per kg of dry ashes). PCDD/Fs for each type of ashes expressed in I-TEQ ng per kg of dry ashes, in ng per kg, and in ng per ton of dry burnt fuel. PCDD/Fs ratios were also presented in the same table. Most of PCDD/Fs are found stored in the exchanger ashes (collecting point numbers 4 and 5) with a value of 84% of total PCDD/Fs. Starting from the exchanger, all collected ashes from the upstream of the combustion chamber (sampling point numbers 6 and 7) show high concentrations of PCDD/Fs. A total close to 90% of PCDD/Fs were measured in the exchanger, cyclone, and the bag filter ashes (sampling point numbers 4, 5, 6, and 7, respectively). This phenomenon has already been observed in municipal solid waste treatment plants and reported since the 1990s. It consists in an enrichment of PCDD/Fs amounts in the fly ashes during the cooling of the gases and the removal of fly ashes within the treatment devices (Zhang et al. 2017, 2018b). Thus, it can be assumed that the formation mechanisms during a biomass combustion could be similar to what has been observed in municipal incineration plants.

During this combustion test, emission factor for PCDD/Fs was also measured in three replicates in exhaust gas. An average was calculated according to the toxic equivalent systems I-TEQ WHO (1998) in ng per Nm$^3$. The maximal value of emitted PCDD/Fs for ICPE (Installation Classified for the Protection of the Environment) type 2910-B installations is 0.1 I-TEQ ng Nm$^{-3}$. The PCDD/Fs emission factor in the exhaust gas overshoot of 0.8 I-TEQ ng Nm$^{-3}$, which is 8 times higher than the allowed emission value.

**Experimental mixture of ashes (EMA)**

Three types of these collected ashes were selected to prepare a mixture of macroscopic composition that was treated afterwards in a macro-TGA and in a crossed fixed-bed reactor.
The choice was made according to the dioxin contents measured in the collected ashes. Used ashes ratios and dioxin contents are reported in the following section. The mixture is now described as EMA for Experimental Mixture Ashes.

**Elementary analysis** Table 2 shows the elemental composition of EMA which was calculated on the basis of the elemental compositions of different ashes from which EMA is composed. EMA is mostly high in chlorine, zinc, sodium, and sulfur. Copper is also present in a smaller amount.

The most abundant chemical elements measured in EMA are chlorine, potassium, sodium, and zinc. Sulfur and sodium are also present but in less significant quantities. The comparison of a mixture of ashes identical to ours from a similar combustion plant is not possible. Characterized ashes in literature are usually reported as a total ashes mixture called “fly ash” collected from the smoke treatment compartments (ESP, cyclone, etc.). Nevertheless, we attempted to compare the composition of our mixture with these kinds of ashes. The percentage of carbon in our mixture is higher than those measured in 3 types of ashes (1.6, 1.7, and 4.7%) collected from bag filters and ESP of several combustion plants. Chlorine percentages (6.2 and 16) of these ashes reported in the same study are higher than chlorine measured in EMA. All other element amounts measured in these 3 types of ashes are higher than amounts measured in EMA (Lundin et al. 2011).

**PCDD/Fs amounts** EMA is a mixture of 10% of exchanger ashes (collect point numbers 4 and 5), 30% of cyclone ashes (collect point number 6), and 60% bag filter ashes (collect point number 7). These proportions are chosen depending on the available quantities of ashes collected from the boiler. These three types of ashes have the highest PCDD/Fs levels compared to other collected ashes. The mixture was prepared in such a way to have a significant dioxin level in order to increase the detection of the phenomena during their future thermal treatments at temperature levels corresponding to those of the de novo synthesis and the precursor pathway. To ensure a significant level of PCDD/Fs, the PCDD/Fs content in the EMA was calculated based on the PCDD/Fs content measured at the selected points of collection and reported to their masses in the mixture (exchanger, cyclone, and bag filter ashes). Among the chosen ashes, exchanger and bag filter ashes contained the highest levels of dioxins: 182,000 and 133,000 ng per kg in the exchanger and 16,700 ng per kg in the bag filter. Values are shown in Table 3.

After thermal experiments in both macro-TGA and crossed fixed-bed reactor, samples were sent for dioxin analysis. An untreated ash sample (EMA) was also sent for analysis to determine the actual amount of PCDD/Fs (see Table 4).

**Macro-TGA and crossed fixed-bed reactors** In order to identify possible release of PCDD/Fs stored in ashes or the formation of additional quantities of PCDD/Fs during a stop action of the thermal facility, a laboratory crossed fixed-bed reactor and a macro-TGA were dedicated to test the impact of different temperature levels on EMA. Then regards to results obtained in macro-TGA, further experiments were performed in FBR at only one temperature, this temperature...

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**Table 2** EMA elemental composition

| Element | Composition (g kg⁻¹ dry burnt fuel) | Composition (mg kg⁻¹ dry burnt fuel) |
|---------|-------------------------------------|-------------------------------------|
| C       | 0.77                                |                                     |
| N       | 0.02                                |                                     |
| Cl      | 1570                                |                                     |
| S       | 210                                 |                                     |
| Cu      | 4                                   |                                     |
| Mn      | 12                                  |                                     |
| Ni      | 0.2                                 |                                     |
| Pb      | 60                                  |                                     |
| Zn      | 775                                 |                                     |
| Na      | 279                                 |                                     |
| K       | 1250                                |                                     |
| Fe      | 159                                 |                                     |

1 In g kg⁻¹ dry burnt fuel
2 In mg kg⁻¹ of dry burnt fuel

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**Table 3** PCDD/Fs amount of EMA

| Ash type   | Ash collecting point | Percentages (%) | Ashes mass (kg) | PCDD/Fs in ashes (I-TEQ ng kg⁻¹ of dry ashes (OMS TEF 1998)) | PCDD/Fs in ashes (ng kg⁻¹ of dry ashes) |
|------------|----------------------|-----------------|-----------------|---------------------------------------------------------------|----------------------------------------|
| Exchanger  | 4                    | 5               | 0.1             | 32,000                                                        | 182,000                                |
|            | 5                    | 5               | 0.1             | 26,000                                                        | 133,000                                |
| Cyclone    | 6                    | 30              | 0.6             | 1300                                                          | 9000                                   |
| Bag filter | 7                    | 60              | 1.2             | 2600                                                          | 17,000                                 |
| EMA        | Total                | 100             | 2               | 4900⁴                                                          | 28,600⁴                                |

⁴PCDD/Fs amount calculated from measured PCDD/Fs concentrations of sampling ash points and corrected by the proportion of these ashes in the mixture. The measured PCDD/F composition of EMA is given in Table 4.
was chosen to be the temperature where the amount of PCDD/Fs was the highest in macro TG tests.

In the first set of experiments, several tests were carried out with a macro-TGA (Nabertherm) using relative important masses at different temperatures and reaction times as shown on Fig. 2. A sample of ashes was placed in a crucible, heated at a selected temperature of 200, 250, 300, 350, 400, 450, and 500°C for a varying period ranging (between 15 min and 2 h). The temperature of the airflow in the oven was measured by two thermocouples (type N) as shown on Fig. 2. The airflow was in the range of 1.2 to 1.5 m³/h at 500°C. Macro-TGA experiments are a representation of what happens when ashes are deposited in the boiler and fumes pass above it, in particular in the exchanger where temperatures are in the same chosen range (between 200 and 500°C).

Ashes were initially dried in an oven for 48 h at 105°C and left to cool in a desiccator for 1 h. A mass close to 15 g of ash was weighed for each experiment. The ashes were then placed in a porcelain crucible and placed in the furnace of the macro-TGA for thermal treatment. At the end of the experiment, ashes were placed in the desiccator for 1 h before weighting, which was carried out using a precision scale type XS205 Mettler Toledo (with an error of

| Period (min) | Total PCDD/PCDFs (I-TEQ μg kg⁻¹ of ashes) | Total PCDD/PCDFs (μg kg⁻¹ of ashes) | Temperature (°C) | PCDD/PCDFs ratios | Enrichment factor |
|--------------|------------------------------------------|-------------------------------------|-----------------|-------------------|------------------|
|              |                                          |                                     |                 |                   | Macro-TGA        |
| 120          | 5.86                                     | 40.06                               | 200             | 0.36              | --               |
| 4.99         | 36.52                                    | 35.25                               | 250             | 0.39              | 0.9              |
| 7.13         | 70.13                                    | 300                                 | 0.36            | 1.2               | 0.9              |
| 44.10        | 590.82                                   | 350                                 | 0.22            | 7.5               | 1.7              |
| 71.30        | 655.49                                   | 400                                 | 0.09            | 12.2              | 16.4             |
| 22.10        | 197.81                                   | 450                                 | 0.11            | 3.8               | 6.1              |
| 1.21         | 13.90                                    | 500                                 | 0.26            | 0.2               | 0.3              |
| 60           | 107.00                                   | 1065.99                             | 0.10            | 18.3              | 9.2              |
| 2.80         | 22.58                                    | 500                                 | 0.17            | 0.5               | 0.3              |
| FBR          | 120                                      | 13.07                               | 400             | 0.23              | 0.3              |
| 60           | 0.95                                     | 10.56                               | 0.29            | 0.2               | 0.2              |

Table 4: Dioxin amount in the initial non-treated ashes (EMA) and in treated ashes in macro-TGA and in crossed fixed-bed reactor (FBR) (I-TEQ μg kg⁻¹ of ashes) and PCDD/Fs ratios at different temperatures.

Fig. 2 Macro thermogravimetric analyzer (macro-TGA) (furnace Nabertherm-balance Kern)
The weighting operation was performed each time using this same scale by the same person. In the second set of experiments, a crossed fixed-bed reactor was used to carry out two tests at 400°C, the first for 1 h and the second for 2 h (Fig. 3). Deposited ashes are passed through by a very low speed air flow of 0.06 m³/h. Experiments in this reactor are an illustration of what occurs during a combustion test, when fly ashes are trapped in the bag filter and crossed by the passing fumes.

As in macro-TGA experiments, ashes were initially dried in an oven for 48 h at 103°C and left to cool in a desiccator for 1 h. A mass close to 10 g of ashes were weighed and deposited on a quartz fiber filter fixed on a metal support which allows the air to flow through. After experiments, treated ashes were placed in a desiccator for 1 h before weighting. Percentages of mass loss of all treated ashes were calculated for both experiments.

The emitted gases at the outlet of the reactor and the macro-TGA were not analyzed to measure PCDD/Fs contents, since both flow rates and experimental duration were too low to collect sufficient matter. The measurements of PCDD/Fs would be included in the error range.

In order to understand the effect of temperature on the PCDD/Fs stored in ashes and the effect of the heating period, ashes recovered after these tests were sent for dioxin analysis.

These two both experiments are fundamentally different. In macro-TGA, ashes will be overflown by the airflow which is the same that occurs in the boiler with ashes deposited in the exchanger, part of the combustion chamber, and in the ash pan. In the fixed-bed reactor, ashes were crossed by the airflow which illustrate what occurs to ashes trapped in the bag filter. In the boiler, ashes are either passed through or overflown by air and gas flow, or both at the same time. In the area where they are deposited and/or trapped, the type of the trap (bag filter, electrostatic filter (ESP), etc.) could determine the phenomenon that the ashes would undergo.

**Diagram of the following stages of the research**

In this section, all the presented works previously are summarized in the diagram shown in Fig. 4 in chronological order. Firstly, a combustion test with biomass fuel is conducted.

The obtained ashes in the boiler are then collected and PCDD/Fs are analyzed (step 1). EMA is prepared from the collected ashes in order to be thermally treated either in macro-TGA (step 3) or in a fixed-bed reactor (step 4). After treatment, PCDD/Fs in treated ashes are analyzed (step 5). Comparing PCDD/Fs analysis in EMA and treated ashes will be useful to understand the formation and/or destruction of PCDD/Fs and the suspected memory effect.

**Results and discussions**

**Characterization of EMA after thermal treatment in macro-TGA**

Several experiments were carried out in a macro-TGA, while keeping the same temperature level, the treatment period was varied. Figure 5 shows the mass loss at different temperatures and reaction times (expressed in mass percentage) for all treated ashes during macro-TGA experiments. Residual carbon in treated ashes samples was measured in a muffle furnace at 850°C for 3 h for only EMA and ashes treated in macro-TGA. Residual carbon shown in Fig. 5 is the average of three replications for each measurement. Values and
Fig. 4 Diagram of the steps followed in the research

Fig. 5 Percentages of mass loss and residual carbon as a function of period and temperature treatment in macro-TGA treated ashes.
standard deviations are given in Supplementary Materials in Table S5.

Results showed that increasing the reaction time and the temperature of treatment in macro-TGA promotes mass loss. The mass losses were progressively more important with increasing temperature; the most important mass loss was about 13% which was measured in ashes after a treatment at 500°C for 2 h.

Residual carbon amounts were measured in treated ashes with the aim to determine a possible correlative link with formation of PCDD/Fs since these molecules can be produced via heterogeneous reaction in flue gas via the de novo mechanism (McKay 2002). In regard to deviation standards given in Supplementary materials in Table S5, before 350°C, the residual carbon did not react. A significant decrease of residual carbon was observed from 350°C and above mainly for samples heated for a duration of 2 h. This decrease is more important for samples treated at higher temperatures and for longer duration; residual carbon measured initially in EMA was 26.6% while the one measured in treated ashes for 2 h was close to 17.8% and 12.5% in ashes for 350°C and 500°C, respectively, and for the same duration.

As reported in the literature by Kakuta et al., the amount of residual carbon decreased as the heating temperature increased while treating fly ashes above 400°C (Kakuta et al. 2005). Two reactions could take place. Several metals as copper in ashes can promote carbon oxidation and gasification at low temperatures (Stanmore 2004). The mass loss in ashes is still higher than the loss of residual carbon leading that if these two reactions could occur in ashes during the thermal treatment, other reactions could also take place.

### PCDD/Fs amounts

Total amounts of PCDD/Fs in the initial and treated ashes in the macro-TGA are given in Table 4. The amount of PCDD/Fs measured in ashes treated at 200 and 250°C for 2 h in macro-TGA is nearly the same as the one measured in the initial ashes considering the measurement error of 0.003 μg kg⁻¹. Considering these error range, at temperature below 300°C, PCDD/Fs amounts are in the same order of magnitude as the initial amount measured in EMA, which means that no change occurs at these temperatures. However, only with a relatively small increase of temperature of 50°C, the amount of PCDD/Fs measured in ashes becomes slightly higher.

Table 4 shows that PCDD/Fs in ashes treated in macro-TGA significantly change depending on heating temperatures. The highest amounts were measured in ashes heated at 350, 400, and 450°C: 44.1, 71.3, and 22.1 I-TEQ μg kg⁻¹ of ashes, respectively, with a maximum at 400°C for 2h.

Above 400°C, the amount of PCDD/Fs measured in the treated ashes begins to decrease from 655.49 μg kg⁻¹ at 400°C to 197.81 μg kg⁻¹ at 450°C for 2h. Moreover, ashes treated at 500°C (for 1 and for 2 h) contained much lower dioxin amounts, even lower than the initial amount measured in non-treated ashes. For the same temperature level, ashes treated for a shorter period contained more PCDD/Fs (at 400°C and at 500°C). Many mechanisms can occur and influence the PCDD/Fs amount in ashes during the thermal treatment, regardless the experimental used set-up (Cunliffe and Williams 2007a). Formation reactions can occur via de novo synthesis from residual carbon/char in presence of an oxygen source (Stanmore 2004) which is available from ashes in the flue gas in our case. Other phenomena can also occur such as dechlorination, destruction, and desorption, particularly at temperature above 400°C. All simultaneously act varying the PCDD/Fs amounts (Cunliffe and Williams 2007a). In our case, the predominant phenomenon is the formation via De novo synthesis considering the high PCDD/Fs measured in ashes in macro-TGA experiments. As reported in a study carried by Kakuta et al. on several types of fly ashes, it showed that dioxin formation via de novo synthesis depended on gasification of carbon at 450°C regardless of the origin of carbon (Kakuta et al. 2007).

Enrichment factors of PCDD/Fs were calculated in treated ashes compared to the initial amounts of these compounds in EMA. The enrichment factor corresponds to the ratio [PCDD/F] in treated EMAash/[Initial PCDD/F] in non-treated EMAash. In the case of an enrichment factor less than 1, the amount of PCCD/Fs was decreased, as found in treated ashes at 200, 250, and 500°C for 2 h and at 500°C for 1 h. When the calculated enrichment factor is close to 1, it can be concluded that PCDD/Fs levels are kept at the same order of magnitude than initial EMA, as in the case of treated ashes at 300°C for 2 h. For all other treated ashes, the enrichment factors were significantly higher than 1 which means that PCDD/Fs amounts are largely increasing, especially in the case of treated ashes at 400°C for 2 h (enrichment factor of about 12). Therefore, it can be confirmed that from 300°C, treated ashes are enhanced with PCDD/Fs: PCDD/Fs amounts are increased by 22%, 653%, 1117%, and 277% in ashes treated respectively at 300, 350, 400, and 450°C for 2 h.

Similar to what has been seen in literature, residual carbon can influence PCDD/Fs behavior during thermal treatment, but it is difficult to evaluate how carbon content affects the formation of PCDD/Fs since no direct correlation was found. In a study investigating several types of ashes resulting from biomass combustion, high levels of residual carbon (also named “unburned carbon”) was found in the studied fly ashes compared to much lower levels in bottom ashes. These high levels of unburned carbon confirm that elevated amounts of PAHs and PCDD/Fs may have origin from the poor combustion performance (Freire et al. 2015). PCDD/Fs amounts were not exclusively related to the residual carbon
and this due to the presence of other factors that can affect the formation of PCDD/Fs (Freire et al. 2015).

Lundin et al. investigated the behavior of PCDD/Fs in ashes during thermal treatment in stainless steel reactor. Fly ashes were placed in a crucible in the middle of the reactor and heated to 300°C and 500°C in air. After the desired temperature of either 300 °C or 500 °C had been reached (after approximately 10 and 15 min, respectively), ashes are maintained for a further 30 min in the reactor. The type of reactor used is similar to the one used in our experiments (macro-TGA). This study showed that a significant increase of PCDD/Fs amount was found in treated ashes at 300°C. Conversely, PCDD/Fs amount measured in treated ashes at 500°C was much lower than both 300°C treated ashes and untreated ashes. The gas outlet was also sampled and analyzed. Results showed that PCDD/Fs was desorbed from ashes to the gas phase and concentrations in gas after treatment at 500°C were higher to the ones at 300°C (Lundin et al. 2011). At 300°C, the desorbed PCDD/Fs in the analyzed gas phases and the PCDD/Fs amounts in the treated ashes are proportional: the more PCDD/Fs the ash contains, the more PCDD/Fs are desorbed in the gas phase. This can lead to the conclusion that during our thermal tests, the increase of PCDD/Fs amounts in ashes after treatment at temperatures between 300 and 450°C should be associated with desorption toward the gaseous phase.

Based on macro-TGA dioxin results, if temperatures levels in the heat exchanger can be controlled to a maximum of 250°C, the release of PCDD/Fs formed and stored in the ash can be significantly reduced. Avoiding the phenomenon of release within the exchanger ensures that it would be automatically avoided after in the emissions (exiting the bag filter).

The PCDD/PCDFs ratios in ashes treated at temperature between 200 and 300°C in macro-TGA are similar to the PCDD/PCDFs ratio of the initial non-treated ashes, which means that the total amounts of PCDDs and PCDFs remains unchanged. However, concerning the 350 to 450°C treated ashes, ratios were lower: the amounts of PCDFs are much higher than those of PCDDs. This was also seen in thermal treatment under post-combustion conditions in which treated ashes predominantly contained PCDFs at temperatures higher to 275°C (Cunliffe and Williams 2007b). While PCDDs result mainly from stable ortho-substituted chlorophenols that have survived from the primary combustion, PCDFs can form from several other reactions, such as the decomposition of carbonaceous compound which leads to phenoxyl radicals. These can combine in the gas phase to form dibenzo-furans. Additionally, chlorophenoxyl radicals can undergo heterogeneous condensation to form PCDF (Cunliffe and Williams 2007b). This may explain the different increase of PDDs and PCDFs.

### PCDD/Fs congeners in treated ashes

Table 5 shows PCDDs congener distribution in ashes treated at different temperatures for 1 and 2 h. The distribution of PCDDs congeners is shown in Table 6. Seventeen congeners were analyzed: 7 PCDDs and 10 PCDFs. Congener amounts are given in μg per kg of treated ashes. Quantification limits of each PCDDs and PCDFs congeners are given in Supplementary Materials in Table S6.

Table 5: PCDDs congeners amounts in EMA and in treated ashes in macro-TGA and fixed-bed reactor at different temperatures for 2 h (table on the left) and for 1 h (table on the right) (μg per kg of ashes)

| PCDDs | 2 h of treatment | 1 h of treatment |
|-------|------------------|------------------|
|       | Macro TG | FBR | Macro TG | FBR |
| 2,3,7,8-TeCDD | 0.69 | 0.61 | 1.41 | 0.14 | 0.22 | 0.46 | 5.41 | 0.13 | 0.85 |
| 1,2,3,7,8-PeCDD | 1.75 | 1.71 | 2.14 | 7.08 | 12.60 | 4.53 | 0.30 | 0.52 | 0.12 | 2.96 |
| 1,2,3,4,7,8-HxCDD | 0.61 | 0.61 | 1.27 | 7.66 | 3.34 | 1.23 | 0.097 | 0.16 | 0.19 | 8.23 |
| 1,2,3,6,7,8-HxCDD | 0.71 | 0.72 | 1.26 | 6.15 | 3.66 | 1.39 | 0.15 | 0.15 | 0.21 | 7.30 |
| 1,2,3,7,8,9-HxCDD | 0.71 | 0.72 | 1.26 | 6.15 | 3.66 | 1.39 | 0.15 | 0.15 | 0.21 | 7.30 |
| 1,2,3,7,8,9-HpCDD | 1.00 | 0.99 | 1.88 | 8.60 | 5.40 | 2.08 | 0.37 | 0.22 | 0.31 | 11.10 |
| 1,2,3,4,6,7,8-HpCDD | 0.46 | 0.41 | 0.61 | 2.31 | 0.097 | 0.16 | 0.19 | 8.23 | 0.12 | 0.67 |
| OCDD | 0.21 | 0.23 | 4.32 | 33.40 | 9.22 | 3.42 | 0.21 | 0.11 | 16.30 | 0.97 |

The initial non-treated ash EMA showed a PCDDs congener distribution mainly composed of the most chlorinated congeners (octa, hepta, and penta-chlorinated). The same distribution was reported in Cunliffe and Williams in the original used fly ashes obtained from an operational municipal solid waste incinerator of a moving grate design (Cunliffe and Williams 2009).

PCDFs congener distribution in non-treated EMA showed less chlorinated congeners (tetra, penta, and hexa-chlorinated). This is similar to what has been shown in the analysis of several types of ashes taken from a waste incineration plant (not thermally treated); the amount of PCDFs is higher than that of PCDDs and the most chlorinated congeners are the most abundant ones (Cunliffe and Williams 2006).
In our analyses of treated ashes in the macro-TGA, both PCDDs and PCDFs families showed an increase of all congener amounts in treated ash between 350 and 450°C. Each congener was impacted by an enrichment in this temperature range and it was found that the most abundant PCDD congeners are the most chlorinated ones, octa-CDD and hepta-CDD, and the most abundant PCDF congeners are hepta-CDF, hexa-CDF, tetra-CDF, and penta-CDF. Mono-, di-, and tri-chlorinated congeners were not included in the analysis and comparison with literature data was not possible. As described by Lundin et al., the distribution of congeners well depends of the origin of ashes trapped in fabric filters or in electrostatic precipitator (ESP) from municipal waste plants (Lundin et al. 2011). These authors treated different ashes from incineration plants at 300°C and 500°C at laboratory scale. They also observed an enrichment in PCDD/Fs at 300°C and losses at 500°C. The enrichment and the distribution of congeners well depend on the origin of the ashes trapped in fabric filters or in electrostatic precipitator (ESP) from municipal waste plants (Lundin et al. 2011). These authors treated different ashes from incineration plants at 300°C and 500°C at laboratory scale. They also observed an enrichment in PCDD/Fs at 300°C and losses at 500°C. The enrichment and the distribution of congeners well depend on the origin of the ashes (fabric filter or ESP) and the elemental composition of ashes. Lundin and al. demonstrated that the enrichment was related to high amounts of residual carbon and copper. In their ESP ashes, the main enrichment both favors tetra and penta-CD/ Fs whereas for fabric filters ash, it could be observed an increase of mono to tri-CD/Fs leading to dechlorination reactions. At 500°C, Lundin et al. observed that tetra- to hepta-chlorinated dioxins and furans were favored.

Characterization of EMA treated in crossed fixed-bed reactor

After treatment in the crossed fixed-bed reactor at 400°C, measured mass losses were about 12% for both ashes treated for 1 and 2 h. Residual carbon measurement was not performed for theses ashes.

PCDD/Fs amounts

Table 4 shows the total amount of PCDD/Fs in the initial ashes and in treated ashes in crossed fixed-bed reactor. This table shows a significant decrease in the amount of PCDD/Fs at least of 75% compared to initial non-treated ashes (EMA). After treatment in a crossed fixed-bed reactor, the initial total amount of PCDD/Fs (in μg) is divided by at least a factor of 7. Enrichment factor was lower than 1 in both experiments at 400°C for 1h and 2h in the crossed fixed-bed reactor. They are quite constant in the range 0.2–0.4 for both experiments.

In a similar study by Lundin et al., ashes treated at 500°C in an experimental set-up under a flue of air resulted in a decrease of the total PCDD/Fs amount in ashes with a reduction minimum of 75% observed but leaded to high PCDD/Fs concentrations in the gas phase (Lundin et al. 2011). These results from Lundin et al. confirm ours results meaning that under a flue crossed of air, the oxygen may diffuse in the ash bed in order to induce oxidative reactions/and or desorption of these molecules in the gas phase at temperatures above 450°C. In addition, at temperatures ranging between 300 and 400°C and in absence of oxygen, PCDD/Fs amounts progressively declined in ashes allowing the desorption of PCDD/Fs in the gas phase (Cunliffe and Williams 2006, 2007b). The same result was shown in a study with fly ashes recovered from waste incineration, in which the amount of PCDD/Fs decreased significantly after being treated in quartz-lined crossed fixed-bed reactor (similar to the one

### Table 6

| PCDFs | Temperature | 2 h of treatment | 1 h of treatment |
|-------|-------------|------------------|------------------|
|       |             | Macro TG FBR     | Macro TG FBR     |
|       |             | 200 250 300 350 400 450 500 400 | 200 250 300 350 400 450 500 400 |
| 2,3,7,8-TeCDF | 4.17 | 3.68 | 3.81 | 14.30 | 78.10 | 22.80 | 1.19 | 1.20 | 2.94 | 70.90 | 0.68 | 4.74 |
| 1,2,3,7,8-PeCDF | 5.54 | 4.94 | 5.31 | 24.90 | 148.00 | 40.20 | 1.75 | 1.73 | 4.10 | 145.00 | 1.05 | 6.10 |
| 2,3,4,7,8-PeCDF | 3.81 | 3.39 | 5.31 | 41.60 | 59.80 | 16.30 | 0.81 | 0.78 | 1.61 | 99.20 | 0.48 | 4.10 |
| 1,2,3,4,7,8-HxCDF | 2.95 | 2.76 | 4.47 | 45.80 | 68.00 | 21.30 | 1.11 | 1.06 | 1.99 | 130.00 | 0.77 | 3.25 |
| 1,2,3,6,7,8-HxCDF | 3.42 | 3.19 | 4.88 | 53.70 | 83.90 | 26.40 | 1.15 | 1.18 | 2.34 | 146.00 | 0.88 | 3.75 |
| 1,2,3,7,8,9-HxCDF | 0.22 | 0.23 | 0.72 | 4.32 | 2.77 | 0.92 | 0.07 | 0.09 | 0.14 | 6.75 | 0.06 | 0.21 |
| 2,3,4,6,7,8-HxCDF | 1.67 | 1.71 | 5.85 | 59.30 | 28.30 | 8.62 | 0.50 | 0.44 | 0.79 | 69.70 | 0.39 | 1.73 |
| 1,2,3,4,6,7,8-HpCDF | 3.43 | 3.52 | 10.90 | 160.00 | 116.00 | 36.90 | 3.32 | 2.94 | 4.27 | 256.00 | 2.69 | 3.73 |
| 1,2,3,4,7,8,9-HpCDF | 0.60 | 0.61 | 2.97 | 29.90 | 6.73 | 1.58 | 0.16 | 0.27 | 0.24 | 19.90 | 0.24 | 0.65 |
| OcCDF | 1.08 | 1.25 | 7.33 | 49.20 | 9.90 | 3.66 | 0.95 | 0.94 | 0.94 | 24.50 | 0.98 | 1.15 |
used in our experiments) at 325, 350, and 400°C (Cunliffe and Williams 2007b). However, these experiments were carried out under simulated flue gas and for 4 days. It was shown in the same study that a considerable desorption of PCDD/Fs from fly ashes is observed at 275°C and above with a maximum at 350°C (Cunliffe and Williams 2007b).

According to the same study conducted by Cunliffe et al., from 325°C and above, the amount of desorbed PCDD/Fs is strongly increased, whereas the amount of remaining PCDD/Fs in ashes is strongly decreased (compared to original ashes and compared to treated ashes at lower temperatures).

The PCDD/PCDFs ratios calculated in the crossed fixed-bed reactor ashes are similar to the ratio calculated in the initial non-treated ashes, even though a remarkable decrease of the total dioxin amount was observed in these treated ashes. The PCDFs congeners were predominant in the untreated ashes (EMA) and also exceeded PCDDs congeners in the treated ashes. A study showed that PCDDs congeners decrease more markedly than did the PCDFs congeners. It also proved that the families behavior mainly depends on ash composition and that their concentrations after treatment vary uniformly: if PCDFs is predominant for example, it will be predominant in the treated ashes (Lundin et al. 2011).

Based on the bibliography, it can conclude that the decrease of PCDD/Fs observed in the treated ashes is due mainly to a phenomenon of desorption of these molecules from solid phase to the gas phase.

**PCDD/Fs congeners in treated ashes**

Table 5 and and Table 6 provide the PCDDs and PCDFs congener distribution in treated ashes in the crossed fixed-bed reactor.

As found in the macro-TGA treated ashes, the most abundant PCDDs congeners that have been analyzed (only 7 molecules) are the most chlorinated ones: octa-CDD and hepta-CDD while, the most abundant PCDF congeners that have been analyzed (only 10 molecules) are hepta-CDF, tetra-CDF and penta-CDF whatever the duration time. The same result was found in a study conducted by Cunliffe et al. in treated fly ashes in a quartz lined reactor (Cunliffe and Williams 2007b).

The total PCDDs congeners measured in ashes after treatment was about 22% of the initial PCDDs in EMA. While, the total PCDFs congeners was about 28% in ashes treated for 1 h and 36% in ashes treated for 2 h. In a similar reactor as the one used in our experiment, ashes treated under a mixture of 8.8% O₂/92.2% N₂ contained 1.4% of the total initial PCDDs content in the original non treated ashes and 10.7% of the total PCDFs content, after 50 min of heating at 398°C (Addink et al. 1995). Considering that although the used reactor and the temperature treatment level are similar in the study of Addink et al., the operating conditions (gas flowrate, the treatment duration and the ash mass) are different. If the quantity of ashes initially used (2 g) and the total gas flowrate (6.64 10⁻³ m³ h⁻¹) were lower than in our experiment, the ratio mass/flowrate is in the same order of magnitude than in our experiment being 300 and 250, respectively, meaning that both experiments are quite similar and could be compared. As in our study, it can be seen that the PCDDs content reduction is more significant than the PCDFs content after a treatment at 400°C especially for 2 h.

**Comparison of EMA characterization from macro-TGA results and crossed fixed-bed reactor**

Figure 6 allows the comparison of both experiments.

The calculated percentages of mass loss were greater in ashes treated in crossed fixed-bed reactor tests than those treated in the macro-TGA. These differences are related to the characteristics of each device and their specific phenomena: in the crossed fixed-bed reactor, the air is directly in contact with ashes and can more easily oxidize the carbonaceous compounds present (soot carbon, organic compounds). In contrast, in macro-TGA, the air circulating in the kiln flows over the superficial layers of ashes but not directly through it.

While treating ashes at temperatures between 200 and 300°C, the effect of the period is rather insignificant even if the mass loss seems to increase but it remains relatively constant if the errors are considered. However, between 350 and 500°C, the influence of the treatment period is significantly more important. At a temperature higher than 300°C, the mass loss is linear with the duration time. In ashes treated at 350°C, the mass loss increased by 50% between 15 and 120 min. As for ashes treated at 500°C, the mass loss increased by 34% between 15 and 120 min.

Table 4 shows the quantities of PCDD/Fs measured in ashes treated in the crossed fixed-bed reactor and in macro-TGA, at the same temperature level (400°C) and for the same period of thermal treatment. Results shows that PCDD/Fs amounts in crossed fixed-bed reactor ashes are much lower than those treated in the macro-TGA. If an enrichment of PCDD/Fs is observed on ashes in macro-TGA, the opposite is true in the fixed-bed reactor.

In both experiments (macro-TGA and crossed fixed-bed reactor), several phenomena on PCDD/Fs can simultaneously occur, such as their oxidation with oxygen from the air, or a catalytic oxidation reaction, or their destruction by the temperature or desorption into the flue gas stream. All these different phenomena act to change PCDD/Fs levels and occur simultaneously (Cunliffe and Williams 2007a). PCDD/Fs can also be directly destroyed only by the effect of temperature or by oxidation, although this cannot be the dominating phenomenon (in both experiments) since these...
Compounds can be stable up to 800°C and their destruction by incineration in the flue gas is only total above 1300°C (Alexander et al. 2017). Nevertheless, several studies show that with thermal treatments above 400 and 500°C, PCDD/Fs in the ashes begin to decrease. Destruction of PCDD/Fs could occur during the trapping of ashes in fabric filters and ESP in incineration plants (Cunliffe and Williams 2007a; Lundin et al. 2011). In addition, dioxin formation reactions can also occur alongside other reactions, since the chosen temperature range is adequate for formation, specifically via heterogenous reactions. Hence, the competition between the different phenomena and the different predominance lead to these different results obtained from both experiments: macro-TGA and crossed fixed-bed reactor.

In one hand, some studies showed that degradation of PCDD/Fs in closed systems (glass ampules) and under a gas flow is possible in an oxidative atmosphere (Hagenmaler et al. 1987; Lundin and Marklund 2005). Degradation can occur either via dechlorination/hydrogenation reactions or via oxidation reactions. In the other hand, other studies showed that when the outlet gas phase is analyzed, high PCDD/Fs concentrations are found after ashes heat treatment (Cunliffe and Williams 2007a, b; Lundin et al. 2011). Comparing our results to heat treatment carried out in similar set-ups, it can conclude that changes observed in PCDD/Fs levels were mainly associated to the desorption of these molecules from the solid phase to the gas phase. Although degradation may occur, it is not the dominant phenomenon.

Based on results shown in Table 5 and Table 6, it can be seen that in both macro-TGA and crossed fixed-bed reactor, the initial PCDFs distribution of EMA changed: most chlorinated PCDFs congeners were significantly more abundant, while there were no remarkable changes in the distribution of PCDDs congeners, even in treated ashes at 500°C with lower PCDDs amounts. According to literature, this can be related to the fact that dechlorination of molecules with few chlorine atoms is faster compared to highly chlorinated ones (Lundin et al. 2011). In addition, it can confirm that dechlorination is more important for PCDFs than PCDDs congeners.

**Conclusion**

Collected ashes from biomass combustion test were heated in macro-TGA for 1h and 2h at different temperatures and in crossed fixed-bed reactor at 400°C for 1 and 2 h.

The macro-TGA results have shown that there is an increase in PCDD/Fs amounts measured in the treated ashes in particular in a range of temperatures between 350 and 400°C. PCDD/Fs amounts were 18 and 12 times higher in treated ashes at 400°C for 1 h and 2 h, respectively, compared to the initial amount measured in the non-treated ash. The increase of PCDD/Fs amounts in the treated ashes in macro-TGA would explain why the formation of PCDD/Fs persists over time, particularly during the cooling phases of the combustion plant and consequently why a memory effect could be observed, if the plant is not cleaned of all solid residues from the previous test to the next one. The increase of dioxin amounts in treated ashes can also be combined and followed by a release of PCDD/Fs in the vapor phase. Since these macro-TGA experiments illustrate the ash cooling process within the boiler and especially in the exchanger, based on these results, at the boiler scale, in order to reduce and/or avoid the phenomenon of release in the exchanger, the temperature...
should be well controlled to a maximum of 250°C. Avoiding this phenomenon within the exchanger may ensure that it would be automatically avoided in the exhaust gas.

In contrast, the heat treatment tests in crossed fixed-bed reactor did not show the same results. PCDD/Fs measured in ashes treated in this reactor were significantly lower than in initial non-treated ashes and in macro-TGA treated ash: 91% of the PCDD/Fs are removed/eliminated after 1h at 400°C. At the same temperature, a 2-h heating treatment can lead to a reduction of 85% of the initial amount of PCDD/Fs. Based on similar experiments in literature, analyzed outlet gas phase showed high PCDD/Fs concentration.

As seen in the crossed fixed-bed reactor, PCDD/Fs stored in ashes are eliminated at 400°C. However, the operating temperature of the bag filter range is between 110 and 180°C; consequently, it would not be possible to raise temperature to 400°C to ensure PCDD/Fs removing. The optimized solution to drastically reduce emissions of PCDD/Fs in the exhaust is to trap and evacuate the flying particles in order to avoid their emission and their storage in an area with a level of temperature allowing a desorption of PCDD/Fs.

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Declarations

Ethics approval The authors attest that this work was not submitted elsewhere in another journal.

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