Characterization of gaseous emissions and ashes from the combustion of furniture waste

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Abstract

Gaseous emissions and ash obtained in the combustion of furniture waste have been studied, with particular emphasis on the emissions of hazardous pollutants, such as PCDD/Fs and dl-PCBS. Two different combustion procedures were carried out, one of them in a conventional residential stove (without an automatic control of combustion air and bad mixing of combustion gases with air), and the other in a laboratory-scale reactor (operating under substoichiometric conditions).

Three different experiments were carried out in the residential stove, in which the gaseous emissions and ashes obtained were analysed. The fuel burnt out in two of the experiments was furniture wood waste and in one of the experiments, the fuel burnt out was briquettes composed of a mixture of furniture wood with 10 wt.% of polyurethane foam. One of the purposes of these experiments was the evaluation of the possible inhibition effect of the higher nitrogen content on the formation of PCDD/Fs. Slight inhibition of the PCDD/F formation was found although, it is noteworthy that the lowest yield of PAHs, volatile and semi-volatile compounds were obtained in the combustion of these briquettes.

In all experiments, the emission factors of polychlorinated dibenzo-*p*-dioxins and dibenzofurans and dioxin-like polychlorinated biphenyls (PCDD/Fs and dl-PCBs) were between 29 and 74 ng WHO-TEQ/kg sample burnt, lower than that obtained by other authors in the burning of pine needles and cones.

PCDD/Fs and dI-PCBs emissions from furniture wood waste combustion were also analysed in the laboratory scale reactor at 850 °C and the results were compared with the values obtained from the combustion of solid wood (untreated wood). The total equivalent toxicity obtained was 21.1 ng WHO-TEQ/kg sample for combustion of furniture wood waste, which is low in comparison with those obtained for other waste combustion in similar conditions.

In the laboratory scale reactor, PCDFs were the dominant compounds in the profiles of PCDD/Fs, by contrast, in the combustion in the residential stove, the majority compounds were PCDDs, due to the different operation conditions.

Keywords: Combustion; Furniture waste; Nitrogenated compounds; PCDD; Fs; PCBs; Organic pollutants

1 Introduction

The European Directive on solid waste management (Directive 2008/98/EC) proposed a hierarchic waste policy, which consists of: (1) prevention; (2) re-use; (3) recycling; (4) other recovery; e.g. energy recovery; and (5) disposal.

Panelboard manufacture, used for animal bedding, or used as bulking agent for composting are different ways of recycling wood. Nevertheless, it must be taken into consideration that the additives present in furniture wood, such as metals, chlorine, pentachlorophenol, etc. could restrict the recycling. For instance, the German Ordinance on the Management of Waste Wood (BMU, 2002) regulates the limits of some elements/compounds for the wood waste used in the manufacture of panelboard; but treated wood usually exceeds these limits. Therefore, combustion for energy recovery can be an appropriate management method for furniture wood waste, avoiding its disposal in landfills.

Lignocellulosic wastes, such as wood, are being widely used as a renewable energy source due to the significant reduction in the emission of acid and greenhouse gases, as well as improved management of natural resources. Therefore, energy recovery is a possible way to manage with these wood wastes, because its use improves the management of environmental resources and wastes.

The additives contained in furniture wood waste hinder their recycling and re-use, so furniture wood combustion shows some disadvantages compared with natural wood combustion, such as NO_x increase, higher heavy metal emissions and increase of PCDD/Fs, dioxin-like compounds and other organic compounds (Lavric et al., 2004).

Furniture wood contains nitrogenated adhesives, such as urea formaldehyde, melamine formaldehyde, melamine-urea-formaldehyde resins, polymer isocyanates (Pizzi and Mittal, 2011), flame retardants, such as ammonium salts (Di Blasi et

al., 2008; Kozlowski and Wladyka-Przybylak, 2001), and amino resins modified with phosphoric acid (Gao et al., 2003). Nitrogen content produces NO_x, NH₃ and HCN predominantly during biomass combustion (Stubenberger et al., 2008). NO_x emissions can come from three routes of formation during combustion: thermal NO_x is produced at temperatures higher than 1100 °C from atmospheric nitrogen, the prompt NO_x is formed from the radical CH as an intermediate at the flame front and the fuel- NO_x is formed from nitrogen of the fuel (Werther et al., 2000). Nevertheless, at temperatures lower than 1000 °C, NO_x is expected to be produced mainly from the nitrogen of the fuel (Roy and Corscadden, 2012).

Not only heavy metal emissions (particles, volatile halides, etc.) are harmful, but also the pollutant retention in the ash, which restricts its use for disposal in agricultural soil (Obernberger et al., 1997).

On the other hand, it must be noted that incomplete combustions cause environmental concerns, mainly due to particulate matter (PM), polycyclic aromatic hydrocarbons (PAHs) and carbon monoxide (CO) emissions. For instance, Bari et al. (2011) reported that the smoke formed during the combustion of wood in residential heating contains small particles, and thus represents a particular health risk because of its respirability and content of polycyclic aromatic hydrocarbons (PAHs).

Some of the most harmful emissions to human health are the polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and dioxin-like polychlorinated biphenyls (PCBs). Their formation is probably via two main pathways (Salthammer et al., 1995): (i) via precursor compounds such as pentachlorophenol, which has been widely used as a preservative in wood, and (ii) the novo mechanism, which consists of the combination of carbon, oxygen and chlorine at low temperatures (between 200 and 400 °C) and catalyzed by a metal, mainly Cu.

The presence of chlorine in wood increases the PCDD/F formation, due to either salt-laden wood or organochlorinated additives, such as pentachlorophenol (Altwicker et al., 1990; Preto et al., 2005; Thuβ et al., 1997; Yasuhara et al., 2003).

Some typical preservatives of wood show Cu in their composition, such as copper chromium arsenate, copper chrome boron, alkaline copper quaternary, copper boron azole, and copper naphthenate. It has been demonstrated that the presence of Cu increases the formation of PCDD/F (Tame et al., 2003b, 2005). The combination of chlorine and copper in wood preservatives shows a higher formation of PCDD/F; for instance, the tebuconazole pesticide, which is a chlorinated compound, present in copper boron azole preservative provides chlorinated precursors for PCDD/F formation and Cu as a catalyst (Tame et al., 2005).

Besides the catalytic effect of copper, Qian et al. (2005) and Pandelova et al. (2007) found that other metal oxides also promote formation of PCDD/Fs. For instance, TiO₂, which is present in furniture wood due to the paints, also shows a promotion effect on PCDD/F formation, although, the strongest catalytic effect was observed with CuO.

Combustion conditions have also been found to be an important factor in the formation and distribution of PCDD/Fs. Salthammer et al. (1995) observed that the type of combustion chamber has a significant influence on the distribution of congeners. A literature survey concludes that the conditions to minimize PCDD/F formation are maximization of combustion temperature, gas residence time and turbulence of the gases, and an excess of oxygen of 3–6% (v/v) (McKay, 2002).

On the other hand, the PCDD/F inhibition due to nitrogen content has been found in studies of wood combustion. For instance, Skodras et al. (2002) studied the combustion and the co-combustion of natural wood, Medium-Density Fibreboard (MDF) (with nitrogen additives), power poles (with high metal content) and lignite and they observed that the lowest PCDD/Fs emissions were during combustion of fuel containing MDF. Bhargava et al. (2002) also studied the PCDD/F emissions from combustions of chipboard and MDF (with nitrogen additives) in a cone calorimeter. They found toxic equivalencies of 20.5 and 15.4 ng TEQ/kg sample for chipboard and MDF, respectively.

Gaseous NH₃ has been also found as an effective inhibitor of PCDD/F formation (Hajizadeh et al., 2012; Ruokojärvi et al., 2004, 1998). Furthermore, the first stage of combustion is a pyrolysis process, in which the ammonia formation is high if the nitrogen content of the fuel is significant (Moreno and Font, 2015).

Therefore, the objective of the present work is the study of the toxic emissions and the toxic content of the ashes from the combustion of furniture waste. Experiments were carried out in a residential stove (without an automatic control of the combustion air and bad mixing of the combustion gases with air) and with a laboratory scale reactor (operating under substoichiometric conditions with airflow and temperature control but a good mixing of volatiles evolved) to observe the formation of pollutants under these conditions.

Three different experiments were carried out in the residential stove. In two of them, the fuel used was furniture wood waste ant the other experiment was carried out with briquettes of furniture wood waste with the addition of polyurethane foam (material with higher N content) to test the possible inhibition of PCDD/F formation by the ammonia formation during the pyrolysis stage. A previous work concluded that briquettes of furniture wood with an addition of 10 wt.% of polyurethane foam show good quality (durability and density of the briquettes) (Moreno et al., 2016). For this reason, this combustion experiment was carried out with briquettes of furniture wood with 10 wt% of polyurethane foam.

PCDD/Fs and dioxin-like PCBs were also analysed in a laboratory reactor under fuel rich conditions with furniture wood waste (treated wood) and solid wood (untreated wood), in order to compare the effect of the global effect of the additives present in furniture wood waste (higher chlorine, metal and nitrogen content). In this reactor, the combustion conditions are perfectly controlled, therefore the differences in the PCDD/F and dl-PCB formation can only be possible due to the different composition of the wood studied. These set-ups were carried out under substoichiometric conditions to promote the formation of products of incomplete combustion.

2 Experimental section

2.1 Characteristics of the materials

Furniture wood waste and polyurethane foam were collected from a Municipal Solid Waste Treatment Plant and solid wood (untreated wood) from a furniture factory. Prior to the experimental runs, the woody samples were dried and milled to a size less than 0.2 mm to obtain representative samples for the further characterization of the samples and for the experimental runs in the laboratory-scale reactor.

The characterization of the materials and the methods used were presented in previous works (Garrido and Font, 2015; Moreno and Font, 2015). For comparison, the results are also shown in Table 1. Note that the nitrogen content of the solid wood is below the limit of detection. For some elements, the standard deviations are high due to the fact that their concentrations are low and close to the detection limit.

Table 1 Characterization of the materials used.

	Furniture wood waste (Moreno and Font, 2015)	Solid wood (Moreno and Font, 2015)	Polyurethane foam (Garrido and Font, 2015)
NCV, MJ/kg (d.b.)	15.8 ± 0.1	19.5 ± 0.5	24.2
Ash content, wt% (d.b.)	1.8 ± 0.1	0.3 ± 0.1	5.5
C, wt% (d.b.)	47.9 ± 0.03	52.7 ± 0.1	57.8
H, wt% (d.b.)	6.0 ± 0.1	6.2 ± 0.1	7.4
N, wt% (d.b.)	2.86 ± 0.58	<0.01	5.95
O, wt% (d.b.)	41.4 ± 0.6	40.8 ± 0.1	23.4
Others elements, mg/kg (d.b.)			
	ICP analysis		XRF analysis
S	540 ± 130	70 ± 50	130
CI	630 ± 70	160 ± 80	390
AI	480 ± 10	30 ± 20	80
Са	1590 ± 240	260 ± 50	>20,000
Fe	280 ± 30	25 ± 4	250
Mg	320 ± 80	100 ± 30	100
Р	100 ± 20	20 ± 10	20
К	400 ± 150	160 ± 90	n.d.
Si	2150 ± 140	109 ± 3	1050
Na	300 ± 120	20 ± 10	270
Ti	1600 ± 200	2.1 ± 0.8	n.d.
As	0.4 ± 0.03	0.011 ± 0.004	n.d.
Cd	1.0 ± 0.1	0.1 ± 0.02	n.d.
Co	1.1 ± 0.1	0.051 ± 0.004	n.d.
Cr	6.7 ± 1.4	2.0 ± 1.3	n.d.
Cu	6.4 ± 0.7	1.4 ± 1.4	n.d.
Hg	0.03 ± 0.04	0.006 ± 0.003	n.d.
Mn	40.0 ± 3.6	46.8 ± 7.1	n.d.
Мо	0.34 ± 0.03	0.02 ± 0.02	n.d.

Ni	1.2 ± 0.3	0.04 ± 0.07	n.d.
Pb	6.3 ± 3.6	0.04 ± 0.06	n.d.
Sb	2.0 ± 0.4	0.01 ± 0.01	n.d.
V	0.85 ± 0.04	0.052 ± 0.002	n.d.
Zn	69.4 ± 2.0	7.7 ± 0.9	n.d.
Br	8.8 ± 0.8	0.02 ± 0.04	n.a.

n.a.: not analysed.

n.d.: not detected (<10 mg/kg in XRF analysis).

Furniture wood waste shows high nitrogen content although the highest N content is in the polyurethane foam. Therefore, the briquettes used in this work (with 10 wt.% of polyurethane foam) show a high nitrogen content (3.17 wt.%).

Furniture wood waste also shows the highest CI content (630 mg/kg). This value slightly exceeds the limit assigned by a German ordinance (BMU, 2002) for waste wood used in the manufacture of panelboard (less than 600 mg Cl/kg), although it is within the European limits proposed for non-industrial briquettes (less than 1000 mg Cl/kg) (CEN, 2010). Therefore, recovery of energy with furniture wood waste is the best option for its management.

A high Ti content in furniture wood waste is also noteworthy, and this element could catalyse the formation of PCDD/Fs. Cu shows a higher catalyst effect; its content is the highest in the furniture wood waste, although its concentration is not very high in comparison with the Ti content.

A high Ca content is also observed in the furniture wood waste and in the polyurethane foam, although this high value is positive for the combustion processes, because Ca increases the ash melting temperature and is also an inhibitor of the PCDD/F formation (Qian et al., 2005).

Briquettes of furniture wood waste with 10 wt.% of polyurethane foam were made with a hydraulic piston press briquette machine, in the same way as indicated in a previous work (Moreno et al., 2016). Emissions and ashes produced in the combustion of these briquettes were also analysed.

Although the use of pentachlorophenol (PCP) and creosote for the treatment of the wood were firstly restricted in the European Union in 1992 by Directive 91/173/CEE, the possible presence of these compounds were tested in furniture wood waste. Analyses of natural woods, such as solid wood and pine wood, were also been carried out for comparison. Extractions of the wood waste were carried out according to the U.S. EPA Method 3545A (2007) and chlorophenols, chlorobenzenes and compounds from the creosote were analysed according to U.S. EPA 8270D (EPA, 2014). Chlorobenzenes were not detected in any of the samples analysed. The results obtained are shown in Table 2.

Table 2 Chlorophenols, PAHs and other organic compounds in furniture wood waste and comparison with other natural woods.

	Furniture wood waste (n = 2) ^a	Solid wood	Pine wood
Chlorophenols (µg/kg dry basis)			
MONO-	2.6 ± 1.4	nd	nd
DI-	15.5 ± 5.8	0.8	0.6
TRI-	11.1 ± 4.5	0.1	0.1
TETRA-	58.3 ± 25.6	0.6	0.4
PENTA-	524.4 ± 211.1	5.9	0.1
Total	611.9 ± 248.4	7.4	1.0
PAHs (µg/kg dry basis)			
Naphthalene	84 ± 13	nd	nd
Acenaphthylene	nd	nd	nd

Acenaphthene	11 ± 2	nd	nd
Fluorene	14 ± 2	nd	nd
Phenanthrene	118 ± 1	11	nd
Anthracene	16 ± 4	nd	nd
Fluoranthene	121 ± 3	8	nd
Pyrene	173 ± 17	nd	nd
Benzo(a)anthracene	66 ± 42	nd	nd
Chrysene	47 ± 7	nd	nd
Benzo(b)fluoranthene	13 ± 19	nd	nd
Benzo(k)fluoranthene	19 ± 1	nd	nd
Benzo(a)pyrene	nd	nd	nd
Indeno(1,2,3-cd)pyrene	nd	nd	nd
Dibenz(a,h)anthracene	nd	nd	nd
Benzo(g,h,i)perylene	nd	nd	nd
Total	645	19	nd
Other organic compounds (µg/kg dry basis)			
Pyridine, 2-methyl	301 ± 206	nd	nd
Ethylbenzene	159 ± 193	23	nd
Xylenes	82 ± 76	17	nd
Cymene	755 ± 138	901	151
Phenol	740 ± 156	nd	nd
Cresol	309 ± 25	202	65
Naphthalene, 1,6-dimethyl-4-(1-methylethyl)-	136 ± 40	nd	nd
nd: values less than limit of detection (I OD \sim 0.1 µg/kg for chlorophenols. \sim 3 µg/kg for PAHs and other org	anic compounds)		

nd: values less than limit of detection (LOD \sim 0.1 µg/kg for chlorophenols, \sim 3 µg/kg for PAHs and other organic compounds).

^a Duplicate analysis.

As can be seen from Table 2, the pentachlorophenol content and PAHs content are the highest in the furniture wood waste. Therefore, this furniture wood waste was treated with PCP and creosote. Due to the PCP content, the use of this furniture wood waste as a bulking agent in composting processes is not recommended, because during composting, the PCP present in the wood could react and produce PCDD/Fs (Gómez-Rico et al., 2007; Muñoz et al., 2010, 2014).

2.2 Experimental procedure

Two different experimental set-ups were used in this work: a conventional residential stove without an automatic control of combustion air and bad mixing of combustion gases with air; and a laboratory-scale horizontal tubular quartz reactor, operating under substoichiometric conditions with airflow and temperature control and good mixing of volatiles evolved in the second part of the reactor. The experiments carried out in the residential stove show the advantage of burning a high amount of fuel (2 kg approximately), whereas, in the laboratory scale reactor, the amount of sample that is burnt is small (between 1 and 2 g for PCDD/F and PCB analysis).

2.2.1 Residential Stovestove

The residential stove operated with natural draft and with manual control of the biomass burning rate observing the CO₂ concentration at the gas exit and an irregular mixing of combustion gases with air. The set-up consisted of a residential stove with a chimney

stack, and the emissions evolved were sampled (SKMM5HS, Apex Instruments, USA) according to the U.S. EPA Method 0023A (Fig. 1). Temperature was measured regularly with a temperature probe at the centre of the stove.

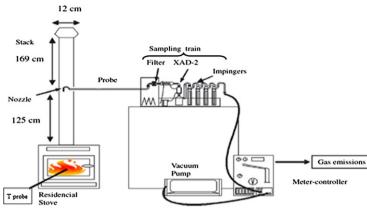


Fig. 1 Scheme of the experimental set-up (residential stove and sampling train).

During the experiments, CO₂, CO, O₂ and nitrogen oxides (NO and NO₂) were continuously analysed with an IM-2800 gas analyser (Environmental Equipment Germany GmbH). In addition, the volumes of the gases evolved were collected in Tedlar bags and they were analysed by gas chromatography using a TCD and FID detector and by a GC-MS with a DB-624 capillary column (30 m × 0.25 mm × 1.4 µm).

PAHs and semi-volatile organic compounds were determined and quantified from a known volume of the XAD-2 resin extracts, and PCDD/Fs and PCBs were determined and quantified from the rest of the volume extract. Analyses of PAHs were carried out with GC-MS with a HP-5MS capillary column (30 m × 0.25 mm × 0.25 µm) by the isotope dilution method. The identification of semi-volatile compounds was done comparing unknown mass spectra with NIST database reference spectra and a semiquantitative determination of the yield was calculated with the response factors of the deuterated internal standard with the nearest retention time, according to the U.S. EPA Method 8270D method. The simultaneous analyses of PCDD/Fs and 12 dioxin-like PCBs were carried out according to a modification of the U.S. EPA Method 1613 (Moltó et al., 2006). The purified extracts were analysed with a high-resolution gas chromatograph (Agilent HP6890) coupled to a high-resolution mass spectrometer (Micromass Autospec UltimaNT, Waters) with a positive electron impact (EI+) source.

Ashes obtained in the different combustions in the residential stove were also analysed for PCDD/Fs and PCBs (in duplicate). Ash samples were extracted with 5% v/v glacial acetic acid in toluene, according to the U.S. EPA Method 3545A and the purified extracts were analysed according to the U.S. EPA Method 1613B. Ash samples were also analysed for elements with an atomic weight higher than that of F, by X-ray fluorescence with an automatic sequential spectrometer model PW2400 (PHILIPS MAGIX PRO).

Blanks of the experiments and the equipment used were also carried out prior to the corresponding runs.

2.2.2 Laboratory reactor

A laboratory scale horizontal tubular reactor was used for the combustion of the furniture wood waste (in triplicate runs) and the solid wood (Fig. 2). Runs were carried out with 300 mL air min⁻¹ (measured at 1 atm and 20 °C). The residence time of the gas inside the central part of the reactor is around 3.5 s at 850 °C. Runs were performed under substoichiometric conditions, although in the end part of the reactor some quartz raschig rings are placed, which promote the secondary cracking reactions and a good mixing of the gas <u>(Font et al., 2003)</u>. PCDD/Fs and PCBs from the gas stream were retained by XAD-2 resin. The resins were extracted with toluene and the analyses of the PCDD/Fs and PCBs were carried out following the same analytical methods as for the extract obtained in the residential stove runs.

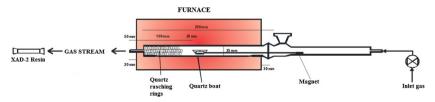


Fig. 2 Scheme of the laboratory scale reactor.

3 Results and discussion

Table 3 shows the operating conditions, volume percentage of the carbon oxides and oxygen, nitrogen oxides and the yields of hydrocarbons and 16 priority PAHs generated in the residential stove experiments.

 Table 3 Volatile gases and 16 priority PAHs evolved in residential stove combustion.

	Furniture wood waste (I)	Furniture wood waste (II)	Briquettes of furniture wood and 10 wt.% of foam
Operating conditions			
Nm³ dry gas/kg burnt	41	37	24
Residence time (s)	~3.5	~3.5	~3.6
Furnace temperature (°C)	420–780	320–740	450–750
Carbon oxides			
CO ₂ (g/kg sample burned)	1650 ± 530	1663 ± 832	1649 ± 768
CO (g/kg sample burnt)	42 ± 12	46 ± 19	40 ± 15
Ratio CO/(CO ₂ + CO)	0.025 ± 0.014	0.035 ± 0.023	0.030 ± 0.018
Oxygen (% vol.)			
O ₂	19.0 ± 0.6	18.6 ± 1.2	17.6 ± 1.7
Nitrogen oxides (g/kg sample burnt)			
NO	1.77 ± 0.45	2.42 ± 0.91	4.43 ± 2.22
NO ₂	<0.05	<0.05	<0.05
Volatiles (mg/kg sample burnt)			
Methane	6030	1750	330
Ethane	820	160	30
Ethene	1890	350	220
Propane	nd	20	30
Propene	480	190	340
Ethyne	560	60	50
Propyne	90	90	230
Toluene	14,130	14,050	1620
Total volatiles (mg/kg sample)	24,000	16,670	2850
nd: value less than LOD \sim 10 mg/kg			
16 priority PAHs (mg/kg sample)			
Naphthalene	19.8	39.2	2.8
Acenaphthylene	6.4	11.7	1.5

Acenaphthene	0.4	0.7	0.1
Fluorene	1.4	2.9	0.5
Phenanthrene	3.4	8.1	1.3
Anthracene	0.8	1.0	0.3
Fluoranthene	1.2	2.4	0.3
Pyrene	1.4	2.0	0.3
Benzo[a]anthracene	0.5	0.5	0.1
Chrysene	0.3	0.6	0.1
Benzo[b]fluoranthene	0.2	0.4	0.1
Benzo[k]fluoranthene	0.2	0.4	0.1
Benzo[a]pyrene	0.2	0.3	nd
Indeno[1,2,3-cd]pyrene	0.1	0.2	nd
Dibenz[a,h]anthracene	nd	nd	nd
Benzo[g,h,i]perylene	0.1	0.2	nd
Total PAHs	36	71	8
Total semi-volatile compounds	807	729	159
nd: value less than LOD \sim 0.1 mg/kg			

The operating conditions are those which are obtained in combustion in the stove without automatic control, the percentage of oxygen was the only variable that was controlled manually (around values of 18% O₂).

The CO emission, in this study, ranged from average values of 40–46 g/kg sample burnt. Similar values were shown in literature from combustions of wood in similar stoves; Evtyugina et al. (2014) obtained CO emissions between 60 and 120 g/kg, and Tissari et al. (2007) found CO emissions between 28 and 120 g/kg. In large industrial combustors, CO emissions are lower (Williams et al., 2012).

Regarding the emissions of nitrogen oxides, the NO yield increased slightly in the co-combustion of furniture wood waste with 10 wt.% of polyurethane foam (4.43 mg NO/kg sample) in comparison with the emissions of furniture wood combustion (without foam; 1.77 and 2.42 mg NO/kg sample). This increase is due to the higher N content in the briquettes used.

On the other hand, the yields of volatile compounds obtained from the combustion of the briquettes are lower than the other two experiments burning furniture wastes without polyurethane foam.

PAH emissions obtained from combustion of furniture waste are in the same order of magnitude (even lower) as those obtained from combustions of natural wood in analogous stoves. McDonald et al. (2000) obtained an average PAH yield from wood stoves of 75 mg/kg. Tissari et al. (2007) found 164 mg PAH/kg wood, from a sauna stove combustion.

PAH emissions in biomass combustion are mainly formed by naphthalene, acenaphthylene, phenanthrene, fluoranthene and pyrene, comprising more than 80% of the total PAHs evolved (Bignal et al., 2008; Johansson et al., 2004; Khalfi et al., 2000; Reisen et al., 2014); the results shown, even for combustion of briquettes with 10 wt.% of polyurethane foam, are in agreement with this trend.

The lowest yield of PAHs volatile and semi-volatiles compounds obtained in the combustion of the briquettes of furniture wood with 10 wt.% of polyurethane foam is also noteworthy. This could be by the effect of polyurethane foam, but, in addition, some authors have found that densified fuels (briquettes or pellets) reduce light hydrocarbons, PAH emissions and particulate matters (PM) (Chen et al., 2004; Shao et al., 2016; Shen et al., 2012).

Furthermore, another 152 semi-volatile compounds were identified and quantified and the results are shown in Table A1 of the Appendix. Table A2, also in the Appendix, shows the percentage contribution of semi-volatiles by groups. Note that the combustion of briquettes of furniture wood and 10 wt.% of foam shows the highest percentage contribution of nitrogenated compounds.

The formation of PCDD/Fs and dioxin-like PCBs during the combustion of furniture waste has also been studied in the residential stove and in a laboratory scale reactor.

Table 4 shows the PCDD/F and dl-PCB yield in the combustion experiments carried out with the residential stove and the laboratory reactor, with their corresponding blank experiments. Blank values were obtained following the same experimental and analysis procedures, without burning any material, and they were subtracted from the analyses carried out. Results from blank experiments are also shown in Table 4, in order to observe their negligible values. Only for the run carried out with solid wood in the laboratory reactor, the blank is similar to the corresponding run, indicating that the PCDD/F and PCB formation was very small.

Table 4 Concentration of PCDD/Fs and dioxin-like PCBs (ng kg⁻¹) in different samples and combustion experiments.

	Gas from residential stove						Gas from laboratory scale reactor			
	Furniture wood waste (run I)	Blank stove (run I)	Furniture wood waste (run II)	Blank stove (run II)	Briquettes of furniture wood and 10 wt.% of foam	Blank stove (run III)	Furniture wood waste (n = 3)ª	Furn. wood blank	Solid wood	Solid wood blank
Operating conditions										
Residence time (s)	~3.5		~3.5		~3.6		~3.5		~3.5	
Furnace temperature (°C)	420–780		320-740		450–750		850		850	
Ratio CO/(CO ₂ + CO)	0.025		0.035		0.030		0.070		0.075	
PCDD/Fs and dioxin-like PCI	Bs (ng kg⁻¹)									
2378-TCDF	3.2	0.3	90	2.0	41	0.1	15.5 ± 4.3	0.2	1.5	0.1
12378-PeCDF	2.2	0.4	42	0.9	15	0.1	10.7 ± 2.2	1.0	1.4	0.7
23478-PeCDF	3.7	0.4	89	1.4	26	0.1	12.5 ± 1.1	0.9	1.4	0.6
123478-HxCDF	3.3	0.8	30	0.6	16	0.1	5.8 ± 1.1	1.1	1.1	0.7
123678-HxCDF	2.8	0.5	28	0.6	13	0.2	7.5 ± 1.7	1.0	0.9	0.7
234678-HxCDF	3.3	0.8	53	0.9	23	nd	11.5 ± 7.9	1.9	1.8	1.3
123789-HxCDF	2.0	0.8	6.7	0.2	4.2	0.1	3.4 ± 4.6	1.2	0.5	0.8
1234678-HpCDF	11.5	2.5	103	1.5	41	0.4	12.2 ± 10.4	4.0	1.1	2.7
1234789-HpCDF	8.0	0.9	8.2	0.6	4.9	0.2	3.5 ± 2.3	1.9	nd	1.3
OCDF	29	2.9	30	0.5	20	0.1	8.7 ± 8.8	3.3	2.2	2.5
2378-TCDD	3.2	0.8	3.1	0.5	1.5	nd	3.9 ± 1.8	0.5	0.3	0.3
12378-PeCDD	12.4	0.5	10.3	0.5	4.6	0.3	5.6 ± 1.1	0.9	0.3	0.6
123478-HxCDD	11.6	0.4	11.4	0.6	3.5	nd	1.3 ± 0.5	0.7	1.0	0.5
123678-HxCDD	33	0.9	20	0.6	8.1	0.5	3.7 ± 2.6	0.5	nd	0.4
123789-HxCDD	30	0.8	15	0.8	8.1	0.3	3.4 ± 1.8	0.9	2.2	0.6
1234678-HpCDD	655	4.2	233	0.9	131	0.6	3.4 ± 1.8	1.8	2.1	1.2
OCDD	2335	11.4	530	180	533	0.8	7.2 ± 9.3	2.9	5.2	2.0
Total WHO-TEQ PCDD/Fs	33	2.1	70	2	28	0.5	19.0 ± 2.9	2.5	2.0	1.7
PCB-81	3.0	0.2	72	0.7	18	nd	9.1 ± 7.4	nd	nd	nd
PCB-77	11.0	0.8	505	9.9	83	1.5	73 ± 69	4.3	4.6	2.9
PCB-123	7.7	0.3	487	4.7	120	0.4	25 ± 30	1.5	2.1	1.0

PCB-118	63.6	2.2	4738	47	1276	5.9	101 ± 114	16.0	25.7	10.8
PCB-114	1.6	0.3	193	2.3	34	0.1	2.4 ± 3.3	0.5	nd	nd
PCB-105	25.9	1.2	2637	21	559	2.0	38 ± 40	7.2	10.3	4.9
PCB-126	2.2	0.3	36	1.6	14	0.4	14.4 ± 9.1	0.5	2.9	0.4
PCB-167	11.4	0.1	276	1.9	91	0.2	6.9 ± 5.6	1.1	0.1	0.1
PCB-156	11.2	0.4	442	4.0	159	0.4	11.7 ± 4.3	2.5	2.7	1.7
PCB-157	1.1	0.1	77	0.9	38	nd	7.2 ± 5.2	0.7	0.5	0.5
PCB-169	1.4	nd	7.4	0.2	4.5	nd	23 ± 37	0.6	4.6	0.4
PCB-189	2.9	nd	66	0.3	18	0.2	3.7 ± 3.3	0.6	1.4	0.4
Total WHO-TEQ PCBs	0.3	0.03	4.2	0.1	1.6	0.05	2.2 ± 0.9	0.07	0.4	0.05
Total WHO-TEQ (PCDD/Fs + PCBs)	33	2	74	2	29	0.6	21.1 ± 2.1	2.6	2.5	1.8

n.d.: value less than the LOD \sim 0.1 ng/kg sample.

^a Triplicate experiment.

The total toxicity equivalence was calculated using the toxicity equivalency factor given by the World Health Organization (Van den Berg et al., 2006).

The residential stove without control of combustion air can cause bad mixing of the combustion gases with air and therefore the combustion emissions can vary widely from one combustion to another. According to the ratio of CO/(CO + CO₂) obtained, the combustion of furniture wood waste (run II) is the worst combustion. Therefore, taking into account that the fuel used in run I and in run II are the same, it can be concluded that the combustion conditions are an important factor in the formation of the PCDD/Fs and PCBs. Consequently, in this kind of stove (without an automatic control of combustion air), it should be really important to promote high turbulence and good mixing of the combustion gases with air, in order to avoid the generation of incomplete combustion areas. In industrial boilers, operating with an excess of oxygen, good mixing will favour the destruction of organic pollutants.

The co-combustion of furniture wood waste with polyurethane foam does not increase the production of PCDD/Fs; it could even be considered that the total toxicity equivalence slightly decreases, as observed by other authors (Bhargava et al., 2002; Samaras et al., 2000; Skodras et al., 2002). It is possible that the ammonia formation due to the higher nitrogen content of the polyurethane foam produces a slightly decrease of PCDD/F formation. In a previous work (Moreno and Font, 2015), the ammonia formation in pyrolysis was found to be high if the nitrogen content of the fuel was significant; it must be taken into consideration that the first stage of combustion is a pyrolysis process, so ammonia can inhibit the PCDD/F formation (Hajizadeh et al., 2012; Ruokojärvi et al., 2004, 1998). Other authors have also found ammonia emissions from biomass burning (Delmas et al., 1995; Goode et al., 2000; Yokelson et al., 2003).

Schatowitz et al. (1994) found emissions of PCDD/Fs between 24 and 176 ng I-TEQ/kg in the combustion of waste wood from demolition, values that are in the same order of magnitude that the obtained in the present work with furniture waste.

From Table 4, it can be observed that the yield of PCDD/Fs and PCBs in the combustion of furniture wood waste in the laboratory scale reactor is higher than that obtained in the combustion of solid wood under the same conditions. The additives present in the furniture wood waste, considering the catalytic effect of TiO₂ (Qian et al., 2005), probably produce the increase of PCDD/F and PCB in comparison with the solid wood combustion, although this increase is not too high.

It can be observed that, in the combustion in the residential stove, the most abundant congener is OCDD. This high emission of OCDD was also observed in biomass combustion (Meyer et al., 2004; Prange et al., 2003) and in treated wood combustion (Salthammer et al., 1995; Wasson et al., 2005).

Some authors found that furan concentrations were higher than dioxin concentrations for treated wood combustion (Salthammer et al., 1995; Samaras et al., 2001; Skodras et al., 2002; Tame et al., 2005; Wasson et al., 2005). In contrast, for the combustion of natural wood, the dioxins were more abundant than furans (Samaras et al., 2001; Skodras et al., 2002). In the present work, in the experiments carried out with the residential stove, the dioxin formation is higher than the furan formation. The opposite occurs with experiments with furniture wood waste using the laboratory reactor. This could be because the laboratory scale reactor set-ups were carried out under substoichiometric conditions but with good mixing of gases, and therefore, a predominance of PCDFs occurred. Nevertheless, in the residential stove with an excess of air, but with bad mixing, PCDDs were the dominant compounds.

Comparing the combustion of different wastes, the PCDD/F emissions from furniture waste combustion cannot be considered high. Table 5 shows a comparison of the yields of PCDD/Fs and PCBs obtained in the combustion of other samples

in the same laboratory reactor and the same residential stove.

Table 5 Comparison of the emissions from combustion of different wastes.

	Ratio CO/(CO + CO ₂)	PCDD/Fs (ng TEQ/kg sample)	Reference
Laboratory reactor at 850 °C			
Furniture wood waste	0.07	19	Present work
PVC	0.09	4500	Conesa et al. (2009)
Sewage sludge with high metal content, mainly Fe	0.11	1700	
Sewage sludge with low metal content	0.08	55	
Waste lube oil	0.46	80	
Polyester textiles	0.11	14	
Pine needles	0.11	49	Moltó et al. (2010)
Pine cones	0.13	30	
Residential stove			
Furniture waste	0.03 - 0.04	30–70	Present work
Pine needles and cones	0.12	175	Moltó et al. (2010)

The presence of metals in the fuel increases the levels of PCDD/Fs generated, as can be observed in Table 5 comparing the emissions of PCDD/Fs from the combustion of sewage sludge with high metal content and sewage sludge with low metal content. Levels of PCDD/Fs obtained in the combustion of furniture wood waste are lower than those obtained in the combustion of sewage sludge (with high and low metal content) and biomass (such as needles and cones of pine).

In order to have a complete study, Table 6 shows the PCDD/F and dI-PCB yields in the ash obtained in the combustion experiments carried out in the residential stove. Blanks of the extraction, clean-up and purification processes are also carried out and their values are also shown in Table 6.

Table 6 Concentration of PCDD/Fs and dioxin-like PCBs (ng kg $^{-1}$) in the ashes from the residential stove combustions.

		Ash from residential stove (ng/kg ash)							
	Furniture wood waste (I) $(n = 2)^{a}$	Blank (I)	Furniture wood waste (II) $(n = 2)^a$	Blank (II)	Briquettes of furniture wood and 10 wt.% of foam $(n = 2)^{a}$	Blank (III)			
Ratio CO/(CO ₂ + CO)	0.025		0.035		0.030				
2378-TCDF	10.0 ± 2.1	nd	58.2 ± 9.2	nd	35.2 ± 2.9	nd			
12378-PeCDF	5.6 ± 0.9	0.2	53.5 ± 6.5	0.1	26.9 ± 2.5	0.2			
23478-PeCDF	7.3 ± 0.6	0.1	71.5 ± 0.1	0.1	36.9 ± 2.7	0.1			
123478-HxCDF	4.2 ± 0.6	0.2	56.4 ± 3.1	0.1	24.9 ± 1.8	0.1			
123678-HxCDF	4.1 ± 0.5	0.2	59.3 ± 4.5	0.1	26.1 ± 0.9	0.2			
234678-HxCDF	7.4 ± 0.8	0.3	86.2 ± 5.2	0.2	41.7 ± 4.9	0.2			
123789-HxCDF	1.2 ± 0.8	0.3	19.3 ± 1.1	0.2	8.4 ± 0.1	0.3			
1234678-HpCDF	18.1 ± 1.6	0.7	175 ± 29	0.5	100 ± 14	0.6			

1234789-HpCDF	1.6 ± 0.02	0.2	17.0 ± 1.5	0.2	6.5 ± 0.5	0.2
OCDF	3.4 ± 1.1	0.7	50.7 ± 3.3	0.5	16.7 ± 1.8	0.6
2378-TCDD	0.4 ± 0.1	0.1	2.7 ± 0.2	0.1	1.2 ± 0.1	0.1
12378-PeCDD	2.1 ± 0.5	0.2	11.3 ± 1.3	0.1	4.7 ± 0.6	0.2
123478-HxCDD	1.1 ± 0.1	0.1	5.2 ± 0.5	0.1	2.1 ± 0.3	0.1
123678-HxCDD	5.9 ± 0.02	0.3	8.6 ± 2.0	0.2	4.2 ± 0.7	0.2
123789-HxCDD	4.0 ± 0.5	0.3	7.3 ± 0.7	0.2	3.7 ± 0.5	0.2
1234678-HpCDD	32.8 ± 1.3	0.4	57.2 ± 13.8	0.3	32 ± 6	0.4
OCDD	111 ± 5	0.7	79.5 ± 6.9	0.5	64 ± 10	0.6
Total WHO-TEQ PCDD/Fs	9.2 ± 0.3	0.5	70 ± 3	0.3	33.9 ± 0.2	0.4
PCB-81	2.4 ± 0.2	nd	37 ± 0.1	nd	22.3 ± 2.6	nd
PCB-77	22.1 ± 4	0.7	181 ± 7	0.5	85.0 ± 3.2	0.6
PCB-123	2.7 ± 0.7	0.3	232 ± 47	0.2	109 ± 17	0.3
PCB-118	13.6 ± 2.8	3.1	2599 ± 571	2.1	1213 ± 149	2.6
PCB-114	0.4 ± 0.3	nd	71 ± 16	nd	34 ± 5	0.1
PCB-105	8.2 ± 2.1	1.3	1277 ± 298	0.9	541 ± 67	1.1
PCB-126	5.8 ± 1.1	0.3	80 ± 4	0.2	28.8 ± 1.9	0.2
PCB-167	3.2 ± 1.6	0.2	112 ± 25	0.1	47.0 ± 7.7	0.2
PCB-156	15.9 ± 18.1	0.2	282 ± 62	0.2	97.5 ± 12.5	0.2
PCB-157	12.0 ± 15.3	nd	86 ± 17	nd	31.8 ± 5.7	nd
PCB-169	1.5 ± 0.2	nd	19 ± 1	nd	7.8 ± 1.8	nd
PCB-189	1.4 ± 0.1	0.6	27 ± 3	0.4	10.3 ± 2.1	0.5
Total WHO-TEQ PCBs	0.6 ± 0.1	0.03	9 ± 0.5	0.02	3 ± 0.3	0.02
Total WHO-TEQ (PCDD/Fs + PCBs)	10 ± 0.4	0.5	78 ± 2	0.4	37 ± 0.4	0.4

n.d.: value less than the LOD \sim 0.1 ng/kg sample.

^a Duplicate analysis.

Regarding the toxicity of the ash, Tame et al. (2003a,b) found an analogous concentration of PCDD/Fs in ash from the combustion of CCA-treated pine wood in a cone calorimeter (27–78 ng WHO-TEQ/kg ash) to that obtained in ash from this present study (10–78 ng WHO-TEQ/kg ash). Freire et al. (2015) found 32 ng I-TEQ/kg ash for bottom ashes from biomass combustion, which is also within the range of the values obtained in the present work. On the other hand, Wunderli et al. (2000) found low concentrations of PCDD/Fs in ash (4–11 ng I-TEQ/kg ash), in urban waste wood bottom ashes from incinerators and wood combustion facilities in Switzerland.

Tame et al. (2007) compared the PCDD/Fs concentrations in ashes from combustion runs with treated and untreated wood. They concluded that the presence of preservatives increased the PCDD/F emissions, with a higher increase of furans.

Ashes from biomass can be used for agricultural applications due to the mineral contribution that they provide to the soil, although the limitation of the alkalinity characteristics of the ashes for soil disposal should be considered (Obernberger and Supancic, 2009; Pitman, 2006; van Loo and Koppejan, 2008).

In the EU, there is no particular legislation for the application of ashes in agriculture use, but the European Commission is reviewing the European Directive on sewage sludge application for agriculture (86/278/EC) to include limits of dioxin content. A recommendation of the 3rd Draft of the Working Document on Sludge (Langenkamp and Part, 2001) established a limit of PCDD/F content of 100 ng I-TEQ/kg. None of the ash samples studied in the present work exceeds this limit proposed.

Heavy metals present in ashes could also restrict the possibility of agricultural use. The European Directive (86/278/EC) and the Spanish legislation (RD 1310/1990) establish limits for some heavy metals in sewage sludge for application in agriculture (Cd: 20, Cu: 1000, Ni: 300, Pb: 750, Zn:2500, Hg: 16, Cr: 1000, in mg/kg).

In this connection, inorganic elements have been quantified for the ashes from the combustion carried out in the residential stove. The results are given in Appendix (Table A.3.). The composition of the three samples of ashes studied was quite similar. Ash samples do not exceed the heavy metal limits of the legislation, except for the Pb content in the ash from the 2nd experiment of combustion of furniture wood waste that is 1300 mg/kg ash.

In comparison with biomass ashes (Freire et al., 2015), it must be noted that ashes from furniture waste show a significance content of Ti (between 3.3 and 8.1 Ti wt.% for furniture waste ashes and around 0.1 wt.% for biomass ashes), higher Cu content (540–800 mg/kg furniture waste ashes and a maximum of 120 mg/kg for biomass ashes), and higher Cr content (120–220 mg/kg for furniture waste ashes and a maximum of 60 mg/kg for biomass ashes). The higher content of Ti is due to the paints present in the furniture wood, and the higher content of Cu and Cr is due to the treatment of the furniture wood with preservatives that contain these elements. The Pb content has shown an important variation in the experiments carried out in the present work (between 20 and 1300 mg/kg ash); the maximum Pb content found in biomass ash by Freire et al. (2015) was 100 mg/kg ash.

4 Conclusions

From the combustion experiments carried out in the residential stove, 16 PAHs and another 152 semi-volatile compounds were identified and quantified. Naphthalene is the most abundant PAH in all the experiments (2–40 mg/kg sample). Regarding the semi-volatile compounds, the oxygenated aromatics are the most abundant in all the experiments. NO emissions increase in the combustion of the briquettes of furniture wood with 10 wt.% of polyurethane foam and the percentage contribution of nitroaromatic compounds also increases in comparison with the other experiments. However, it is noteworthy that the yields of PAHs, volatile and semi-volatile compounds obtained in the combustion of furniture wood with 10 wt.% of polyurethane foam are the lowest. This fact could be explained by the composition of the fuel and also by the densification of the fuel.

The co-combustion of the furniture wood with the presence of polyurethane also decreases the formation of PCDD/Fs and dioxin-like PCBs. PCDD/F and dI-PCB emissions obtained from the combustions carried out in the residential stove range between 29 and 74 ng WHO-TEQ/kg sample and PCDD/F and dI-PCB concentration of the ashes range between 10 and 78 ng WHO-TEQ/kg ash. These values are not high in comparison with those obtained in other works.

From the runs carried out in the laboratory scale reactor, it can be concluded that the higher emissions of PCDD/Fs and PCB in the combustion of furniture wood waste is due to the additives present in this treated wood, although, this value obtained is not too high in comparison with those obtained in combustions of other wastes. The total equivalent toxicity obtained were: 21.1 ng WHO-TEQ/kg sample for combustion of furniture wood waste and 2.5 ng WHO-TEQ/kg sample for combustion of solid wood.

Results can be helpful for practice because the PCDD/F formation in the combustion of furniture waste is not very high in comparison with combustion of other wastes. The combustion of briquettes of furniture wood waste with 10 wt.% of polyurethane foam also shows a favourable result because: on one hand, emissions of VOCs, PAHs and semivolatile compounds decrease, and on the other hand, PCDD/F emissions do not increase, even it can be considered that they decrease slightly. Nevertheless, the NOx emission should be carefully controlled. Consequently, furniture waste would not be adequate for combustion in residential stoves, but energy recovery of this waste can be carried out in large industrial combustors without special problems due to the volatiles evolved.

5 Uncited reference

Font et al. (2003).

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.wasman.2016.09.046.

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Appendix A. Supplementary material

Multimedia Component 1

Supplementary data 1

Graphical abstract



Highlights

- · Co-combustion with polyurethane foam can be carried out without toxic risk.
- More than 150 semi-volatile compounds, PCDD/Fs and dl-PCBs evolved have been quantified.
- PCDD/F + PCB emissions are low (29-74 ng WHO-TEQ/kg) in comparison with biomass combustions.

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