

Pollutant Emissions during the Pyrolysis and Combustion of Flexible Polyurethane Foam

María A. Garrido, Rafael Font, Juan A. Conesa*

Department of Chemical Engineering, University of Alicante, P.O. Box 99, E-03080
Alicante

*Email: mangeles.garrido@ua.es

GRAPHICAL ABSTRACT



ABSTRACT

Thermal decomposition of flexible polyurethane foam (FPUF) was studied under nitrogen and air atmospheres at 550°C and 850°C using a laboratory scale reactor to analyse the evolved products. Ammonia, hydrogen cyanide and nitrile compounds were obtained in high yields in pyrolysis at the lower temperature, whereas at 850°C polycyclic aromatic hydrocarbons (PAHs) and other semivolatile compounds, especially compounds containing nitrogen (benzonitrile, aniline, quinolone and indene) were the most abundant products. Different behaviour was observed in the evolution of polychlorodibenzo-p-dioxins and furans (PCDD/Fs) at 550°C and 850°C. At 550°C, the less chlorinated congeners, mainly PCDF, are more abundant. Contrarily, at 850°C the most chlorinated PCDD are dominant. In

20 addition, the total yields of PCDD/Fs in the pyrolysis and combustion runs at 850°C were
21 low and quite similar.

22 **Keywords:** Polyurethane; Pyrolysis; Combustion; PAHs; PCDD/Fs; dlPCBs

23

ABBREVIATIONS

ClBzs	Chlorobenzenes
ClPhs	Chlorophenols
dlPCBs	dioxin like Polychlorobiphenyls
FPUF	Flexible Polyurethane Foam
GC-FID	Gas Chromatography-Flame Ionization Detector
GC-MS	Gas Chromatography-Mass Spectrometry Detector
GC-TCD	Gas Chromatography-Thermal Conductivity Detector
HRGC-HRMS	High Resolution Gas Chromatography-High Resolution Mass Spectrometry
HRGC-MS	High Resolution Gas Chromatography-Mass Spectrometry
PAHs	Polycyclic Aromatic Hydrocarbons
PCDDs	Polychlorodibenzo-p-dioxins
PCDFs	Polychlorodibenzofurans

1. INTRODUCTION

Polyurethanes are polymers made up of polyethers or polyester long chains covalently bonded by a urethane linkage ($-\text{NH} - \text{COO} -$). The manufacture of these plastics involves the reaction between polyfunctional isocyanates and polyfunctional alcohols (Zhang et al., 2009).

Flexible polyurethane foam (FPUF) is mainly employed in upholstered furniture and mattresses and is therefore automatically linked with the end of life of these products. Mattresses and furniture have two important characteristics that make their recycling really complex. The first one is their high volume that is a disadvantage in the transport of these products to the recycling plant and the second characteristic is their heterogeneous composition, with materials such as wood, metals and textiles, which require dismantling prior to recycling. In addition, dismantling can cause hygienic and health-related problems due to bacteria content, sweat and dust; these drawbacks can be avoided with a thermal process (ISOPA, 2012).

On the other hand, polyurethane contains practically the same amount of energy as coal or heavy fuel oil, which makes it a substitute for fossil fuels in cement kilns or provides assistance in waste treatment plants, such as municipal solid waste incineration plants.

Thermal degradation of different types of polyurethanes has been studied by other authors in the past. Boettner et al. (1973) analysed some volatiles evolved during the combustion of four polyurethane foams from automobile seats, under three different atmospheres, heating them at controlled rates from 5 to 50°C/min. Infrared spectroscopy and gas chromatography-mass spectrometry were employed in the qualitative and quantitative analysis of combustion products. Carbon dioxide, carbon monoxide, hydrogen cyanide, acetaldehyde and methanol were the most abundant gas products in all the runs. As the atmosphere was more oxidative,

the concentration of carbon dioxide, carbon monoxide and acetaldehyde increased, and that of methanol and hydrogen cyanide decreased.

A study was developed by Font et al. (2001) analysing the pyrolytic degradation of polyurethane-based adhesive at 600 and 850°C in a fast pyrolysis apparatus and a laboratory furnace by GC-MS. The results obtained showed an increase in the yield of methane, ethylene, benzene, ammonia, hydrogen cyanide, aniline, benzonitrile and naphthalene with a temperature increase.

Polycyclic aromatic hydrocarbons (PAHs) were analysed by Herrera et al. (2002) from the thermal degradation of two different thermoplastic polyurethanes, under two different atmospheres (N₂ and air) at 800 and 950°C. Naphthalene, phenanthrene and acenaphthylene were the most abundant in all runs. In addition, carbon dioxide, cyclopentanone, 2-cyclopentanone, phenylisocyanate, benzonitrile and 1,4-butanediol were the main products detected by thermogravimetric analysis-mass spectrometry (TG-MS) and thermogravimetric analysis coupled with Fourier transformed infrared spectroscopy (TG-FTIR).

A review of the literature did not reveal any previous work that undertook measurement of chlorinated compounds in the exhaust gases from the thermal degradation of FPUF. It is known that some chlorinated compounds such as polychlorodibenzo-p-dioxins and furans (PCDD/Fs) present a health risk for people and can be evolved from materials with chlorinated flame retardants as is the case of the flexible polyurethane foams. Therefore, it is important to analyse the emissions of these compounds, among others, under the extreme degradation conditions which could be reached in cement kilns or incineration plants which will be the common destinations for used mattress in future years, bearing in mind that the rate of wastes sent to landfills should decrease progressively.

On the other hand, a really low number of papers developed this type of analysis in duplicate because it involves a great amount of work, mainly for analysing the

polychlorodibenzo-p-dioxins and furans (PCDD/Fs) and dioxin-like polychlorobiphenyls (dlPCBs) so it is important to evaluate the reproducibility of this analytical procedure.

The main objective of the present work is to characterise the emission, from pyrolysis and combustion under fuel rich conditions at 550 and 850°C of FPUF waste in a laboratory scale reactor with the aim of including the extreme feasible conditions that could be reached in incineration systems. The extensive study comprises the analysis of ammonia, nitric oxide, carbon oxides, light hydrocarbons, polycyclic aromatic hydrocarbons (PAHs) and more than 180 other semivolatile compounds increasing the number of compounds detected with respect to those presented in other papers with similar materials. The novelty of the present work is the analysis of other organic pollutants such as chlorobenzenes (ClBzs), chlorophenols (ClPhs), polychlorodibenzo-p-dioxins and furans (PCDD/Fs) and dioxin-like polychlorobiphenyls (dlPCBs) which have not been previously determined during the thermal degradation of these type of polymers. Duplicated runs and analysis of all compounds was done to test for the reproducibility of the results obtained.

2. MATERIALS AND METHODS

2.1. Material

The flexible polyurethane foam (FPUF) employed comes from mattresses disposed of in a landfill in Alicante (Spain), with an apparent density of 19.62 kg m⁻³. The elemental analysis of the sample was performed in a Flash EA 1112 Elemental Analyzer and a content of C, O, H and N equal to 57.79, 23.43, 7.36 and 5.95% was obtained, respectively. The characterization of the sample and the thermogravimetric study by thermal decomposition under inert and two oxidative atmospheres was previously studied (Garrido and Font, 2015). With a view to employing this waste as fuel in the cement industry or in waste incineration plants, the reduced content of chlorine (0.0253% ± 0.0003%) that came from the flame

retardants present in the foam, and the high net calorific value (24.23 MJ/kg) meet the criteria proposed in CEN/TC 343 regulation (European Committee for Standardization) for solid recovered fuel.

2.2. Experimental Setup

In order to study the gases evolved from the combustion and pyrolysis of FPUF, a horizontal, laboratory scale reactor described previously (Aracil et al., 2005) was employed. The sample was introduced into the reactor at a constant speed (0.8 mm/s). The reactor was located inside a furnace that allowed the temperature to be maintained at a set value. Synthetic air (purity of 99.995%) or nitrogen (purity of 99.9992%) (Carbueros Metalicos, Barcelona, Spain) was introduced in parallel with the sample, at a constant flow of 300 mL/min, to remove the volatiles evolved.

The gases passed through a packing of quartz rings situated at the end of the reactor where they were mixed and underwent further reaction. For each atmosphere, two different temperatures were studied, 550°C and 850°C. The first temperature was chosen because FPUF at this temperature had reached the total decomposition in both atmospheres (Garrido and Font, 2015) and simulates low temperature zones that are sometimes presented in the combustion chambers. On the other hand, 850°C was selected because the EU establishes this temperature as a reference which should be maintained for two seconds in the post-combustion zone of incineration plants. In the experimental system, the calculated residence times of gases at the maximum temperature (the furnace presents a parabolic temperature distribution) were 5 s at 550°C and 3 s at 850°C.

Approximately 50 mg of sample was employed to perform the experiments. With this mass the CO ratio obtained ($R_{CO} = CO / (CO + CO_2)$) in the combustion run at 850°C was about 10% which ensured that all runs were carried out under fuel-rich conditions. Also with the sample mass, the oxygen ratio for the combustion runs, defined as the ratio between the actual

oxygen flow and the stoichiometric oxygen flow for the complete combustion (Font et al., 2010), was $\lambda=0.84$ (slightly sub-stoichiometric conditions).

2.3. Analytical Procedure

Accurate reactor cleanings were performed after each run employing water, toluene, acetone and high temperature (1000°C) for 30 min. in order to avoid interferences between samples. Additionally, blank runs were done using the same experimental conditions (temperature, reactor, atmosphere,...) but without sample, before the eight experiments which means that eight runs and eight blanks were analysed in the experimental campaign.

2.3.1. Ammonia Content

The U.S. EPA CTM 027 method was used for determining the emissions of ammonia (US EPA, 1997). This method consists of passing off the exhaust gases through two impinges which contain 10 mL of H₂SO₄ 0.1 N (purity of H₂SO₄ used was 95% (AnalaR NORMAPUR)), where the ammonia is trapped by the acid solution as ammonium ion (NH₄⁺). The solutions were analysed using a Dionex DX500 ion chromatography apparatus. The exhaust gases were sampled for 8 minutes in all the runs performed including the blank experiments.

2.3.2. Gases and Volatile Compounds

Gases and volatile compounds from both experiments with and without sample were collected in Tedlar® bags at the outlet of the reactor for 8 minutes (sufficient time to ensure a correct analysis). Carbon dioxide and carbon monoxide were analysed in a Shimadzu GC-14A Gas Chromatograph coupled to a Thermal Conductivity Detector (GC-TCD) equipped with a concentric packed Alltech CTR I column. A Shimadzu GC-17A Gas Chromatograph

with a Flame Ionization Detector (GC-FID) using a capillary column Alumina KCl Plot, was employed to analyse the light hydrocarbons (ranging from methane to xylene). An external standard calibration for each compound was carried out prior to the identification and quantification with high purity samples of all gases.

The IM 2800-P portable gas analyzer (from the same , Germany) was employed to analyse the nitric oxide collected in the Tedlar® bags, calibrating the analyzer before each run.

Other non-condensable products were collected in the same Tedlar® bags as gases and volatile compounds and were analysed using an Agilent 5973N mass spectrometer coupled to an Agilent 6890N gas chromatograph (HRGC-MS) with a capillary DB-624 column, working in the SCAN mode. For its calibration, EPA 502/524.2 VOC Mix (Supelco, USA) was employed as the external standard.

2.3.3. Semivolatile Compounds

A separate round of runs (including blank experiments) was carried out for 15 minutes to retain the semivolatile compounds generated in a small tube containing Amberlite XAD-2 resin (Supelco, Bellefonte, USA). To determine the concentration of PAHs, ClPhs and ClBzs in the samples, three different internal standards (5 µL of deuterated PAH Mix 26 (Dr. Ehrenstorfer-Schäfers, Augsburg, Germany) , 10 µL of ¹³C-labelled ClPh and 10 µL ¹³C-labelled ClBz (Wellington Laboratories, Ontario, Canada)) were added to the resin before extraction in a mixture of dichloromethane-acetone (1:1) by Accelerated Solvent Extraction (ASE-100 Dionex-Thermo Fisher Scientific, California, USA) following the U.S. EPA method 3545A (US EPA, 2007a).

The extract was concentrated in a rotary evaporator and with a moderate stream of nitrogen up to 1.5 mL. Finally, 3 µL of a solution 2000 µg/mL anthracene-d10 (AccuStandard, New Haven, USA) was spiked as a recovery standard.

The 16 priority PAHs established by U.S. EPA (1998) and other semivolatile compounds were quantified and identified following the U.S. EPA method 8270D (US EPA, 2007b) as reference. The analysis of these pollutants was performed in a GC-MS (Agilent GC 6890N/Agilent MS 5973N, Agilent Technologies, USA), in the SCAN mode with a HP-5 MS capillary column (Agilent Technologies, USA).

ClPhs and ClBzs were analysed in the same equipment but employing the SIR mode to confirm each isomer with the ratio between the areas of the primary and secondary ions (they differ in the presence of ^{35}Cl and ^{37}Cl).

ClPhs, ClBzs and 16 priority PAHs were quantified by internal standard calibration. The rest of semivolatile compounds and non-condensable products detected by HRGC-MS were identified comparing the mass spectrum of each compound with that of the NIST database guaranteeing a confidence higher than 80%.

2.3.4. PCDD/Fs and dioxin-like PCBs

To analyse PCDD/Fs and dioxin-like PCBs, additional pyrolysis and combustion experiments were performed, collecting the exhaust gases coming from 20 runs under the same conditions (temperature and atmosphere) in a single XAD-2 resin, in order to accumulate the produced volatiles from at least 1 g of sample burnt. The same procedure was followed for the blank experiments.

U.S. EPA method 1613 (US EPA, 1994b) and U.S. EPA method 1668C (US EPA, 2010) were used to analyse PCDD/Fs and dioxin-like PCBs, respectively.

After the runs, ^{13}C -labeled analogues were added to the resin as internal standards (10 μL of LCS-1613 for PCDD/Fs and 10 μL WP-LCS for PCBs (Wellington Laboratories, Ontario, Canada)) and an accelerated extraction with toluene was performed in an ASE 100 Dionex apparatus.

All extracts, including those that came from blank runs, were purified and fractionated in an automated Power Prep[®] system (FMS, Inc., Boston, MA), obtaining two fractions: one for the PCDD/Fs analysis and another for PCBs. Both fractions were concentrated in nonane with a stream of nitrogen and, finally, recovery standards were added (10 µL of ISS-1613 for PCDD/Fs and 10 µL WP-ISS for PCBs (Wellington Laboratories, Ontario, Canada)). The final detection of these compounds was performed in an Agilent HP5890 High Resolution Gas Chromatographer equipped with programmable temperature vaporization (PTV), coupled to a Micromass Autospec Ultima NT High Resolution Mass Spectrometer (HRGC-HRMS) with an Agilent DB-5MS column (60x0.25x0.25).

Quantitative determination of PCDD/Fs and dlPCBs was performed by the isotope dilution method employing the relative response factor for each congener obtained previously from five calibration standards (CS0.5-CS4, Wellington Laboratories, Ontario, Canada).

All solvents for the organic trace analysis were purchased from Merck (Germany).

3. RESULTS AND DISCUSSION

Runs were carried out in duplicate in order to keep track of the reproducibility of the results obtained. The average values and the standard deviations calculated from these two runs are shown in Tables and Figures but the detected values for each duplicate run are shown in the Supporting Information. The limit of detections (LOD) have been calculated for each type of compound (e. g. gases and volatile compounds, PAHs, other semivolatile compounds, chlorophenols,...) and in Tables “nd” has been employed to indicate that the detected level was lower than the corresponding LOD.

3.1. Ammonia Emissions

The emissions of ammonia obtained in the runs performed under two different atmospheres, at 550 and 850°C, are shown in **Table 1** where, PYRO and COMB refer to the

pyrolysis and combustion runs respectively, and the number accompanying them refers to the temperature of the runs, in °C. Blank runs done in the same conditions showed levels lower than 3 mg/kg sample, this value being the calculated LOD for NH₃.

As can be seen in **Table 1**, the yields of ammonia decreased more than 70% and 85% from pyrolysis to combustion at 550°C and 850°C, respectively, as was expected bearing in mind that this compound together with HCN is a common product from the incomplete combustion of high nitrogen containing material such as FPUF (Boettner et al., 1973). The effect of temperature is similar in both atmospheres because there was a decrease from 20100 ± 665 ppm to 11915 ± 440 ppm in pyrolysis and from 5960 ± 362 ppm to 1771 ± 102 ppm in combustion.

The behaviour observed under pyrolytic conditions is comparable to the results reported previously by Font et al. (2001) during their pyrolytic degradation of polyurethane-based adhesive at 600 and 850°C. The possible explanation for this unexpected behaviour, could be attributed to the higher heating rate of the runs at higher temperature, due to the fact that the sample was introduced with the same speed at 550 and 850°C. The rise of NH₃ from 850 to 550°C, together with the decrease of HCN, could be a result of the hydrogenation of HCN to NH₃ under low heating rate whereas at high heating rate (850°C) the HCN progressed to NO increasing the emission of this compound respect to the level detected at 550°C (**Table 1**) (Nielsen et al., 1995).

Under an N₂ atmosphere, 28% and 14% of nitrogen content in the initial sample was transformed to ammonia at 550 and 850°C, respectively, following the trend observed in the values presented by Leichtnam et al. (2000) from fast pyrolysis of polyamide at high temperature. However, in combustion runs, the yield of ammonia reached values of 7% and 2% for runs at 550°C and at 850°C, consequently there was an oxidation of ammonia in the combustion runs as reported previously by Guo et al. (2012) employing ASR residue (which

accounts for a high proportion of FPUF) to analyze the ammonia emitted during the pyrolysis and combustion in a wide range of temperatures.

Table 1. Average emissions and standards deviations of gases and volatile emissions in pyrolysis and combustion is given (nd<LOD).

Experiment	PYRO 550			PYRO 850			COMB 550			COMB 850		
Compound	<i>mg compound/kg sample</i>											
NO	103	±	4	132	±	4	95384	±	493	111243	±	341
NH ₃	20100	±	665	11915	±	440	5960	±	362	1771	±	102
<i>Carbon oxides (GC-TCD)</i>												
CO ₂	13594	±	220	15204	±	100	955951	±	2026	1460095	±	1288
CO	26746	±	230	31125	±	127	120877	±	1468	134060	±	3665
R _{CO} (%)=CO/(CO+CO ₂)	66%			67%			12%			9%		
<i>Light hydrocarbons (GC-TCD)</i>												
methane	28080	±	1219	135261	±	13831	8918	±	41	20464	±	712
ethane	11832	±	580	6859	±	524	1092	±	92	1697	±	69
ethylene	18054	±	521	102987	±	12210	11478	±	2443	4479	±	315
propane	11279	±	814	332	±	62	211	±	59	82	±	10
propylene	97732	±	7088	17909	±	1471	15957	±	455	3937	±	342
isobutane	340	±	43	nd			nd			nd		
acetylene	169	±	13	6344	±	528	863	±	25	2273	±	163
n-butane	nd			1437	±	70	nd			nd		
isobutene	2379	±	36	159	±	28	305	±	53	279	±	10
cis-2-butene	1237	±	10	229	±	25	170	±	12	163	±	10
isopentane	337	±	61	nd			nd			nd		
n-pentane	117	±	27	nd			nd			nd		
propyne	378	±	129	759	±	173	nd			358	±	49
1,3-butadiene	5710	±	432	7915	±	464	385	±	88	200	±	10
1-pentene	737	±	15	nd			nd			nd		
2-butyne	nd			648	±	128	nd			nd		
n-hexane	288	±	10	2992	±	78	nd			660	±	35
1-hexene	284	±	10	nd			nd			nd		
benzene	821	±	25	33334	±	2748	2070	±	90	1318	±	240
1-heptene	224	±	16	nd			nd			nd		
xylene (m-, p-, o-)	2262	±	207	nd			nd			nd		
<i>Total</i>	<i>182254</i>	±	<i>4462</i>	<i>317163</i>	±	<i>154916</i>	<i>41478</i>	±	<i>1808</i>	<i>35907</i>	±	<i>1230</i>
<i>Other non-condensable products (GC-MS)</i>												
Acetaldehyde	200580	±	2854	nd			40717	±	1868	nd		
Propene	114815	±	995	48298	±	962	22417	±	1886	27130	±	741
Hydrogen cyanide	23870	±	3216	54330	±	1087	12267	±	1744	1445	±	422
Acetone	43041	±	575	555	±	183	9743	±	1825	nd		

Formaldehyde	37332	±	360	nd		10265	±	571	nd
2-Propanone	30496	±	7947	nd		2113	±	188	nd
Ethene, ethynyl-	nd			13048	±	669	nd		9324 ± 835
Acrylonitrile	2617	±	210	12206	±	118	2490	±	193 4400 ± 430
Diisopropyl ether	19505	±	2655	nd		nd			nd
Acetonitrile	1337	±	114	11764	±	144	1546	±	139 2915 ± 634
Methyl Alcohol	4358	±	110	1953	±	135	11057	±	181 nd
Pyridine, 2-Methyl-	nd			14984	±	3100	nd		nd
Propanal	13215	±	3199	nd		1325	±	211	nd
Methylglyoxal	9514	±	789	nd		nd			nd
1,3-Cyclopentadiene	nd			7700	±	121	nd		737 ± 110
Oxirane, tetramethyl-	6279	±	782	nd		nd			nd
Total	429164	±	18340	168742	±	42061	102769	±	4961 50460 ± 6144

3.2. Gases and Volatile Compounds

Table 1 also shows the analysis of gases and volatile compounds, identified by GC-TCD (carbon oxides) and GC-FID (aliphatic and aromatic hydrocarbons) in the pyrolysis and combustion runs at different temperatures. In the blank runs, the only gases detected in the Tedlar® bags were N₂ and O₂ for the combustion experiments and N₂ in the pyrolysis runs and a percentage of other compounds less than 0.01%. The calculated detection limits were 1 ppm for NO and 10 ppm for carbon oxides and light hydrocarbons.

Nitric oxide (NO) was detected in all the runs showing an important increase in the yields from pyrolysis to combustion, mainly due to the oxidation of HCN to NO (Zevenhoven, 2003) as can be confirmed observing the HCN evolution in **Table 1**. Assuming this hypothesis, it would be expected that at COMB 850 the yield of NO would be much higher than COMB 550 observing the great decrease of HCN in these runs. However, a smooth increase was observed in combustion when the temperature rose, and this trend can be explained considering the hypothesis proposed by Zevenhoven and Kilpinen (2002). They postulated that under an oxidative atmosphere, an increase of temperature produced the oxidation of HCN to NO and at the same time, the nitric oxide obtained reacted with the

NCO radical to form N₂O, which could be accepted bearing in mind the great amount of isocyanate groups present in the molecular structure of polyurethanes.

The presence of CO and CO₂ in significant quantities in pyrolysis runs can be attributed to the oxygen content in the FPUF structure and also these compounds can be formed from the decomposition of carboxylic acids evolved at low temperatures (Leichtnam et al., 2000). The production of both compounds increased with temperature as a consequence of the thermal degradation of heavier compounds (Paabo and Levin, 1987).

The main light hydrocarbons obtained (**Table 1**) were methane, ethylene, benzene, ethane, 1,3-butadiene, propane and acetylene; methane was the most abundant in all runs. In general, the total yields of light hydrocarbons are higher in pyrolysis runs than in combustion ones at the same temperature as a consequence of the oxidative destruction of about 77% and 89% of pyrolytic products formed at 550°C and 850°C, reactively (Aracil et al., 2010; Conesa et al., 2000).

It is known that under an inert atmosphere, an increase of temperature involves two types of reactions: thermal cracking and pyrosynthesis reactions which involve a rise in some compound yields such as methane, ethylene, benzene, acetylene, hexane, butane, and 1,3-butadiene which are responsible for the increase of the total yield, whereas, there is also a decrease in the rest of light hydrocarbons.

Under an oxidative atmosphere, the increase of temperature involves a decrease of yields of nearly all organic compounds mainly due to the oxidation to carbon oxides and water. Methane and acetylene do not follow this behaviour as they are the most likely products from the decomposition of oxygenated compounds, such as ketones and aldehydes (Conesa et al., 2009).

The most abundant non-condensable products analysed by GC-MS and the total yields obtained are shown in **Table 1** but the rest of the products can be found in Table S1 in

Supporting Information. In this case the “nd” makes reference to levels lower than 10 mg/kg sample (LOD).

As expected, the pyrolytic degradations generated more non-condensable compounds than the combustions at both temperatures, from 429164 ± 18340 ppm to 102769 ± 4961 ppm at 550°C and from 168742 ± 42061 ppm to 50460 ± 6144 ppm at 850°C, the total yields detected in pyrolysis runs being higher than the emission during the combustion. This means that the pyrolysis at 550°C and combustion at 850°C presented the highest and the lowest levels, respectively.

Propylene is one of the most abundant products in all conditions as a consequence of the product from simultaneous degradation of urethane, polyether and aliphatic oxygenated functional groups present in the polymeric structure (Adeosun, 2014). Nitrile compounds (acrylonitrile, acetonitrile) and hydrogen cyanide present a significant health hazard (Boettner et al., 1973) because these compounds hamper the absorption of oxygen by the cells, which produces asphyxiation (Stec and Hull, 2011). They are products from an incomplete combustion showing their highest yields in the run performed under a nitrogen atmosphere at 850°C, due to the thermal breaking of heavier compounds. This behaviour agrees with the results obtained by Blomqvist et al. (2007) in their study of production of HCN, NH₃, and NO among others, from the thermal degradation of flexible polyurethane foam mattress in a tube furnace with well-ventilated (650°C) and vitiated (825°C) conditions, which can be compared to combustion (550°C) and pyrolysis (850°C) runs performed in the present study. They found yields of 4 mg/g and 9 mg/g for HCN under well-ventilated and vitiated conditions, respectively, whereas NO was found only at well-ventilated (4 mg/g) and NH₃ only at vitiated conditions (1.5 mg/g). Despite that they obtained similar trends to those presented in this study for all compounds, the total yields were lower than the average values presented in **Table 1** for the considered runs (combustion at 550°C and pyrolysis at 850°C).

This fact can be explained bearing in mind that in the tube furnace tests performed by Blomqvist et al. (2007), the exhaust gases were diluted in a mixing chamber in order to analyse them with a FTIR spectrometer.

The study of the effect of temperature in the degradation of FPUF at different atmospheres performed in this work, allows us to know the yields of compounds that present a risk for people (HCN, NH₃ and NO) in the extreme conditions that could be reached in incineration systems or accidental fires (Blomqvist, 2005).

In **Table 1** it can be observed that, in general, the standard deviations values are small, in comparison with the average values, and only when the average values are small, can the standard deviation be somewhat greater but always, less than 30% of average value.

3.3. PAHs and Other Semivolatile Compounds

The profiles of the 16 priority PAHs are shown in **Figure 1**, whereas other semivolatile compounds detected in the SCAN mode can be found in the Supporting Information (Table S2). In the blank runs, PAHs compounds detected showed levels lower than 1 mg/kg sample which was the calculated limit of detection (LOD), whereas for other semivolatile compounds the LOD considered was 10 ppm.

More than 180 other semivolatile compounds were identified and quantified (Table S2), observing that the run performed under a N₂ atmosphere at 850°C shows the maximum total yield followed by pyrolysis at 550°C, combustion at 550°C and finally combustion at 850°C. In order of abundance, benzonitrile and styrene are the most abundant products in all runs with the highest concentration in pyrolysis at 850°C and the lowest in combustion at 850°C. These compounds, along with ether compounds, such as 1-2-(1-methylethoxy)-Propanol, and 1-propoxy-2-Propanol, come from the direct degradation of long chains of polyurethane polymer. On the other hand, nitrogen containing compounds are one of the most important

groups of products evolved in pyrolysis runs with 75 different compounds detected. Some of these products such as benzonitrile, aniline, indole and isoquinoline have previously been reported by other authors (Adeosun, 2014; Esperanza et al., 2000; Esperanza et al., 1999), whereas in this study apart from these compounds indene, 4-methyl-benzonitrile, isocyanate benzene and quinolone have also been detected with relatively high yields. Total yields for nitrogen obtained in pyrolysis runs were 490 ± 30 mg of N /kg_{sample} at 550°C and 2370 ± 90 mg of N /kg_{sample} at 850°C, whereas in the combustion runs these levels decreased from 210 ± 20 mg N /kg_{sample} at 550°C to 50 ± 10 mg N /kg_{sample} at 850°C. These latter yields would account for the 0.8, 3.9, 0.4 and 0.1% of the nitrogen content in the initial sample.

The increase of yields with the temperature under an inert atmosphere, for almost all the semivolatile organic compounds detected can be explained considering the pyrosynthesis reactions from aliphatic hydrocarbons formed in the primary decomposition of polyurethane and their relatively high thermal stability (Ji et al., 2006).

With reference to 16 priority PAHs the total yields follow the same trend as the semivolatile compounds explained previously, pyrolysis at 850°C presented the highest emissions with a total yield of 6871 ± 76 mg/kg sample, followed by pyrolysis at 550°C (191 ± 32 mg/kg sample), combustion at 550°C (44 ± 5 mg/kg sample) and, finally combustion at 850°C (18 ± 2 mg/kg sample), which means that the yields of PAHs at 850°C decreased more than 90% from pyrolysis to combustion. Naphthalene, acenaphthylene, phenanthrene, pyrene and fluorene, in this order, are the most abundant compounds (**Figure 1**). This profile agrees with the results obtained by Herrera et al. (2002), although in their study, they did not detect a great difference between the PAH yields in the combustion under fuel-rich conditions and pyrolysis runs of two thermoplastic polyurethane elastomers. Herrera et al. (2002) explained the congener distribution employing the precursor theory which establishes that initially, the first aromatic ring (benzene) is formed and then begins growing to heavier PAHs. For this

reason, the concentration of naphthalene is higher than acenaphthylene, whose concentration is higher than phenanthrene. This theory can be accepted as a possible explanation of the profiles obtained in the present study.

The PAH yields under an inert atmosphere increased from 550 to 850°C. Similar behaviour was observed with other organic wastes (Aracil et al., 2010; Esperanza et al., 2000) due to the fact that when increasing the pyrolysis temperature, the primary products (aliphatic hydrocarbons) evolve into light gases and aromatics, mainly, polycyclic aromatic hydrocarbons (Mastral et al., 2002). Liu et al. (2000) found a rise with the temperature of PAHs in the gas phase from the pyrolysis of coal in a laboratory scale fluidized bed reactor, relating it with cyclization reactions to form heavier compounds.

Under an oxidative atmosphere, the increase of temperature together with the presence of oxygen involves the destruction of most of the aromatic compounds.

Finally, it is important to observe that the 7 most carcinogenic PAHs (benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene and dibenz(a,h)anthracene) were detected in the pyrolysis run at 850°C with a total yield of 381 ± 77 mg/kg_{sample}.

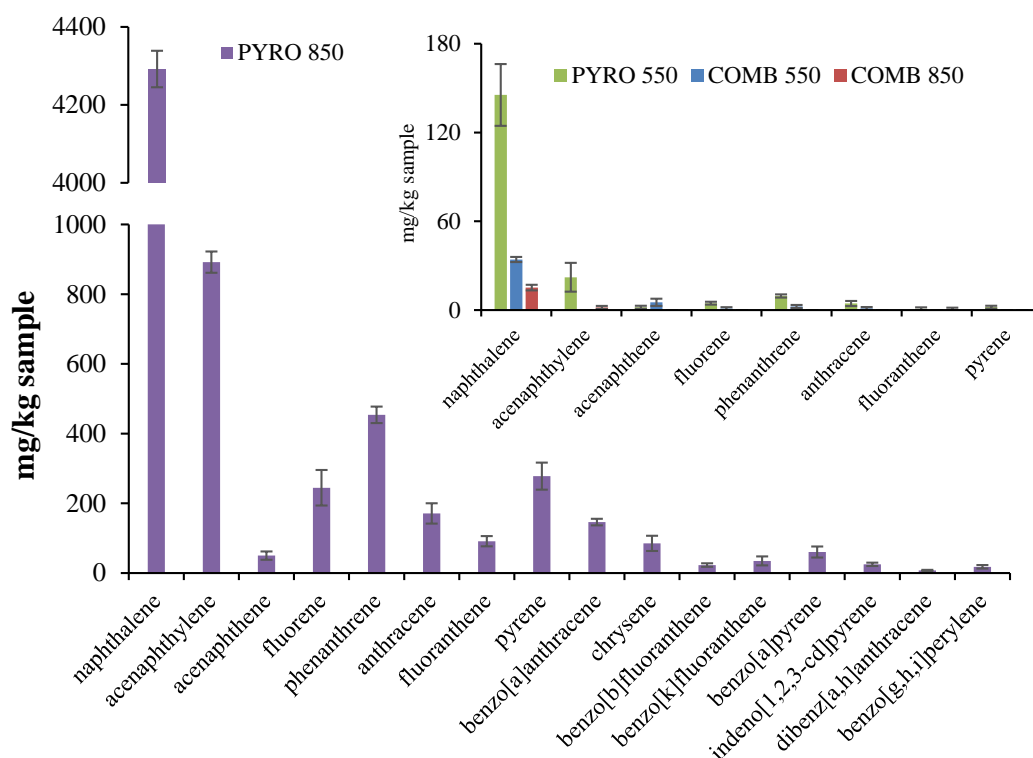


Figure 1. Evolution of 16 priority PAHs during the thermal degradation of FPUF at two different temperatures and two different atmospheres. Average values with the error bars from the duplicated runs.

3.4. Chlorobenzenes and chlorophenols

Chlorobenzenes

In this case the LOD calculated was 0.1 ppm and the levels of the congeners detected in blank runs were lower than this value.

The results of the ClBzs analyses are shown in **Table 2**. Pyrolysis and combustion runs show an opposite trend with the temperature; the total yields of ClBzs rose when the temperature increased, from 42.0 ± 5.6 to 359.4 ± 32.1 mg/kg_{sample} in pyrolysis and decreased from 27.2 ± 16.5 to 4.1 ± 1.5 mg/kg_{sample} in combustion. Despite the great variation of total yields from the combustion to pyrolysis runs, both at 550°C and 850°C, no important

difference in the congener profiles has been detected, and monochlorobenzene was the most abundant in all runs. The predominance of mono-ClBz could be explained assuming the precursor theory for PAH formation explained previously, bearing in mind the low level of chlorine in the initial sample (0.0253%). In pyrolysis, benzene could react with chlorine to obtain mono-ClBz mainly, whereas in combustion benzene is decomposed to more light hydrocarbons avoiding the formation of ClBzs. The trends of mono-ClBz yields observed in both, pyrolysis and combustion runs, with temperature agree with the benzene profile observed previously which could confirm the hypothesis proposed before.

Table 2. Average and standards deviations yields of ClBzs in pyrolysis and combustion runs at different temperatures (nd<LOD=0.1 mg/kg sample).

Experiment	PYRO 550			PYRO 850			COMB 550			COMB 850		
Compound	mg compound/kg sample											
Mono-	41.2	±	5.9	359.4	±	32.0	27.2	±	16.5	2.3	±	0.3
1,3-	0.2	±	0.1	nd			nd			nd		
1,4-	0.6	±	0.4	0.2	±	0.1	nd			nd		
1,2-	nd			nd			nd			1.9	±	1.8
1,3,5-	nd			nd			nd			nd		
1,2,4-	nd			nd			nd			nd		
1,2,3-	nd			nd			nd			nd		
1,2,3,5-+1,2,4,5-	nd			nd			nd			nd		
1,2,3,4-	nd			nd			nd			nd		
penta-	nd			nd			nd			nd		
hexa-	nd			nd			nd			nd		
Total	42.0	±	5.6	359.6	±	32.1	27.2	±	16.5	4.1	±	1.5

Chlorophenols

No significant variation has been detected in total yields of chlorophenols (**Table S4**) with the temperature in combustion (7.8 ± 0.1 mg/kg_{sample} at 550°C and 6.5 ± 0.1 mg/kg_{sample} at 850°C) whereas in pyrolysis, there is a slight decrease from 4.8 ± 0.6 mg/kg_{sample} at 550°C to 2.4 ± 0.1 mg/kg_{sample} at 850°C.

The oxidation of corresponding ClBzs precursors can be responsible for the formation of the isomers of ClPhs under oxidative conditions (Aracil et al., 2010) which usually involves the increase of ClPhs total yields from pyrolysis to combustion. Data in **Table S4** confirms this fact.

Congener 3-+ 4-ClPh is the most abundant product in all runs except in pyrolysis at 550°C where 3,4,5-Cl₃Ph is the predominate product, as can be seen in **Figure 2**.

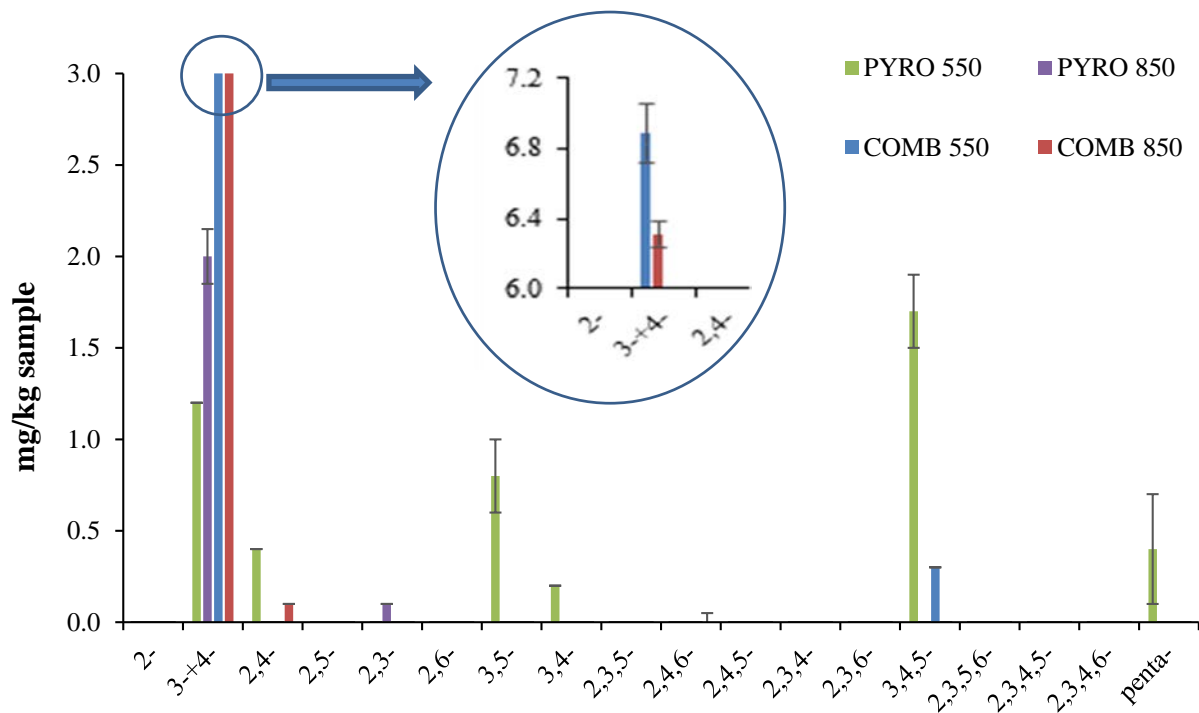


Figure 2. Average values and the error bars for the ClPhs congeners evolved during the pyrolysis and combustion of FPUF at 550°C and 850°C.

The 3-+ 4-ClPh and 3,5-Cl₂Ph congeners, presented significant yields in pyrolysis at 550°C, apart from 3,4,5-Cl₃Ph. With these results, it can be observed that the isomers with chlorine atoms situated in meta- and para- positions are favoured in these conditions. When the temperature increased under an inert atmosphere, polychlorophenols decreased their yields and this fact contributed to the decrease of total yields. On the other hand, no

significant variation was observed in the yield of monochlorophenol (3-+ 4-ClPh) with the temperature which was not the expected trend. The possible explanation for this behaviour could be the oxidation of some mono-ClBz obtained at these conditions (Ballschmiter et al., 1988). This behaviour is complex to explain but it can be considered that the high content of oxygen in the FPUF structure and the possible presence of oxygen in the furnace could produce the oxidation of ClBzs to ClPhs in the pyrolytic runs at higher temperature.

In combustion runs, an increase in the temperature (**Table S4**) produced a slight decrease of total yields which was the expected behaviour due to the thermal cracking of aromatic compounds under an oxidative atmosphere. Also, under oxidative conditions the monochlorophenol (3-+ 4-) did not present an important reduction in its yield with the temperature in spite of the thermal destruction. Perhaps, the oxidation of mono-ClBz to 3-+ 4-ClPh is more important than the thermal cracking.

3.5. PCDD/Fs and dioxin-like PCBs

Table 3 presents the yields of 17 congeners of 2,3,7,8-Cl-substituted PCDD/Fs obtained in the pyrolysis and combustion runs at 550 and 850°C in pg/g, pg I-TEQ /g and pg WHO-TEQ /g sample. Details of the analyses in the runs performed in duplicate are available as Supporting Information (**Table S5**). The values shown have been calculated subtracting the yields obtained in the blank experiments which have also been included in **Table 3** in order to show that in all cases, the data obtained in the blank runs were much lower than these obtained in the experiments with FPUF, the LOD calculated being equal to 1 pg/g sample not only for PCDD/Fs but also for dlPCBs.

Total yields in pyrolysis and combustion at 850°C are higher than those obtained at lower temperature, as reported previously (Aracil et al., 2010). Comparing these total yields at the highest temperature there is not a great difference between pyrolysis and combustion, despite

the fact that the formation of PCDD/Fs is favoured at intermediate oxygen ratios (Conesa et al., 2011).

On the other hand, the high level of ammonia obtained in the pyrolysis run at 550°C could be responsible for the low formation of total PCDD/Fs, compared to the combustion run at the same temperature, due to the inhibitory effect of ammonia on PCDD/F formation and the dechlorination of more highly substituted congeners (Ruokojärvi et al., 1998)

Combustion at 850°C of FPUF produced 10 times more PCDD/Fs than the combustion at 550°C. This behaviour is difficult to explain because it is known that chlorinated phenols are precursors of PCDD/Fs formation (Ballschmiter et al., 1988) and bearing in mind that the yields of these compounds did not change significantly with the temperature (**Figure 2**), it could be expected that there was no increase in the emissions of PCDD/F. However, the decrease of the NH₃ yield with the increase of temperature under an oxidative atmosphere (**Table 1**) could explain the rise of PCDD/Fs observed in this study due to the inhibitor effect of ammonia in the formation of dioxins commented previously (Ruokojärvi et al., 1998).

476 **Table 3.** Average and standard deviations of emission of PCDD/Fs obtained in pyrolysis and combustion at different temperatures from
477 both sample and blank runs (nd<LOD=1 pg/g sample).

pg/g sample																
Experiment	PYRO 550				PYRO 850				COMB 550				COMB 850			
Compound	Blank		Sample		Blank		Sample		Blank		Sample		Blank		Sample	
2,3,7,8-TCDF	nd		1	± 1	nd		nd		nd		4	± 4	nd		1	± 1
1,2,3,7,8-PeCDF	nd		3	± 3	nd		3	± 3	1	± 1	5	± 5	nd		2	± 1
2,3,4,7,8-PeCDF	1	± 1	3	± 3	nd		4	± 4	2	± 2	58	± 12	nd		2	± 1
1,2,3,4,7,8-HxCDF	nd		2	± 2	1	± 1	6	± 4	nd		30	± 4	1	± 1	2	± 2
1,2,3,6,7,8-HxCDF	nd		1	± 1	1	± 1	5	± 2	nd		14	± 14	1	± 1	2	± 2
2,3,4,6,7,8-HxCDF	1	± 1	1	± 1	1	± 1	8	± 4	nd		76	± 9	nd		3	± 3
1,2,3,7,8,9-HxCDF	1	± 1	nd		1	± 1	2	± 2	1	± 1	15	± 15	nd		1	± 1
1,2,3,4,6,7,8-HpCDF	2	± 2	nd		nd		4	± 4	nd		56	± 43	5	± 1	50	± 25
1,2,3,4,7,8,9-HpCDF	nd		nd		nd		nd		nd		24	± 7	nd		2	± 2
OCDF	nd		nd		nd		nd		nd		54	± 15	nd		6	± 6
2,3,7,8-TCDD	nd		6	± 6	nd		nd		nd		nd		nd		3	± 3
1,2,3,7,8-PeCDD	1	± 1	15	± 11	2	± 1	17	± 2	1	± 1	28	± 2	1	± 1	57	± 13
1,2,3,4,7,8-HxCDD	nd		3	± 3	1	± 1	7	± 7	nd		5	± 1	nd		42	± 3
1,2,3,6,7,8-HxCDD	nd		2	± 2	1	± 1	23	± 23	1	± 1	21	± 8	nd		133	± 20
1,2,3,7,8,9-HxCDD	nd		17	± 17	1	± 1	17	± 17	1	± 1	16	± 9	nd		137	± 22
1,2,3,4,6,7,8-HpCDD	nd		6	± 6	1	± 1	433	± 9	nd		51	± 27	3	± 3	1221	± 130
OCDD	2	± 2	nd		8	± 1	1614	± 196	3	± 3	39	± 20	3	± 3	2458	± 468
Total PCDD/Fs	8	± 6	60	± 14	17	± 4	2143	± 234	10	± 9	496	± 97	14	± 5	4122	± 699
Total I-TEQ PCDD/Fs	1	± 1	18	± 12	2	± 1	24	± 5	2	± 2	63	± 2	1	± 0	80	± 17
Total WHO-TEQ PCDD/Fs	1	± 1	25	± 17	2	± 1	30	± 3	2	± 2	65	± 1	1	± 1	106	± 23

478

PCDD congeners are more abundant than PCDFs in all runs except in combustion at 550°C. The 1,2,3,4,6,7,8-HpCDD and OCDD congeners represent about 30% and 70% of total levels, respectively, both in pyrolysis and combustion at 850°C, whereas at 550°C less chlorinated compounds are the predominant. This is the expected trend because the most chlorinated congeners are usually more stable at high temperature (Kim et al., 2004).

Less chlorinated congeners, tetrachlorodibenzo-p-dioxin being the least chlorinated congener considered in this work, are more toxic than more chlorinated ones; the isomer 1,2,3,7,8-PeCDD was the one that contributed most to the total WHO-TEQ in all cases. This fact caused the toxicity levels in pg WHO-TEQ/g of PCDDs to be higher than PCDFs in nearly all the experiments except in combustion at 550°C, where the 2,3,4,7,8-PeCDF congener presented a level of 17 ± 5 pg WHO-TEQ/g and contributed significantly to the total level of PCDFs which was 32 ± 2 pg WHO-TEQ/g, i.e., practically equal to 33 ± 1 pg WHO-TEQ/g of total PCDDs. Similar results were obtained by Fiedler et al. (2000) from the analysis of 109 stack emission samples coming from three different thermal emitters such as the iron and steel industries, municipal solid waste incinerations and hazardous waste incinerations. They concluded that the 2,3,4,7,8-PeCDF isomer was the major contributor to the I-TEQ of 17 samples.

The emissions of PCDD/Fs during the combustion at 850°C of different wastes employing the same reactor used in the present work have been studied previously. Combustion of tomato plant (Moltó et al., 2010b) and pine needles and cones (Moltó et al., 2010a) generated PCDD/F levels in the same range as those obtained in this work.

With respect to the total yields of dlPCBs, the effect of temperature was similar in pyrolysis and combustion because there was an increase of more than 80% when the temperature rose in pyrolysis, from 244 ± 45 to 1212 ± 207 pg/g and also a much slighter increase in combustion, from 1431 ± 122 to 1904 ± 102 pg/g (**Figure 3**). PCB-118, PCB-105 and PCB-

77 show the highest concentrations in all the runs (**Figure 3**) but due to the low toxicity of these congeners, the total WHO-TEQ PCBs obtained were 0.4 ± 0.1 , 0.9 ± 0.2 and 0.9 ± 0.3 pg WHO-TEQ/g (**Table S5**) in pyrolysis at 550 and 850°C and combustion at 850°C, respectively. These values correspond to 2, 3 and 1% of total toxicity (WHO-TEQ PCDD/Fs+PCBs) in runs mentioned previously. On the other hand, combustion at 550°C presented a toxicity of 15.4 ± 0.2 pg WHO-TEQ/g (**Table S5**) due to the presence of the PCB-126 congener that has the highest toxicity and in this case the contribution of PCBs in the total toxicity rose to 19%. A similar dioxin-like PCB profile obtained in combustion at 550°C, was reported by Font et al. (2011) in the combustion at 500°C of mobile phone case made of acrylonitrile-butadiene-styrene (ABS)/polycarbonate (PC) blend, performed in the same reactor used in this study. On the other hand, the predominance of PCB-77, PCB-105 and PCB-118 has been related with the incineration of municipal solid waste (Abad et al., 2006; Sakai et al., 2001).

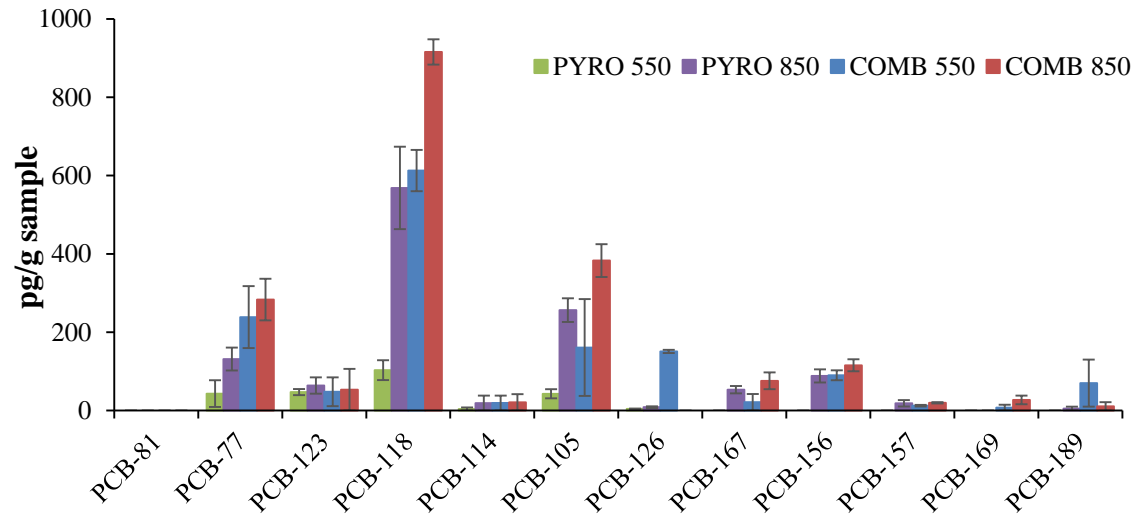


Figure 1. Average levels of dioxin like PCBs congener patterns obtained in pyrolysis and combustion of FPUF at 550°C and 850°C with the error bars from the two runs.

Analysing the results from PCDD/Fs and dlPCBs, it can be concluded that the formation of these chlorinated compounds is favoured at high temperature and under sub-stoichiometric conditions, however the less toxic congeners are the majority. This fact, along with its high net caloric value, makes FPUF a suitable fuel as an example in cement kilns.

4. CONCLUSIONS

In spite of the fact that pyrolytic degradation at 550°C involved high yields of volatile organic compounds, the concentration of toxic products, such as nitrile compounds (acrylonitrile, acetonitrile) and hydrogen cyanide were higher at 850°C.

The 16 priority PAHs and more than 180 other semivolatile compounds were detected in the analysis of samples obtaining the highest levels in pyrolysis run at 850°C. Benzonitrile, styrene and naphthalene were the most abundant compounds in all cases. The 7 most carcinogenic PAHs were only detected in pyrolysis runs at 850°C but with relatively low levels.

Also, the pyrolysis run at 850°C showed the highest yields of ClBzs with the main contribution of mono-ClBz which agrees with the precursor theory assumed by the PAH explanation. No significant difference was obtained in the yields of ClPhs.

Combustion at 850°C produced the highest yields of PCDD/Fs followed by pyrolysis at 850°C. The inhibitory effect of ammonia resulted in the fact that, instead of having a similar amount of ClPhs, under an oxidative atmosphere, the run performed at 850°C generated 10 times more PCDD/Fs than the combustion at 550°C. Congeners 1,2,3,4,6,7,8-HpCDD and OCDD were the most abundant compounds in the runs performed at 850°C at both atmospheres whereas less chlorinated isomers such as 1,2,3,7,8,9-HxCDD and 1,2,3,7,8-

PeCDD and 2,3,4,6,7,8-HxCDF and 2,3,4,7,8-PeCDF presented the highest levels in pyrolysis and combustion at 550°C, respectively.

Low toxicity levels were obtained not only in PCDD/Fs but also in dI PCBs which makes FPUF a suitable supplementary fuel in cement kilns or in incineration plants with energy recovery where there is enough amount of oxygen to move away from the pyrolytic conditions, avoiding the formation of carcinogenic compounds, such as PAHs, and health hazard gases, nitriles, HCN and NH₃.

Acknowledgment

Support for this work was provided by the Spanish Ministry of Culture and Sport and by the CTQ2013-41006-R project from the Ministry of Economy and Competitiveness (Spain) and the PROMETEOII/2014/007 project from the Valencian Community Government (Spain).

References

- Abad, E., Martínez, K., Caixach, J., Rivera, J., 2006. Polychlorinated dibenzo-p-dioxins, dibenzofurans and 'dioxin-like' PCBs in flue gas emissions from municipal waste management plants. *Chemosphere* 63, 570-580.
- Adeosun, D.O., 2014. Analysis of Fire Performance, Smoke Development and Combustion Gases from Flame Retarded Rigid Polyurethane Foams. University of Waterloo.
- Aracil, I., Font, R., Conesa, J.A., 2005. Semivolatile and volatile compounds from the pyrolysis and combustion of polyvinyl chloride. *Journal of Analytical and Applied Pyrolysis* 74, 465-478.
- Aracil, I., Font, R., Conesa, J.A., 2010. Chlorinated and Nonchlorinated Compounds from the Pyrolysis and Combustion of Polychloroprene. *Environmental Science & Technology* 44, 4169-4175.
- Ballschmiter, K., Braunmiller, I., Niemczyk, R., Swerev, M., 1988. Reaction pathways for the formation of polychloro-dibenzodioxins (PCDD) and —dibenzofurans (PCDF) in combustion processes: II. Chlorobenzenes and chlorophenols as precursors in the formation of polychloro-dibenzodioxins and —dibenzofurans in flame chemistry. *Chemosphere* 17, 995-1005.

574 Blomqvist, P., 2005. Emissions from Fires Consequences for Human Safety and the Environment.
575 Lund University.

576 Blomqvist, P., Hertzberg, T., Tuovinen, H., Arrhenius, K., Rosell, L., 2007. Detailed determination
577 of smoke gas contents using a small-scale controlled equivalence ratio tube furnace method. *Fire*
578 *and Materials* 31, 495-521.

579 Boettner, E.A., Ball, G.L., Weiss, B., 1973. Combustion products from the incineration of plastics.
580 DTIC Document.

581 Conesa, J.A., Font, R., Fullana, A., Martín-Gullón, I., Aracil, I., Gálvez, A., Moltó, J., Gómez-Rico,
582 M.F., 2009. Comparison between emissions from the pyrolysis and combustion of different
583 wastes. *Journal of Analytical and Applied Pyrolysis* 84, 95-102.

584 Conesa, J.A., Fullana, A., Font, R., 2000. Tire Pyrolysis: Evolution of Volatile and Semivolatile
585 Compounds. *Energy & Fuels* 14, 409-418.

586 Conesa, J.A., Rey, L., Egea, S., Rey, M.D., 2011. Pollutant Formation and Emissions from Cement
587 Kiln Stack Using a Solid Recovered Fuel from Municipal Solid Waste. *Environmental Science*
588 *& Technology* 45, 5878-5884.

589 Esperanza, M.M., Font, R., García, A.N., 2000. Toxic byproducts from the combustion of varnish
590 wastes based on polyurethane in a laboratory furnace. *Journal of Hazardous Materials* 77, 107-
591 121.

592 Esperanza, M.M., García, A.N., Font, R., Conesa, J.A., 1999. Pyrolysis of varnish wastes based on a
593 polyurethane. *Journal of Analytical and Applied Pyrolysis* 52, 151-166.

594 Fiedler, H., Lau, C., Eduljee, G., 2000. Statistical analysis of patterns of PCDDs and PCDFs in stack
595 emission samples and identification of a marker congener. *Waste Management & Research* 18,
596 283-292.

597 Font, R., Fullana, A., Caballero, J.A., Candela, J., Garcia, A., 2001. Pyrolysis study of polyurethane.
598 *Journal of Analytical and Applied Pyrolysis* 58, 63-77.

599 Font, R., Gálvez, A., Moltó, J., Fullana, A., Aracil, I., 2010. Formation of polychlorinated compounds
600 in the combustion of PVC with iron nanoparticles. *Chemosphere* 78, 152-159.

601 Font, R., Moltó, J., Egea, S., Conesa, J.A., 2011. Thermogravimetric kinetic analysis and pollutant
602 evolution during the pyrolysis and combustion of mobile phone case. *Chemosphere* 85, 516-524.

603 Garrido, M.A., Font, R., 2015. Pyrolysis and combustion study of flexible polyurethane foam. *Journal*
604 *of Analytical and Applied Pyrolysis* 113, 202-215.

605 Guo, Q., Zhang, X., Li, C., Liu, X., Li, J., 2012. TG-MS study of the thermo-oxidative behavior of
606 plastic automobile shredder residues. *Journal of Hazardous Materials* 209-210, 443-448.

607 Herrera, M., Matuschek, G., Kettrup, A., 2002. Thermal degradation of thermoplastic polyurethane
608 elastomers (TPU) based on MDI. *Polymer Degradation and Stability* 78, 323-331.

609 ISOPA, 2012. Recycling and recovery of polyurethanes.

610 Ji, L., Hervier, A., Sablier, M., 2006. Study on the pyrolysis of polyethylene in the presence of iron
611 and copper chlorides. *Chemosphere* 65, 1120-1130.

612 Kim, K.-S., Hong, K.-H., Ko, Y.-H., Kim, M.-G., 2004. Emission Characteristics of PCDD/Fs, PCBs,
613 Chlorobenzenes, Chlorophenols, and PAHs from Polyvinylchloride Combustion at Various
614 Temperatures. *Journal of the Air & Waste Management Association* 54, 555-562.

615 Leichtnam, J.N., Schwartz, D., Gadiou, R., 2000. The behaviour of fuel-nitrogen during fast pyrolysis
616 of polyamide at high temperature. *Journal of Analytical and Applied Pyrolysis* 55, 255-268.

617 Liu, K., Xie, W., Zhao, Z.-B., Pan, W.-P., Riley, J.T., 2000. Investigation of polycyclic aromatic
618 hydrocarbons in fly ash from fluidized bed combustion systems. *Environmental Science &
619 Technology* 34, 2273-2279.

620 Mastral, F.J., Esperanza, E., García, P., Juste, M., 2002. Pyrolysis of high-density polyethylene in a
621 fluidised bed reactor. Influence of the temperature and residence time. *Journal of Analytical and
622 Applied Pyrolysis* 63, 1-15.

623 Moltó, J., Font, R., Gálvez, A., Muñoz, M., Pequenín, A., 2010a. Emissions of
624 Polychlorodibenzodioxin/Furans (PCDD/Fs), Dioxin-Like Polychlorinated Biphenyls (PCBs),
625 Polycyclic Aromatic Hydrocarbons (PAHs), and Volatile Compounds Produced in the
626 Combustion of Pine Needles and Cones. *Energy & Fuels* 24, 1030-1036.

627 Moltó, J., Font, R., Gálvez, A., Rey, M.D., Pequenín, A., 2010b. Analysis of dioxin-like compounds
628 formed in the combustion of tomato plant. *Chemosphere* 78, 121-126.

629 Nielsen, M., Jurasek, P., Hayashi, J., Furimsky, E., 1995. Formation of toxic gases during pyrolysis
630 of polyacrylonitrile and nylons. *Journal of Analytical and Applied Pyrolysis* 35, 43-51.

631 Paabo, M., Levin, B.C., 1987. A review of the literature on the gaseous products and toxicity
632 generated from the pyrolysis and combustion of rigid polyurethane foams. *Fire and Materials*
633 11, 1-29.

634 Ruokojärvi, P.H., Halonen, I.A., Tuppurainen, K.A., Tarhanen, J., Ruuskanen, J., 1998. Effect of
635 Gaseous Inhibitors on PCDD/F Formation. *Environmental Science & Technology* 32, 3099-
636 3103.

637 Sakai, S.-I., Hayakawa, K., Takatsuki, H., Kawakami, I., 2001. Dioxin-like PCBs Released from
638 Waste Incineration and Their Deposition Flux. *Environmental Science & Technology* 35, 3601-
639 3607.

640 Stec, A.A., Hull, T.R., 2011. Assessment of the fire toxicity of building insulation materials. *Energy
641 and Buildings* 43, 498-506.

642 US EPA, 1994b. Method 1613. Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope
643 Dilution HRGC/HRMS. United States Environmental Protection Agency. Office of Solid Waste,
644 Springfield: National Technical Information Service.

645 US EPA, 1997. Procedure for collection and analysis of ammonia in stationary sources (CTM-027).
646 United States Environmental Protection Agency, Washington, D.C.

647 US EPA, 1998. Handbook for air toxic emission inventory development. Volume I: Stationary
 648 sources. United States Environmental Protection Agency. Office of Air Quality Planning and
 649 Standards.

650 US EPA, 2007a. Method 3545A: Pressurized Fluid Extraction (PFE). Revision 1. United States
 651 Environmental Protection Agency. Office of Solid Waste, Washington, D.C., pp. 1-16.

652 US EPA, 2007b. Method 8270D. Semivolatile organic compounds by GC/MS. United States
 653 Environmental Protection Agency. Office of Solid Waste, Washington, D.C.

654 US EPA, 2010. Method 1668 C: Chlorinated byphenil congeners in water, soil, sediment, biosolid
 655 and tissue by HRGC/HRMS. United States Environmental Protection Agency. Office of Water.
 656 Office of Science and Technology, Washington, D.C.

657 Zevenhoven, R., 2003. Treatment and disposal of polyurethane wastes:options for recovery and
 658 recycling, in: Protection, H.U.o.T.E.E.a.E. (Ed.), Espoo

659 Zevenhoven, R., Kilpinen, P., 2002. Chapter 4: Nitrogen, in: Technology, H.U.o. (Ed.), Control of
 660 pollutants in flue gases and fuel gases.

661 Zhang, Y., Xia, Z., Huang, H., Chen, H., 2009. Thermal degradation of polyurethane based on IPDI.
 662 Journal of Analytical and Applied Pyrolysis 84, 89-94.

663