Pollutant formation in the pyrolysis and combustion of Automotive Shredder Residue

Lorena Rey, Juan A. Conesa, Ignacio Aracil, Maria A. Garrido, Nuria Ortuño*

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

Phone: +(34) 96 590 38 67 Fax: +(34) 96 590 38 26

**Author's email:* ja.conesa@ua.es

ABSTRACT

The present work has been carried out to verify the feasibility of thermal valorization of an automobile shredder residue (ASR). With this aim, the thermal decomposition of this waste has been studied in a laboratory scale reactor, analyzing the pollutants emitted under different operating conditions. The emission factors of carbon oxides, light hydrocarbons, PAHs, PCPhs, PCBzs, PBPhs, PCDD/Fs, dioxin-like PCBs and PBDD/Fs were determined at two temperatures, 600 and 850ºC, and under different oxygen ratios ranging from 0 (pure pyrolysis) to 1.5 (over-stoichiometric oxidation). After analyzing all these compounds, we conclude that thermal valorization of ASR is a clean way to treat this waste.

Keywords:

ASR; ELV; PCDD/Fs; dl-PCBs; PBDD/Fs; semivolatile compounds

1. Introduction

In the last decades, the industrial sector devoted to End-of-Life Vehicles (ELV) has changed significantly due to the publication of Directive 2000/53/EC. This evolution has involved a leap from the old scrapyards to the authorized treatment facilities (ATF) (Cossu and Lai, 2015).

This Directive established clear objectives of reuse, recovery and recycling of ELV with the aim of reducing the negative effects in the environment. The Directive dictated that "no later than 1st January 2015, for all end-of-life vehicles, the reuse and recovery shall be increased to a minimum of 95 % by an average weight per vehicle and year. Within the same time limit, the reuse and recycling shall be increased to a minimum of 85 % by an average weight per vehicle and year" (Cossu and Lai, 2015).

The EU generates among 7-8 million tons of ELV every year; and it is estimated that the total amount of ELV generated in Europe by 2030 will reach among 14-17 million tons (Andersen et al., 2008; Cossu and Lai, 2015).

After depolluting, dismantling and shredding of ELV, a remaining fraction appears. This fraction, called automobile shredder residue (ASR), is a heterogeneous material (Gonzalez-Fernandez et al., 2008; Santini et al., 2011) composed by a complex mixture of plastics (19-35%), rubber (20%), textile (10-40%), wood (2-5%), metals (8%), oils (5%) and other unidentifiable materials (10%) (Morselli et al., 2010). ASR accounts for 10–25% of the initial ELV's mass and used to be mostly sent to landfill (Gonzalez-Fernandez et al., 2008; Morselli et al., 2010; Reddy et al., 2008; Santini et al., 2011).

In order to comply with the European Directive, energy recovery might be feasible using ASR as a secondary fuel in thermal treatments. Some previous work was focused on the energy recovery from the combustible part of ASR. However, there is not extensive information of the emissions from thermal degradation processes of ASR neither in oxidative atmosphere nor inert one. Only some authors (Braslaw et al., 1991; Day et al., 1999; de Marco et al., 2007; Donaj et al., 2009; Galvagno et al., 2001; Zolezzi et al., 2004) characterized the emissions generated in thermal treatments using ASR as raw material so further research is needed to minimize some of the uncertainty regarding the use of such wastes as secondary fuel. Mancini et al. (Mancini et al., 2014a; Mancini et al., 2014b) showed that the slag and bottom ash from the combustion process of ASR can be classified as non-hazardous wastes, according to the EU waste acceptance criteria. Furthermore, the authors recommend to pre-treat the ASR before combustion to increase the heat of combustion by reducing fines, which further enhance dust deposit problems.

The aim of the present work is to study the thermal degradation of ASR to assess the emission of pollutants under different operating conditions in a laboratory scale reactor. The study comprises the analysis of CO, CO_2, light hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), polychlorinated phenols (PCPhs), polychlorinated benzenes (PCBzs), polybrominated phenols (PBPhs), polybromo- and polychlorodibenzo- p-dioxins and furans (PBDD/Fs and PCDD/Fs) and dioxin-like polychlorobiphenyls (dl-PCBs). The determination of these compounds is not generally found in the existing literature to the point that some of these contaminants such as PCPhs, PCBzs, PBPhs or PBDD/Fs have not been analyzed for ASR thermal treatments in any previous work. Hence, the present work reports additional findings concerning thermal decomposition of ASR.

2. Experimental/Material and Methods

2.1. Raw material / ASR

The material employed in this study was ASR collected from a cement factory owned by the CEMEX group sited in Alicante (Spain), where it is used as alternative fuel. ASR is a highly heterogeneous material, so prior to its use more than 5 kg of the sample were crushed using immersion in liquidnitrogen in order to homogenize it, but should be considered for discussion of results that it is very difficult to homogenize.

Characterization of this ASR and thermogravimetric study about its thermal decomposition under inert and oxidative atmospheres were previously published (Conesa et al., 2015). The results of the elemental analysis (three repetitions, standard deviation indicated) are: 56.61 $\pm$ 2.1 % C, 7.22$\pm$ 0.58 % H, 3.73 $\pm$ 0.4 % N, 0.01 $\pm$ 0.03 % S and 13.36 % O. The ash content is 22.1 wt. % and the moisture of the material is 2.0 wt. %. The net calorific value is 18750 kJ kg^{-1}.

Cl^- and Br^- anions were analyzed over five different samples using the EPA Method 5050 by ionic chromatography (DIONEX DX500) and the average values found were 277.0 and 5.56 mg/kg respectively.

2.2. Experimental setup

A moving tubular reactor was employed to perform the experiments. The reactor consisted of a quartz tube (10 mm internal diameter) where the ASR was uniformly placed in four quartz boats (70 mm long each) along the tube. This tube was introduced at an accurately controlled speed in a horizontal furnace while a constant flow of gas was passing through. A detailed description of the system can be found elsewhere (Barneto et al., 2014; Conesa et al., 2011).

Combustion and pyrolysis runs were conducted to study ASR decomposition products. During the study, different operating conditions were modified such as temperature, carrier gas and oxygen ratio (Conesa et al., 2009; Conesa et al., 2000).

Both pyrolysis and combustion experiments were carried out at two different temperatures, 600 and 850 ºC. The temperature of 850 ° C was used because it is the temperature reached in the post-combustion treatment plants. Also, the selection of two temperatures was done in order to allow comparing the formation of pollutants in worse conditions to determine the possible ways of their formation / elimination in the combustion process.

A sample of approximately 1 g of ASR spread over the four boats was employed in each experiment. For each run, synthetic air (combustion runs) or nitrogen (pyrolysis runs) was introduced in parallel flow to the sample at a constant flow rate of 300 mL min^{-1} (measured at 20ºC, 1 atm).

On the other hand, the effect of the presence of oxygen was studied by varying oxygen ratio (λ). This ratio was defined (Aracil et al., 2010) as the fraction between the actual air flow rate and the stoichiometric air flow rate necessary for complete combustion. It is an indicator of the quantity of oxygen present in the process ($\lambda = 0$ for pyrolysis processes, $\lambda = 1$ when the oxygen present is the stoichiometric necessary one for a complete combustion and $\lambda > 1$ for the run with excess of oxygen). The oxygen ratio is easily modified by changing the input speed of the boats. In this sense, the residence time in the hot zone of the furnace is approximately 560 seconds at the minimum input speed (0.5 mm/s) and 150 seconds for the higher input speed (1.9 mm/s), measured at 850 ºC, as indicated in previous work (Conesa and Domene, 2015).

2.3. Sampling and analytical procedure

For the pyrolysis and combustion of ASR, the outlet gas stream was sampled to analyze different types of pollutants:

- Gases and volatile compounds were collected using Tedlar® bags (Restek, USA) for a time long enough to collect all the compounds (Conesa et al., 2009). CO_2, CO, oxygen and nitrogen were analyzed using gas chromatography with thermal conductivity detector (GC-TCD) (Shimadzu GC-14A). Light hydrocarbons (from methane to xylenes) were analyzed by gas chromatography with flame ionization detector (GC-FID) (Shimadzu GC-17A).

- Semivolatile organic compounds (PAHs, PCPhs, PCBzs, BrPhs, PCDD/Fs, dl-PCBs and PBDD/Fs) were collected using a polyaromatic Amberlite® XAD-2 resin as adsorbent (Supelco, Bellefonte, USA). It was placed at the exit of the furnace during the entire run. The Tedlar® bags were placed after the XAD-2 resin.

The resin was consecutively extracted with toluene, a mixture of dichloromethane/acetone (1:1 vol.) and hexane using Accelerated Solvent Extraction (ASE-100, Dionex-Thermo Fisher Scientific Inc., California, USA). The extracted solution was divided into two fractions: 30 wt.% was employed to analyze PAHs (USEPA 8270D method), PCPhs, PCBzs and BrPhs and the other 70 wt.% was used for the analysis of PCDD/Fs, dl-PCBs (EPA 1613 and 1668A methods) and PBDD/Fs (EDF 5408 method).

The compounds of the first fraction (PAHs, PCPhs, PCBzs and BrPhs) were analyzed by HRGC-MS in a gas chromatograph coupled to a mass spectrometer (Agilent GC 6890N/Agilent MS 5973N, Agilent Technologies, USA).

Prior to the analysis of PCDD/Fs, dl-PCBs and PBDD/Fs, a cleanup was performed using an automated clean-up system (Power Prep, FMS, Inc., Boston, MA) with three different columns: silica, alumina, and activated carbon. The purified extract was analyzed by HRGC/HRMS using an Agilent HP5890 gas chromatograph equipped with programmable temperature vaporization (PTV) inlet, coupled to a Micromass Autospec Ultima-NT mass spectrometer. For the analysis of PCDD/Fs and dl-PCBs an Agilent DB5-MS chromatographic column (60m×0.25mm×0.25µm) was used, whereas for the analysis of PBDD/Fs a Restek TRB-Meta X5 column (15m×0.25mm×0.25µm) was employed. For PBDD/Fs, the laboratory material was protected from light with aluminum foil throughout the whole experimental process to avoid photodegradation of the brominated compounds.

Blank runs in the reactor were performed before each run reproducing the same experimental conditions. This means that a repetition of each run was performed without the ASR sample. Values found in these blank runs were subtracted from the corresponding values of the samples. In a recent paper (Garrido et al., 2016) it was evaluated the reproducibility of similar runs to that presented in this work, where it is shown that the reproducibility is quite good for all kind of compounds analysed in the emissions from pyrolysis and combustion of polyurethane foams.

3. Results and discussion

3.1. Gases and volatile compounds

Results regarding carbon oxides and light hydrocarbons analyzed by GC-TCD and GC-FID for pyrolysis and combustion runs at 600ºC and 850ºC are shown in Table 1. As stated before, the runs where performed at different values of the oxygen ratio, λ, between 0 and 1.5 approximately.

The most remarkable peculiarity in the results shown in Table 1 is the significant amounts of CO and CO_2 in ASR pyrolysis gases; this fact was also reported by other authors (Braslaw et al., 1991; Day et al., 1999; de Marco et al., 2007; Galvagno et al., 2001; Zolezzi et al., 2004). These gases come from the decomposition of polymers such as polycarbonates and polyurethanes present in the ASR and from the decomposition of carbonate fillers present in automotive plastics.

With regard to the effect of temperature in pyrolysis experiments, the release of CO increases with temperature meanwhile the CO_2 suffers a slight decrease. This is in agreement with the results presented by Haydary et al.(Haydary et al., 2016), Galvagno et al. (Galvagno et al., 2001) and Zolezzi et al. (Zolezzi et al., 2004) in which they studied the pyrolysis of ASR in different types of reactors.

On the other hand, in combustion runs the evolution of CO and CO_2 with temperature for a given λ is not equal for all λ values: for low λ values, CO and CO_2 behave as in pyrolysis runs, indicating that the effect of the temperature is more important that the presence of small amounts of oxygen in the atmosphere; however, at higher λ values the behavior changes, presenting a decrease of CO with temperature while CO_2 increased. This fact indicated that high temperature and high λ values provide a better combustion.

It can be also analyzed the evolution of carbon oxides with oxygen ratio at a definite temperature. The expected behavior is that the higher λ, the more CO_2 is present in the gas; and the higher λ, the less CO is present in the gas. This trend is evident in runs at 850ºC. Nevertheless, the tendency does not occur at 600ºC, where the trend is almost the opposite, although the differences are not as high as in the case of 850ºC. Summarizing, the effect of the oxygen ratio is different depending on the temperature considered, similarly to what was observed for the effect of the temperature at a given oxygen ratio.

From the data presented, it can be calculated the percentage of the carbon present in the sample that evolves as carbon oxides, i.e., that are converted to CO and CO_2. In the combustion runs, the carbon percentage of the sample evolved as CO is in the range of 0.13 - 13.7%, while the corresponding percentage as CO_2 ranges from 8.9 to 30.9%. In the pyrolysis runs these percentages are logically much lower, ranging from 1.8 - 4.6 for the CO and 4.2 - 5.2 for the CO_2, denoting that major part of the carbon remains in the solid phase (apart from that evolved as hydrocarbons).

[Table 1]

Regarding the formation of light hydrocarbons, the most abundant compounds are methane, ethylene and propylene for both pyrolysis and combustion runs. Under pyrolytic conditions light hydrocarbons show in general higher yields which indicate that these compounds react with oxygen in combustion experiments (Conesa et al., 2009; Conesa et al., 2000; Fullana et al., 2000). As for the temperature, most of them decrease their yields with increasing temperature, although there are some few exceptions at low (or zero) oxygen ratios, such as the case of methane, ethylene, benzene or toluene. As can be observed in Table 1, the combination of high temperatures and high oxygen ratios implies an important decrease in the volatile compounds yields.

3.2. PAHs, PCBzs, PCPhs and PBPhs

Figure 1 shows the results on the emissions of PAHs for all the experiments. Data is also available as Supplementary Material in Table SM1. In all the runs the profile of compounds is similar. Naphthalene is clearly the most abundant product, which is in agreement with the results presented by Conesa et al. (Conesa et al., 2009).

The maximum formation of the 16 priority PAHs occurs under pyrolytic conditions at high temperature (850ºC), as expected since it is known that pyrolytic reactions are the primary source of PAH formation (Thomas and Wornat, 2008). In relation to the effect of temperature, higher yields of PAHs are produced at 850ºC in all the experiments, in accordance with previous literature (Fullana et al., 2000), where it is shown that PAHs have maximums at 750-850ºC.

With respect to the effect of the presence of oxygen, the trend is different depending of the temperature considered. At 850ºC, PAHs clearly show a minor emission as the oxygen ratio increases. This indicates that PAHs are pyrolytic products that are easily eliminated in oxygen rich environments at this temperature (Fullana et al., 2000). But at 600ºC, the behavior changes. The reason for that can be explained if we consider that, when comparing at the same time both the presence of oxygen and the temperature, two different and competitive behaviors can be observed. At 850ºC, an oxidative destruction effect of the PAHs takes place when increasing the oxygen ratio. However, at 600ºC the formation of free radicals is enhanced with the presence of oxygen, which boost the pyrolytic reactions. This produces an initial increase in the PAHs yields until stoichiometric conditions followed by a decrease at elevated oxygen ratios when the oxidative destruction effect is dominant (Thomas and Wornat, 2008).

[Figure 1]

Van Caneghem et al. (Van Caneghem et al., 2010) reported that adding ASR to the refuse-derived fuel (RDF) and wastewater treatment sludge in the usual waste feed to a real-scale fluidized bed combustor not only did not increase the concentration of PAHs in the flue gas but decreased it. Their results showed that the formation of new pollutants during the cooling of the flue gas were independent of the pollutants concentration in the incinerated raw wastes.

With regard to PCBzs, PCPhs and PBPhs, relatively low quantities of these compounds were detected. The total emission of chlorobenzenes, chlorophenols and bromophenols are presented in Table 2. The total yields of polychlorinated and polybrominated phenols were nearly negligible and varied between 1-6.6 mg/kg, and 0.2-2.63 mg/kg respectively. Details on each isomer analysis can be found in Supplementary Material (Tables SM2, SM3 and SM4).

The emissions from the pyrolysis experiments are lower than those of the combustion experiments at low λ values. That is similar to the behavior observed for PAHs at 600ºC. For these λ values, the oxygen favours the formation of free radicals and so pyrolytic reactions that can help to form PCPhs take place. The difference with PAHs is that, since PCPhs are oxygenated compounds, in the case of PCPhs the effect of oxygen in the increase of PCPhs yields is observed also at 850ºC, not only at 600ºC. Finally, the decrease in PCPh yields is only observed at high λ values."

[Table 2]

The yields of chlorobenzenes decreased with temperature in combustion experiments meanwhile in pyrolysis the results were in the same order of magnitude at both temperatures, and in general lower than in the presence of oxygen. The most abundant congener was monochlorobenzene as can be found in Table SM3 in the Supplementary Material. Apart from this, no other formation pattern was observed. However, based upon the data presented in Table SM3, it can be stated that an increase in the temperature implies the destruction of such pollutants in the presence of oxygen and so the yields emitted were very low, as expected (Conesa et al., 2009).

No many references were found in the literature in order to compare the results obtained for PAHs and no data were found about the formation of chlorobenzenes, chlorophenols and bromophenols in the thermal decomposition of ASR.

3.3. PCDD/Fs, dl-PCBs and PBDD/Fs

PCDD/Fs and dl-PCBs congener distribution, expressed as pg WHO-TEQ/g, of the different combustion and pyrolysis runs performed are plotted in Figures 2 and 3, respectively. Specific data can be found in Tables SM4 and SM5. Emission factors for PCDD/Fs and PCBs were calculated according to the World Health Organization toxicity equivalence factor (WHO-TEF- 2005) (van den Berg et al., 2006), since it considers the dl-PCBs.

[Figures 2 and 3]

As can be observed in Fig. 2, in all runs furans contributed more than dioxins to the total emission factor. This is due to the fact that furans have a higher thermal stability than dioxins (Conesa et al., 2002), and of the limited presence of oxygen (Stanmore, 2004).

Combustion results show that congener 2,3,4,7,8-PeCDF contributed with the highest value to the total WHO-TEQ. Congener 2,3,4,7,8-PeCDF was found to be the most represented isomer in industrial incinerators emissions (Fiedler et al., 2000). The run with the maximum total emission factor was done at 600ºC and λ= 0.9, with a value of 26077.2 pg WHO-TEQ/g sample burnt.

Concerning pyrolysis results, at 600ºC congener 2,3,4,7,8-PeCDF contributed with the highest value to the total WHO-TEQ as it occurs in combustion. Whereas, at 850ºC, congener 1,2,3,7,8-PeCDD contributed the most to the total WHO-TEQ.

As to the emission factor of 2,3,7,8-Cl substituted PCDD/F, in almost every run (at 600ºC and 850ºC) OCDD and OCDF were the compounds with the highest yields as can be found in Table SM5. This is expected because, at high temperature, the most stable compounds usually are the most chlorinated isomers (Christmann et al., 1989; Kim et al., 2004).

Both combustion and pyrolysis experiments at 600 ºC generally generated much higher PCDD/F yields (expressed as pg/g) than the runs at 850 ºC. This is an expected finding since these compounds are destroyed at high temperatures (Abad et al., 2002; Conesa et al., 2009; Van Caneghem et al., 2010) .

In relation to the emissions of the dl-PCBs, as can be found in Table SM6, all combustion and pyrolysis runs at 600ºC produced higher yields than at 850ºC, being the main congeners PCB-118, PCB-105 and PCB-126. As can be observed in Figure 3 the compounds that contribute the most to the total toxicity are PCB-126 and PCB-169.

Several scientific papers have been published reporting PCDD/F emission data from thermal treatments of ASR. Van Caneghem et al. (Van Caneghem et al., 2012) studied the PCDD/F fingerprints of the outputs in a fluidized bed combustor (FBC) in which ASR was co-incinerated with refuse derived fuel (RDF) and wastewater treatment sludge at 850ºC. The authors reported the PCDD/F fingerprints of the outputs fractions emitted in the FBC during the ASR co-incineration trial. Total amount of 2,3,7,8-Cl substituted PCDD/F congeners in the gas fraction was approximately 30000 pg/g_{DW}, corresponding to approximately 1600 pg I-TEQ/g_{DW}, which is similar to the results shown in the present work. The PCDD/F fingerprints were dominated by PCDFs, mainly HpCDF and

OCDF, as it occurs in the present work. Oxygen content has been also confirmed as an important factor influencing the relative abundance of PCDF and PCDD formations: lower oxygen content favors greater amounts of PCDFs than PCDDs (Stanmore, 2004). Moreover Van Caneghem et al. stated that the average copper concentration in the ASR was 5940 mg/kg_{DW}, which is relatively high, might have enhanced PCDD/F formation during the post combustion stage since it is known that copper is a catalyst of the de novo synthesis (Hatanaka et al., 2004; Karstensen, 2008; Lasagni et al., 2009; Ryu et al., 2005). The authors concluded that adding ASR to the RDF and sewage sludge in the usual waste feed to a real-scale fluidized bed combustor increased the concentration of PCDD/Fs in the flue gas.

Edo et al. (Edo et al., 2013) studied the performance of the different fractions of the ASR. To do so, combustion trials of the different ASR fractions were conducted at 850ºC under substoichiometric oxygen ($\lambda = 0.65–0.70$). The authors reported that fines would be the most toxic fraction (800 pg I-TEQ/g), followed by 20–50 mm (298 pg I-TEQ/g) and 50–100 mm (11 pg I-TEQ/g), whereas in the present work, the maximum emission at 850 ºC has been 82.9 pg WHO-TEQ/g. Edo et al. also stated the total PCDD/Fs emissions generated by each fraction during the combustion runs: 29000 pg/g dry sample in fines, 14000 pg/g dry sample in 20–50 mm fraction and 4700 pg/g dry sample in 50–100 mm fraction.

Joung et al. (Joung et al., 2006) studied the effects of oxygen, catalyst and chlorine content on the formation of PCDD/Fs and dl-PCBs in pyrolysis runs at 600ºC. They reported that addition of oxygen to pyrolysis increased by 360 times the I-TEQ of PCDD/Fs, whereas the addition of a catalyst only increased the TEQ by 16 times. In the present work, the addition of limited amount of oxygen also increased very much the emission factor, but the effect is more pronounced at 600 ºC, when the conditions are not severe enough to destroy these pollutants. In this way, for PCDD/Fs the effect of oxygen is more pronounced that the effect of catalysts. Regarding dl-PCBs, they found that the total amount of dl-PCBs increased 2.6 times and 12.4 times with either oxygen or a catalyst, respectively.

Ishikawa et al. (Ishikawa et al., 2007) studied the PCB emissions during combustion of ASR in a rotary kiln at 850ºC. They reported that the I-TEQ for dl-PCB were 110 ng I-TEQ Nm^{-3} (kiln exit) and that the ratios of the TEQ for dl-PCB to the I-TEQ for dioxins at kiln exit were 1.5%.

Figure 4 shows the distribution congeners of the PBDD/Fs ("brominated dioxins"), expressed as pg WHO-TEQ/g. In 2013, a joint expert panel from the World Health Organization (WHO) and United Nations Environment Programme (UNEP) proposed the use of similar interim Toxic Equivalence Factors (TEF) for chlorinated and brominated dioxins. Therefore, in this paper total toxic equivalence (TEQ) of PBDD/Fs was calculated according to WHO-TEF- 2005 (van den Berg et al., 2013).

[Figure 4]

As can be observed in Figure 4, the emission factors of PBDD/Fs at 600ºC were higher than at 850ºC, as occurred in chlorinated congeners. This fact would show the lower thermal stability of these compounds. The congener that contributed the most to the toxicity of the emissions was the 2,3,7,8-TBDD among dioxins and the 2,3,4,7,8-PeBDF among furans. The run with the highest WHO-TEQ values was that with λ= 0.3. Nevertheless, the emission factor in pyrolytic conditions is relatively high compared with the PCDD/Fs emissions at 600 ºC. Different studies tried to explain the formation and destruction of such pollutants, being for now not clear the formation pathways. For example, Evans and Dellinger (Evans and Dellinger, 2003, 2005) studied the evolution of PBDD/Fs both with temperature and oxygen presence. They also found evidence that some congeners, especially those of furans, decrease in the presence of oxygen, pointing out the significant effect of oxygen on the mechanisms of dioxin and furans formation.

Table SM7 in the supplementary material shows the emission factor of 2,3,7,8-Br substituted PBDD/Fs and total WHO_{2005}-TEQ for the emissions of the different combustion and pyrolysis runs performed from the ASR. The most abundant isomer was 1,2,3,4,6,7,8-HpBDF either in combustion and pyrolysis at 600ºC as also reported by Ortuño et al. treating electronic wastes (Ortuño et al., 2014).

The run with the maximum total emission of PBDD/Fs was that of combustion at 600ºC with a λ= 0.3. This is consistent with the study reported by Conesa et al. (Conesa et al., 2009) in which a comparison between the emission rates from pyrolysis and combustion of different wastes was presented, showing that the presence of a small amount of oxygen could promote the formation of some pollutants.

No data were found in literature in which brominated dioxin formation in ASR thermal treatments was reported so it was not possible to do a comparison.

4. Conclusions

In order to better understand the environmental impact during the pyrolysis and combustion of ASR, runs from pure pyrolysis to over-stoichiometric combustion at two different temperatures in a laboratory scale reactor were performed. The products have been analyzed and quantified in order to evaluate whether the thermal valorization of ASR might be feasible. The main conclusions that we can extract from the study are:

- Significant amounts of CO and CO_2 are generated in pyrolysis. These gases come from the decomposition of polymers (polycarbonates and polyurethanes) present in the ASR and from the decomposition of carbonate fillers present in automotive plastics.

- The combination of high temperatures and high oxygen ratio causes the drastic reduction of light hydrocarbons.
- The maximum emissions of the 16 priority PAHs are obtained in pyrolysis at 850 ° C. The most abundant compound, in all experiments, is naphthalene.
- Chlorobenzenes, chlorophenols and bromophenols yields are almost negligible.
- The greatest yields of PCDD/Fs, dl-PCBs and PBDD/Fs are obtained at 600°C. Furans contribute more than dioxins to total emissions.

Based on the results obtained in this study, it can be stated that thermal recovery may be a feasible method for accomplishing the recovery rates established in the Directive 2000/53/EC.

Acknowledgments

Support for this work was provided 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). The authors are grateful to CEMEX ESPAÑA, S.A. for supplying the samples.

References

Abad, E., Adrados, M.A., Caixach, J., Rivera, J., 2002. Dioxin abatement strategies and mass balance at a municipal waste management plant. Environ. Sci. Technol. 36, 92-99.

Andersen, F., Larsen, H., Skovgaard, M., 2008. Projection of end-of-life vehicles: development of a projection model and estimates for ELVs for 2005-2030, Copenhagen.

Aracil, I., Font, R., Conesa, J.A., 2010. Chlorinated and nonchlorinated compounds from the pyrolysis and combustion of polychloroprene. Environ. Sci. Technol. 44, 4169-4175.

Barneto, A.G., Moltó, J., Ariza, J., Conesa, J.A., 2014. Thermogravimetric monitoring of oil refinery sludge. Journal of Analytical and Applied Pyrolysis 105, 8-13.

Braslaw, J., Melotik, D.J., Gealer, R.L., Wingfield Jr, R.C., 1991. Hydrocarbon generation during the inert gas pyrolysis of automobile shredder waste. Thermochimica Acta 186, 1-18.

Conesa, J.A., Domene, A., 2015. Gasification and pyrolysis of Posidonia oceanica in the presence of dolomite. Journal of Analytical and Applied Pyrolysis 113, 680-689.

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

Conesa, J.A., Fullana, A., Font, R., 2000. Tire pyrolysis: Evolution of volatile and semivolatile compounds. Energy Fuels 14, 409-418.

Conesa, J.A., Fullana, A., Font, R., 2002. De novo synthesis of PCDD/F by thermogravimetry. Environ. Sci. Technol. 36, 263-269.

Conesa, J.A., Galvez, A., Martín-Gullón, I., Font, R., 2011. Formation and Elimination of Pollutant during Sludge Decomposition in the Presence of Cement Raw Material and Other Catalysts. Advances in Chemical Engineering Science 1, 183-190.

Conesa, J.A., Rey, L., Aracil, I., 2015. Modeling the thermal decomposition of automotive shredder residue. J. Therm. Anal. Calorim. 124, 317-327.

Cossu, R., Lai, T., 2015. Automotive shredder residue (ASR) management: An overview. Waste Manage. (Oxford) 45, 143-151.

Christmann, W., Kasiske, D., Kloppel, K.D., Partscht, H., Rotard, W., 1989. Combustion of polyvinylchloride - An important source for the formation of PCDD/PCDF. Chemosphere 19, 387-392.

Day, M., Shen, Z., Cooney, J.D., 1999. Pyrolysis of auto shredder residue: experiments with a laboratory screw kiln reactor. Journal of Analytical and Applied Pyrolysis 51, 181-200.

de Marco, I., Caballero, B.M., Cabrero, M.A., Laresgoiti, M.F., Torres, A., Chomón, M.J., 2007. Recycling of automobile shredder residues by means of pyrolysis. Journal of Analytical and Applied Pyrolysis 79, 403-408.

Donaj, P., Yang, W., Blasiak, W., Forsgren, C., 2009. Kinetic study of decomposition of ASR residues after pyrolysis in inert and oxidative atmosphere, Joint Conference: International Thermal Treatment Technologies (IT3) and Hazardous Waste Combustors (HWC), pp. 465-483.

Edo, M., Aracil, I., Font, R., Anzano, M., Fullana, A., Collina, E., 2013. Viability study of automobile shredder residue as fuel. J. Hazard. Mater. 260, 819-824.

Evans, C.S., Dellinger, B., 2003. Mechanisms of Dioxin Formation from the High-Temperature Pyrolysis of 2-Bromophenol. Environmental Science & Technology 37, 5574-5580.

Evans, C.S., Dellinger, B., 2005. Mechanisms of Dioxin Formation from the High-Temperature Oxidation of 2-Bromophenol. Environmental Science & Technology 39, 2128-2134.

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

Fullana, A., Font, R., Conesa, J.A., Blasco, P., 2000. Evolution of products in the combustion of scrap tires in a horizontal, laboratory scale reactor. Environ. Sci. Technol. 34, 2092-2099.

Galvagno, S., Fortuna, F., Cornacchia, G., Casu, S., Coppola, T., Sharma, V.K., 2001. Pyrolysis process for treatment of automobile shredder residue: Preliminary experimental results. Energy Convers. Manage. 42, 573-586.

Garrido, M.A., Font, R., Conesa, J.A., 2016. Pollutant emissions during the pyrolysis and combustion of flexible polyurethane foam. Waste Manage. (Oxford) 52, 138-146.

Gonzalez-Fernandez, O., Hidalgo, M., Margui, E., Carvalho, M.L., Queralt, I., 2008. Heavy metals' content of automotive shredder residues (ASR): Evaluation of environmental risk. Environ. Pollut. 153, 476-482.

Hatanaka, T., Kitajima, A., Takeuchi, M., 2004. Role of copper chloride in the formation of polychlorinated dibenzo-p-dioxins and dibenzofurans during incineration. Chemosphere 57, 73-79.

Haydary, J., Susa, D., Gelinger, V., Čacho, F., 2016. Pyrolysis of automobile shredder residue in a laboratory scale screw type reactor. Journal of Environmental Chemical Engineering 4, 965-972.
Ishikawa, Y., Noma, Y., Yamamoto, T., Mori, Y., Sakai, S.i., 2007. PCB decomposition and formation in thermal treatment plant equipment. Chemosphere 67, 1383-1393.
Joung, H.T., Seo, Y.C., Kim, K.H., 2006. Effects of oxygen, catalyst and PVC on the formation of PCDDs, PCDFs and dioxin-like PCBs in pyrolysis products of automobile residues. Chemosphere 65, 1481-1489.
Karstensen, K.H., 2008. Formation, release and control of dioxins in cement kilns. Chemosphere 70, 543-560.
Kim, K.S., Hong, K.H., Ko, Y.H., Kim, M.G., 2004. Emission Characteristics of PCDD/Fs, PCBs, Chlorobenzenes, Chlorophenols, and PAHs from Polyvinylchloride Combustion at Various Temperatures. Journal of the Air and Waste Management Association 54, 555-562.
Lasagni, M., Collina, E., Grandesso, E., Piccinelli, E., Pitea, D., 2009. Kinetics of carbon degradation and PCDD/PCDF formation on MSWI fly ash. Chemosphere 74, 377-383.
Mancini, G., Viotti, P., Luciano, A., Fino, D., 2014a. On the ASR and ASR thermal residues characterization of full scale treatment plant. Waste Manage. (Oxford) 34, 448-457.
Mancini, G., Viotti, P., Luciano, A., Raboni, M., Fino, D., 2014b. Full scale treatment of ASR wastes in a modified rotary kiln. Waste Manage. (Oxford) 34, 2347-2354.
Morselli, L., Santini, A., Passarini, F., Vassura, I., 2010. Automotive shredder residue (ASR) characterization for a valuable management. Waste Manage. (Oxford) 30, 2228-2234.
Ortuño, N., Conesa, J.A., Molto, J., Font, R., 2014. Pollutant emissions during pyrolysis and combustion of waste printed circuit boards, before and after metal removal. Sci. Total Environ. 499, 27-35.
Reddy, M.S., Kurose, K., Okuda, T., Nishijima, W., Okada, M., 2008. Selective recovery of PVC-free polymers from ASR polymers by ozonation and froth flotation. Resources, Conservation and Recycling 52, 941-946.
Ryu, J.-Y., Mulholland, J.A., Takeuchi, M., Kim, D.-H., Hatanaka, T., 2005. CuCl2-catalyzed PCDD/F formation and congener patterns from phenols. Chemosphere 61, 1312-1326.
Santini, A., Morselli, L., Passarini, F., Vassura, I., Di Carlo, S., Bonino, F., 2011. End-of-Life Vehicles management: Italian material and energy recovery efficiency. Waste Manage. (Oxford) 31, 489-494.
Stanmore, B.R., 2004. The formation of dioxins in combustion systems. Combust. Flame 136, 398-427.
Thomas, S., Wornat, M.J., 2008. The effects of oxygen on the yields of polycyclic aromatic hydrocarbons formed during the pyrolysis and fuel-rich oxidation of catechol. Fuel 87, 768-781.
Van Caneghem, J., Block, C., Vermeulen, I., Van Brecht, A., Van Royen, P., Jaspers, M., Wauters, G., Vandecasteele, C., 2010. Mass balance for POPs in a real scale fluidized bed combustor co-incinerating automotive shredder residue. J. Hazard. Mater. 181, 827-835.
Van Caneghem, J., Vermeulen, I., Block, C., Van Brecht, A., Van Royen, P., Jaspers, M., Wauters, G., Vandecasteele, C., 2012. Destruction and formation of PCDD/Fs in a fluidised bed combustor co-incinerating automotive shredder residue with refuse derived fuel and wastewater treatment sludge. J. Hazard. Mater. 207-208, 152-158.
van den Berg, M., Birnbaum, L.S., Denison, M., De Vito, M., Farland, W., Feeley, M., Fiedler, H., Hakansson, H., Hanberg, A., Haws, L., Rose, M., Safe, S., Schrenk, D., Tohyama, C., Tritscher, A., Tuomisto, J., Tysklind, M., Walker, N., Peterson, R.E., 2006. The 2005 World Health Organization reevaluation of human and mammalian toxic equivalency factors for dioxins and dioxin-like compounds. Toxicol. Sci. 93, 223-241.
van den Berg, M., Denison, M.S., Birnbaum, L.S., DeVito, M., Fiedler, H., Falandysz, J., Rose, M., Schrenk, D., Safe, S., Tohyama, C., Tritscher, A., Tysklind, M., Peterson, R.E., 2013. Polybrominated

Dibenzo-p-dioxins (PBDDs), Dibenzofurans (PBDFs) and Biphenyls (PBBs) - Inclusion in the Toxicity Equivalency Factor Concept for Dioxin-like Compounds. Toxicol. Sci.

Zolezzi, M., Nicolella, C., Ferrara, S., Iacobucci, C., Rovatti, M., 2004. Conventional and fast pyrolysis of automobile shredder residues (ASR). Waste Manage. (Oxford) 24, 691-699.

FIGURE CAPTIONS AND TABLE LEGENDS

Table 1. Emissions of gases and volatile compounds.

Table 2. Total emissions of chlorobenzenes, chlorophenols and bromophenols

Figure 1. Emissions of PAHs (mg/kg sample).

Figure 2. Distribution congeners of the PCDD/Fs (pg WHO-TEQ/g)

Figure 3. Dioxin-like PCBs emission factor (pg WHO-TEQ/g)

Figure 4. Distribution congeners of the PBDD/Fs (pg WHO-TEQ/g)

Table 1. Emissions of gases and volatile compounds.

	Experiment									
	600ºC					850ºC				
	Pyrolysis	Combustion				Pyrolysis	Combustion			
	λ=0	**λ=0.35**	**λ=0.56**	**λ=0.96**	**λ=1.56**	**λ=0**	**λ=0.32**	**λ=0.55**	**λ=0.98**	**λ=1.54**
Compound	mg compound/kg sample burnt (ppm)									
Analysis by GC-TCD										
CO_2	108700	515500	419800	352700	186200	86900	470300	505800	641700	382000
CO	37300	119600	125000	140200	69500	94600	284500	211800	64300	2700
$R_{CO} = CO/(CO + CO_2)$	0.255	0.188	0.229	0.284	0.272	0.521	0.377	0.295	0.091	0.007
Analysis by GC-FID	mg compound/kg sample burnt (ppm)									
methane	20200	8780	9340	6760	1450	69800	42200	155	2830	
ethane	10900	1790	1730	920	142	5230	2260	6770	89.7	
ethylene	24200	18600	26600		6550	96800	60300		3420	
propane	5520	788	671	230	30.5	341	107			
propylene	75200	35100	33000	16200	2830	29800	8520	327	282	
n-butane	531	257		142	24.0			42.9	74.4	
trans-2-butene	5120									
cis-2-butene	6830	188		90.3	135	121	223			
1.3-butadiene					128				48.3	
2-butino	64.3									
n-hexane	1310	76.5					1110			
benzene	47.3	6590	6480	4610	1620	18500	2360	3080	2300	16.2
toluene	15700					39000	18600			
xilene (p-.m-.o-)		3420			460					

Table 2. Total emissions of chlorobenzenes, chlorophenols and bromophenols

	Experiment									
	600ºC					850ºC				
	Pyrolysis	Combustion				Pyrolysis	Combustion			
	λ=0	**λ=0.35**	**λ=0.56**	**λ=0.96**	**λ=1.56**	**λ=0**	**λ=0.32**	**λ=0.55**	**λ=0.98**	**λ=1.54**
	mg compound/kg sample burnt (ppm)									
Total PCPh	1	4.8	6.6	0.03	0.2	2.2	5.7	3.9	0.1	0.4
Total PCBz	4.94	213	237	303	245	18	63	14	14	1.72
Total PBPh	1.15	0.2	1.04	1.13	2.63	0.04	0.07	0.06	0.03	0.11

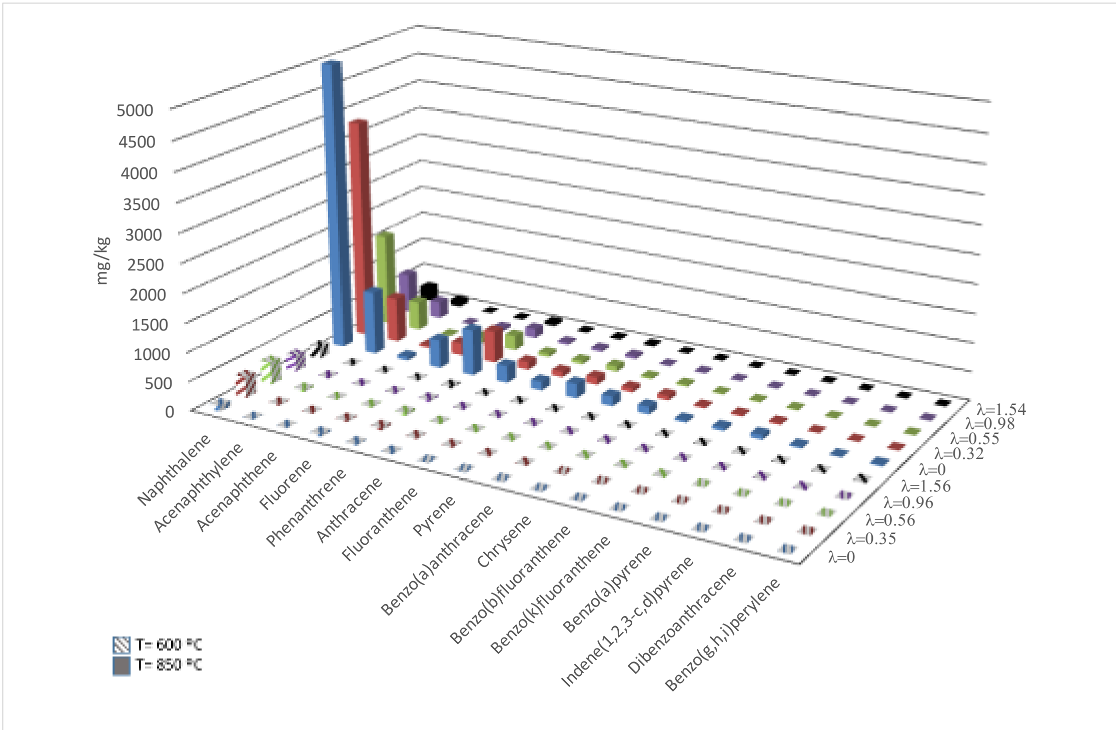

Figure 1. Emissions of PAHs (mg/kg sample).

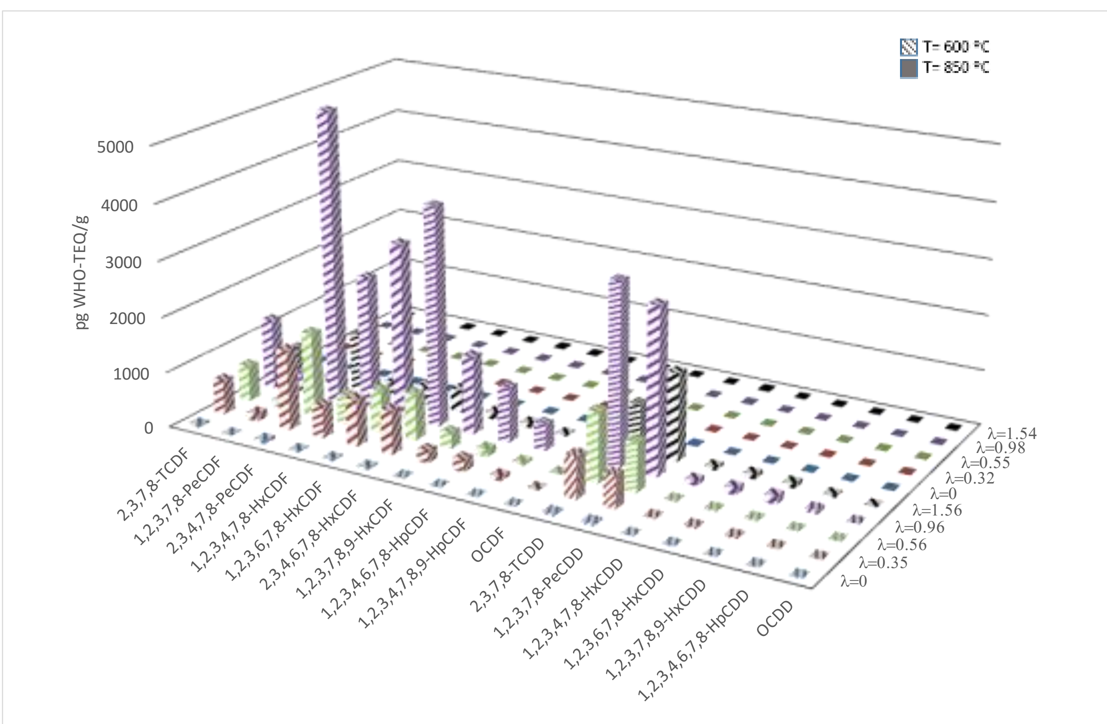

Figure 2. Distribution congeners of the PCDD/Fs (pg WHO-TEQ/g)

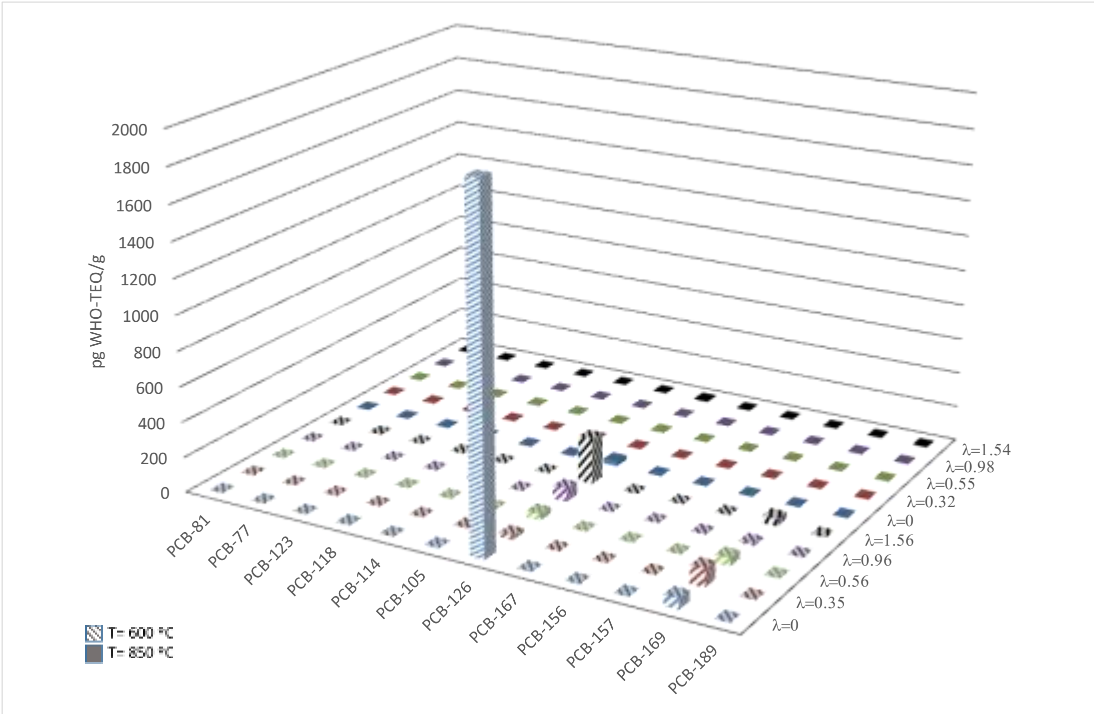

Figure 3. Dioxin-like PCBs emission factor (pg WHO-TEQ/g)

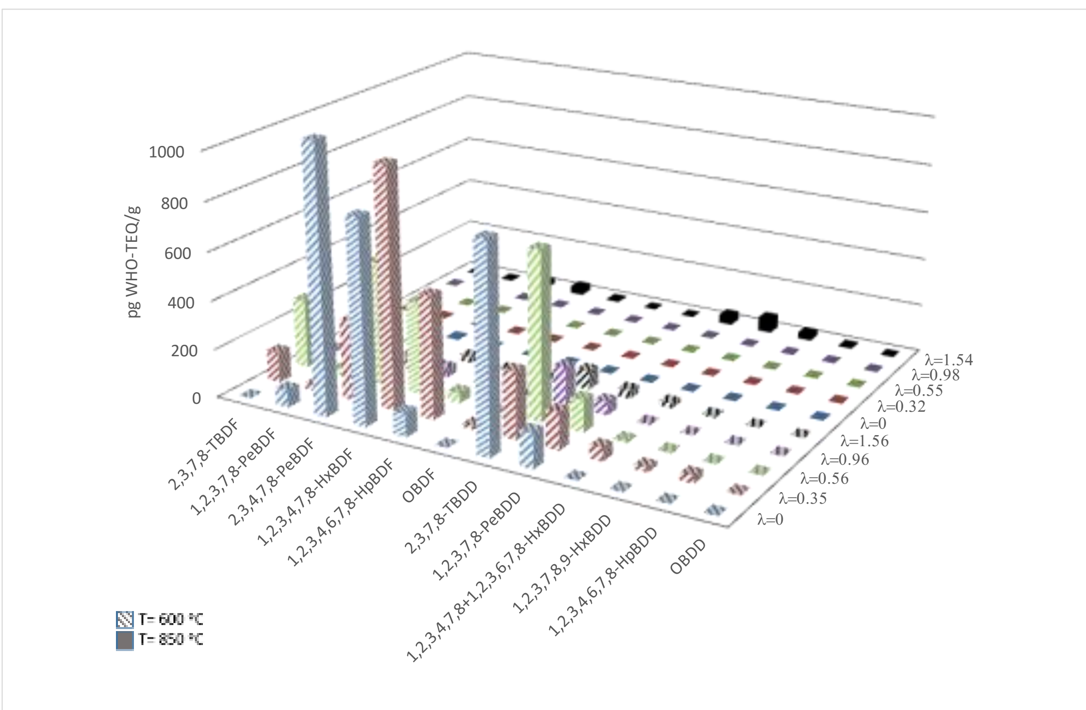

Figure 4. Distribution congeners of the PBDD/Fs (pg WHO-TEQ/g)

Supplementary material

Table SM1. Yields of US EPA priority PAHs in the pyrolysis and combustion of ASR.

	Experiment									
	600ºC					850ºC				
	Pyrolysis	Combustion				Pyrolysis	Combustion			
	λ=0	**λ=0.35**	**λ=0.56**	**λ=0.96**	**λ=1.56**	**λ=0**	**λ=0.32**	**λ=0.55**	**λ=0.98**	**λ=1.54**
	mg compound/kg sample burnt (ppm)									
Naphthalene	96.1	358	385	271	202	5540	3840	1610	689	239
Acenaphthylene	4.0	16.0	34.3	18.0	5.0	1100	779	504	295	106
Acenaphthene	4.0	6.0	5.0	3.0	2.0	63.0	40.0	11.0	4.0	1.0
Fluorene	35.4	20.1	17.1	9.0	8.0	493	213	99.0	54.0	13.0
Phenanthrene	15.7	41.5	45.4	30.6	27.8	799	556	253	160	63.0
Anthracene	9.0	12.4	10.9	6.0	3.5	295	137	59.4	37.8	12.9
Fluoranthene	4.6	7.6	10.0	6.6	4.6	151	96.2	58.3	43.4	18.7
Pyrene	5.3	4.2	5.6	9.4	2.5	250	126	92.7	47.4	23.9
Benzo(a)anthracene	3.6	3.1	3.2	5.1	1.0	166	72.3	27.1	11.4	3.8
Chrysene	4.2	5.4	7.4	8.7	3.0	130	75.7	30.7	13.5	5.8
Benzo(b)fluoranthene	2.4	1.4	2.3	4.4	1.1	36.3	21.7	13.1	6.8	2.1
Benzo(k)fluoranthene	1.1	0.70	1.2	2.1	0.45	52.6	24.0	16.5	6.2	0.90
Benzo(a)pyrene	1.3	0.60	1.0	1.8	0.33	75.5	25.8	15.9	4.8	1.8
Indene(1,2,3-c,d)pyrene	-	-	-	-	-	27.0	7.0	5.0	2.0	1.0
Dibenzoanthracene	-	-	-	-	-	9.0	3.1	2.3	-	-
Benzo(g,h,i)perylene	-	-	-	-	-	19.0	6.0	6.0	4.0	2.0

Table SM2. Yields of bromophenols in the pyrolysis and combustion of ASR.

	Experiment									
	600ºC					850ºC				
	Pyrolysis	Combustion				Pyrolysis	Combustion			
	λ=0	**λ=0.35**	**λ=0.56**	**λ=0.96**	**λ=1.56**	**λ=0**	**λ=0.32**	**λ=0.55**	**λ=0.98**	**λ=1.54**
	mg compound/kg sample burnt (ppm)									
2-	0.20	0.05	0.99	1.1	2.6	0.01	0.06	0.03	0.01	0.04
3-+4-	-	-	-	-	-	-	-	0.03	0.02	0.07
2,4-	0.09	0.01	0.01	0.01	0.03	-	-	-	-	-
2,3-+2,5-	0.04	0.01	0.01	-	-	-	-	-	-	-
2,6-	0.75	0.04	0.01	0.02	0.02	0.02	0.01	-	-	-
3,5-	-	-	-	-	-	-	-	-	-	-
3,4-	-	-	-	-	-	-	-	-	-	-
2,3,5-	0.01	-	0.01	-	-	-	-	-	-	-
2,4,6-	0.03	-	-	-	-	0.01	-	-	-	-
2,3,4-	-	-	0.01	-	-	-	-	-	-	-
2,4,5-	0.01	0.01	-	-	-	-	-	-	-	-
2,3,6-	-	-	-	-	-	-	-	-	-	-
3,4,5-	-	-	-	-	-	-	-	-	-	-
2,3,5,6-	0.01	0.04	-	-	-	-	-	-	-	-
2,3,4,5-+2,3,4,6-	0.01	0.04	-	-	-	-	-	-	-	-
penta-	-	-	-	-	-	-	-	-	-	-
Total mono-BrPh	0.20	0.05	0.99	1.1	2.6	0.01	0.06	0.06	0.03	0.11
Total di-BrPh	0.88	0.06	0.03	0.03	0.05	0.02	0.01	-	-	-
Total tri-BrPh	0.05	0.01	0.02	-	-	0.01	-	-	-	-
Total tetra-BrPh	0.02	0.08	-	-	-	-	-	-	-	-
Total penta-BrPh	-	-	-	-	-	-	-	-	-	-
TOTALS	1.2	0.20	1.0	1.1	2.6	0.04	0.07	0.06	0.03	0.11

Table SM3. Yields of chorobenzenes in the pyrolysis and combustion of ASR.

	Experiment									
	600ºC					850ºC				
	Pyrolysis	Combustion				Pyrolysis	Combustion			
	λ=0	**λ=0.35**	**λ=0.56**	**λ=0.96**	**λ=1.56**	**λ=0**	**λ=0.32**	**λ=0.55**	**λ=0.98**	**λ=1.54**
	mg compound/kg sample burnt (ppm)									
mono-	4.6	204	231	289	199	17.3	62.8	13.4	13.3	1.5
1,3-	0.02	0.96	0.98	1.7	5.4	0.10	0.12	0.05	0.02	-
1,4-	0.08	3.2	1.9	2.1	4.6	0.12	0.14	0.07	0.03	0.01
1,2-	0.08	2.3	1.8	3.9	13.2	0.12	0.13	0.13	0.01	0.04
1,3,5-	-	0.07	0.06	0.19	0.61	-	0.01	-	0.01	-
1,2,4-	0.10	1.8	0.78	2.5	7.7	0.06	0.02	0.27	0.53	0.12
1,2,3-	-	0.23	0.16	2.1	8.8	0.19	0.01	0.01	-	0.01
1,2,3,5-+1,2,4,5-	0.01	0.20	0.08	0.55	1.8	0.03	0.01	-	-	-
1,2,3,4-	0.08	0.15	0.07	0.56	2.2	0.08	0.01	-	-	0.01
penta-	-	0.07	0.05	0.29	0.96	0.01	0.01	-	0.01	0.02
hexa-	0.01	-	-	0.04	0.19	-	-	0.01	0.01	0.02
Total mono-ClBz	4.6	204	231	289	199	17.3	62.8	13.4	13.3	1.5
Total di-ClBz	0.18	6.5	4.7	7.7	23.2	0.34	0.39	0.25	0.06	0.05
Total tri-ClBz	0.10	2.1	1.0	4.8	17.1	0.25	0.04	0.28	0.54	0.13
Total tetra-ClBz	0.09	0.35	0.15	1.1	4.0	0.11	0.02	-	-	0.01
Total penta-ClBz	-	0.07	0.05	0.29	0.96	0.01	0.01	-	0.01	0.02
Total hexa-ClBz	0.01	-	-	0.04	0.19	-	-	0.01	0.01	0.02
TOTALS	5.0	213	237	303	245	18.0	63.3	13.9	13.9	1.7

Table SM4. Yields of chorophenols in the pyrolysis and combustion of ASR.

	Experiment									
	600ºC					850ºC				
	Pyrolysis	Combustion				Pyrolysis	Combustion			
	λ=0	**λ=0.35**	**λ=0.56**	**λ=0.96**	**λ=1.56**	**λ=0**	**λ=0.32**	**λ=0.55**	**λ=0.98**	**λ=1.54**
	mg compound/kg sample burnt (ppm)									
2-	-	-	-	-	-	-	-	-	-	-
3-+4-	-	-	-	-	-	-	-	-	-	-
2,4-	-	-	-	2.4	17.0	-	-	0.03	0.05	0.03
2,5-	-	-	-	-	6.8	-	-	0.03	-	-
2,3-	1.0	1.2	1.4	0.27	0.70	0.14	-	-	-	-
2,6-	-	-	-	1.6	4.6	-	-	-	0.01	-
3,5-	-	3.6	5.0	-	-	2.1	5.7	3.9	-	0.32
3,4-	-	-	-	-	-	-	-	-	-	-
2,3,5-	-	-	-	0.04	5.2	-	-	-	-	-
2,4,6-	-	-	0.19	0.42	6.2	-	-	-	-	-
2,4,5-	-	-	-	0.05	0.24	-	-	-	-	-
2,3,4-	-	-	-	-	0.22	-	-	-	-	-
2,3,6-	-	-	-	-	-	-	-	-	-	-
3,4,5-	-	-	-	-	-	-	-	-	-	-
2,3,5,6-	-	-	-	0.02	0.22	-	-	-	0.01	-
2,3,4,5-	-	-	-	-	-	-	-	-	-	-
2,3,4,6-	-	-	-	0.10	0.72	-	-	0.01	0.04	0.02
penta-	-	-	-	0.03	0.17	-	-	-	0.05	0.03
Total mono-ClPh	-	-	-	-	-	-	-	-	-	-
Total di-ClPh	1.0	4.8	6.4	4.3	29.1	2.2	5.7	4.0	0.06	0.35
Total tri-ClPh	-	-	0.19	0.51	11.9	-	-	-	-	-
Total tetra-ClPh	-	-	-	0.12	0.94	-	-	0.01	0.05	0.02
Total penta-ClPh	-	-	-	0.03	0.17	-	-	-	0.05	0.03
TOTALS	1.0	4.8	6.6	5.0	42.1	2.2	5.7	4.0	0.16	0.40

Table SM5. Yields of PCDD/Fs in the pyrolysis and combustion of ASR.

	Experiment									
	600ºC					850ºC				
	Pyrolysis	Combustion				Pyrolysis	Combustion			
	λ=0	**λ=0.35**	**λ=0.56**	**λ=0.96**	**λ=1.56**	**λ=0**	**λ=0.32**	**λ=0.55**	**λ=0.98**	**λ=1.54**
	pg compound/g sample burnt (ppt)									
2,3,7,8-TCDF	412	6200	6480	12800	5010	61.6	270	-	-	-
1,2,3,7,8-PeCDF	272	4830	4350	12600	2310	11.1	88.9	-	-	3.1
2,3,4,7,8-PeCDF	196	4820	5070	17700	3400	17.7	29.0	20.9	24.6	30.5
1,2,3,4,7,8-HxCDF	208	5750	5060	24400	2640	-	56.2	31.1	26.9	63.7
1,2,3,6,7,8-HxCDF	248	8320	7550	31700	3300	-	37.7	22.5	41.8	73.6
2,3,4,6,7,8-HxCDF	305	7850	8280	39500	4100	-	23.9	55.2	115	171
1,2,3,7,8,9-HxCDF	120	2180	2820	14100	1250	-	-	55.4	97.6	127
1,2,3,4,6,7,8-HpCDF	484	22200	13200	98300	7480	44.1	-	176	342	581
1,2,3,4,7,8,9-HpCDF	136	7720	4720	47000	2220	25.3	-	-	97.7	148
OCDF	182	23800	9390	192300	7360	-	483	681	1070	1150
2,3,7,8-TCDD	37.7	749	1250	3260	866	1.5	18.7	-	-	-
1,2,3,7,8-PeCDD	45.3	578	874	2970	1570	9.3	-	-	8.4	17.5
1,2,3,4,7,8-HxCDD	-	109	162	877	500	-	-	-	-	10.3
1,2,3,6,7,8-HxCDD	-	232	227	1160	767	-	-	-	-	13.9
1,2,3,7,8,9-HxCDD	-	211	231	1400	749	-	-	-	-	12.3
1,2,3,4,6,7,8-HpCDD	148	789	653	6810	3010	9.7	-	27.4	-	94.8
OCDD	347	1250	-	12700	2690	-	-	111	268	323

Table SM6. Yields of PCBs in the pyrolysis and combustion of ASR.

	Experiment									
	600ºC					850ºC				
	Pyrolysis	Combustion				Pyrolysis	Combustion			
	λ=0	**λ=0.35**	**λ=0.56**	**λ=0.96**	**λ=1.56**	**λ=0**	**λ=0.32**	**λ=0.55**	**λ=0.98**	**λ=1.54**
	pg compound/g sample burnt (ppt)									
PCB-81	1790	1460	843	1360	3240	479	12.6	4.5	2.1	24.7
PCB-77	10400	9130	6950	7760	12500	4960	-	-	12.5	118
PCB-123	9420	11100	4790	4920	5400	2020	37.4	5.0	-	1.9
PCB-118	92700	77900	49100	41500	40000	13900	282	67.7	-	32.7
PCB-114	1910	1330	828	840	1270	289	1.7	-	-	7.4
PCB-105	43400	31500	21100	18700	17000	4670	50.7	-	-	12.8
PCB-126	19900	216	348	735	2570	249	15.9	11.6	-	56.4
PCB-167	5420	4730	2650	2090	2270	407	-	-	-	5.8
PCB-156	9670	10600	5490	4620	4810	629	-	-	9.8	28.5
PCB-157	3300	3310	2520	1370	1610	163	-	-	5.9	15.1
PCB-169	1980	3350	1500	346	1390	-	-	3.5	23.3	14.4
PCB-189	223	169	509	244	476	19.2	-	5.6	12.1	24.6

Table SM7. Yields of PBDD/Fs in the pyrolysis and combustion of ASR.

	Experiment									
	600ºC					850ºC				
	Pyrolysis	Combustion				Pyrolysis	Combustion			
	λ=0	**λ=0.35**	**λ=0.56**	**λ=0.96**	**λ=1.56**	**λ=0**	**λ=0.32**	**λ=0.55**	**λ=0.98**	**λ=1.54**
	pg compound/g sample burnt (ppt)									
2,3,7,8-TBDF	-	1260	2860	98.1	87.7	-	-	-	-	10.1
1,2,3,7,8-PeBDF	1640	820	907	57.5	1120	-	-	-	2.6	80.4
2,3,4,7,8-PeBDF	2480	1100	1710	153	65.1	16.0	-	-	3.8	84.4
1,2,3,4,7,8-HxBDF	7470	9870	3800	410	237	-	-	4.4	11.1	321
1,2,3,4,6,7,8-HpBDF	9600	50300	4170	1100	369	-	14.4	10.7	31.5	576
OBDF	-	47300	422	639	193	-	-	-	-	382
2,3,7,8-TBDD	755	274	693	157	77.2	-	-	-	-	2.7
1,2,3,7,8-PeBDD	143	152	133	54.1	34.3	-	-	-	-	37.2
1,2,3,4,7,8+1,2,3,6,7,8-HxBDD	-	530	69.9	43.6	189	-	-	-	-	598
1,2,3,7,8,9-HxBDD	-	181	35.4	28.1	64.0	-	-	-	-	267
1,2,3,4,6,7,8-HpBDD	-	2900	92.1	126	113	-	18.8	13.5	14.9	527
OBDD	-	5530	-	-	94.8	-	-	-	-	774