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## EMISSIONS FROM PYROLYSIS AND COMBUSTION OF AUTOMOTIVE SHREDDER RESIDUE

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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 in order to analyze 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 850°C, and under varying 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 may be an efficient way to achieve the targets established in the Directive 2000/53/EC.

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.

The results on the emissions of PAHs for all the experiments show that 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. and is also the typical behavior that PAH emissions show from thermal treatment of any material.

The maximum formation of the 16 priority PAHs occurs under pyrolytic conditions at high temperature (850°C), as expected since it is known that pyrolytic reactions are the primary source of PAH formation 20. In relation to the effect of temperature, higher yields are produced at 850°C in all the experiments. This is due to the fact that PAHs belong to the type of compounds that have maximums at these temperatures (750-850°C) as reported by Fullana et al.

With respect to the effect of the presence of oxygen, the trend is different depending of the temperature considered. At 850°C, PAHs clearly show a lesser emission as the oxygen ratio increases. This indicates that PAHs are pyrolytic products that are easily eliminated in oxygen rich environments at these temperatures, as stated previously in different studies 19. But at 600°C, 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 behaviours can be observed. At 850°C, an oxidative destruction effect of the PAHs takes place when increasing the oxygen ratio. However, at 600°C the formation of free radicals is enhanced with the presence of oxygen, which boost the pyrolytic reactions. This means 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.

In all runs furans contributed more than dioxins to the total emission factor. This is due to the fact that furans have a major thermal stability than dioxins.

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 24. The run with the maximum total emission factor was the combustion at 600°C and oxygen ratio= 0.9.

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

The emission factors of PBDD/Fs at 600°C were higher than at 850°C. 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 oxygen ratio= 0.3.

Table S7 in the SI shows the concentration of 2,3,7,8-Br substituted PBDD/Fs and total WHO2005-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 600°C as also reported by Ortuño et al.

The products have been analyzed and quantified in order to evaluate whether the thermal valorization of ASR might be feasible. The main conclusion that we can extract from the study are:

- Significant amounts of CO and CO<sub>2</sub> 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.

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