

# CHLORINATED COMPOUNDS FORMED IN THE EMISSIONS FROM PYROLYSIS AND COMBUSTION OF WASTE VEGETABLE OIL

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## Introduction

Large amount of waste vegetable oils (WVO) is generated every day in industries, businesses and homes. In Spain, edible vegetable oil consumption is approximately 928 million litres per year and it is estimated that about 150 million litres of WVO are produced per year<sup>1,2</sup>. Used vegetable oil has numerous uses, including use as a direct fuel, as well as in the production of biodiesel, soap, animal feed, pet food, detergent, and cosmetics. The pyrolysis and combustion of WVO have been studied in a laboratory horizontal reactor with the objective of determining the compounds emitted. The study comprises the identification and quantification of the gases, volatile and semi-volatile compounds, with special focus on PAHs, ClPhs, ClBzs, PCDD/Fs and PCBs.

## Materials and methods

The WVO employed in this study came from a cafeteria of the University of Alicante. The pyrolysis and combustion experiments were carried out at 500°C in a laboratory scale tubular reactor equipped with a liquid injector. The gas flow (either air or N<sub>2</sub>) was fixed at 300 mL/min, the injector temperature was 500°C, and a mass of around 80 mg of waste oil was injected for all runs except for PCDD/Fs and PCBs runs in which the mass was around 0.85 g. The compounds leaving the reactor were collected either in Tedlar bags or over XAD-2 resin.

The outlet gas collected in the Tedlar bags was analysed by GC-TCD, GC-FID and GC-MS to determine the gases and volatile compounds. The semivolatile compounds such as polycyclic aromatic hydrocarbons (PAHs), chlorophenols (ClPhs), chlorobenzenes (ClBzs), polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs) and dioxin-like PCBs were adsorbed over XAD-2 resin placed in a tube at the outlet of the reactor. These resins were extracted by Accelerated Solvent Extraction with dichloromethane (for semivolatile compounds and PAHs) and toluene (for PCDD/Fs and PCBs). Semivolatile compounds and PAHs analysis were carried out by GC-MS and PCDD/Fs and PCBs analysis were performed by HRGC-HRMS.

## Results and discussion

From the results obtained in the analysis of gases and volatile compounds by GC-TCD, GC-FID and GC-MS, the next statements can be highlighted:

- Ethylene and propylene are among the most abundant compounds in both combustion and pyrolysis.
- The total yield of light hydrocarbons (by GC-FID and GC-MS) obtained at two different atmospheres increase from 219230 ppm in pyrolysis to 377180 ppm in combustion due to the presence of oxygen.

The semivolatile compounds detected can be classified in different classes: aliphatic hydrocarbons (1-decene, 1-undecene, cyclododecene, etc.), substituted monoaromatic compounds (propylbenzene, butylbenzene, etc.), PAHs from two to six aromatic rings (naphthalene, acenaphthylene, etc.) and oxygenated compounds (carboxylic acids, benzaldehyde, phenol, etc.). In this case, the maximum amount of total semivolatile compounds was obtained in pyrolysis with 46070 ppm in comparison with 31660 ppm in combustion.

Table 1 shows the results obtained for the 16 EPA priority PAHs. The maximum level of these compounds occurs in combustion conditions. This trend has also been observed by other researchers<sup>3</sup>. The major contributor to total PAH yield in both runs is naphthalene.

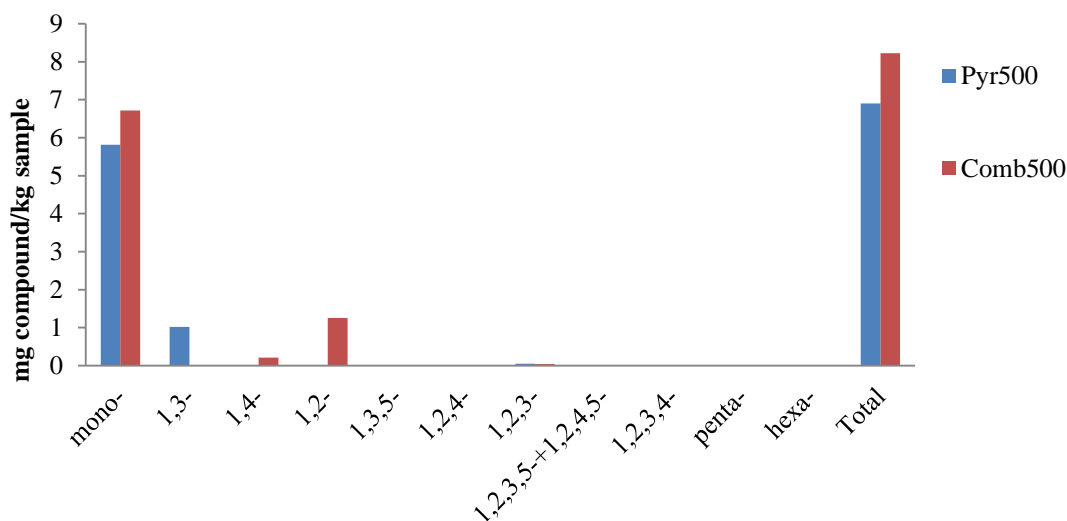
**Table 1. Yields of PAHs in Pyrolysis and Combustion Experiments.**

| Compound               | T = 500°C   |            |
|------------------------|-------------|------------|
|                        | Pyrolysis   | Combustion |
| mg compound/kg sample  |             |            |
| naphthalene            | 11          | 393        |
| acenaphthylene         | 1.0         | 10         |
| acenaphthene           | 2.8         | 2.9        |
| fluorene               | -           | 25         |
| phenanthrene           | -           | 40         |
| anthracene             | -           | 5.0        |
| fluoranthene           | -           | 5.8        |
| pyrene                 | 1.6         | 5.3        |
| benzo(a)anthracene     | -           | 1.2        |
| chrysene               | -           | -          |
| benzo(b)fluoranthene   | -           | 2.3        |
| benzo(k)fluoranthene   | -           | 1.0        |
| benzo(a)pyrene         | -           | 1.6        |
| indeno(1,2,3-cd)pyrene | -           | 2.7        |
| dibenz(a,h)anthracene  | -           | 4.6        |
| benzo(g,h,i)perylene   | -           | 1.0        |
| <b>Total</b>           | <b>16.4</b> | <b>501</b> |

(-) not detected or <1 mg/kg

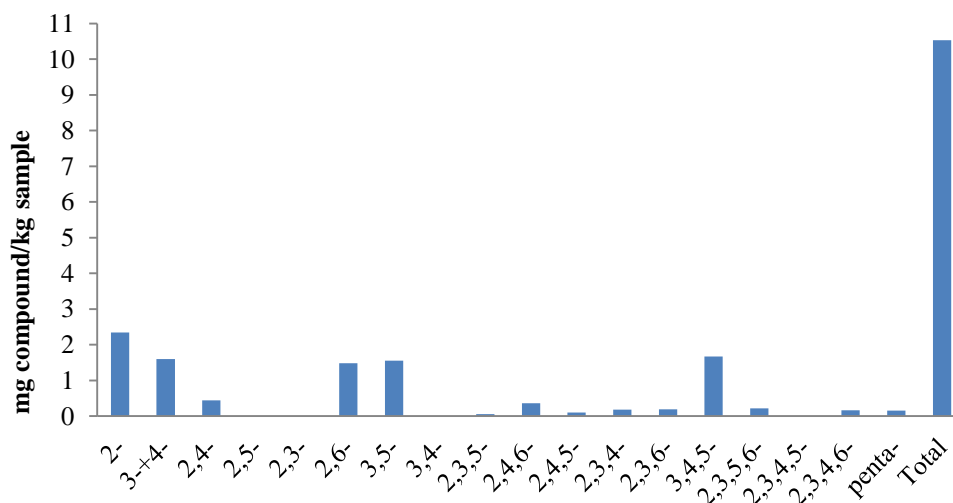
Chlorobenzenes and chlorophenols have been analysed separately. The amount detected for both group of compounds is low.

Regarding chlorobenzenes, the total yield in pyrolysis has been 6.9 ppm and in combustion 8.2 ppm. The highest value is obtained in combustion at 500°C. Figure 1 shows the pattern of chlorobenzene emissions where a clear predominance of monochlorobenzene is observed.



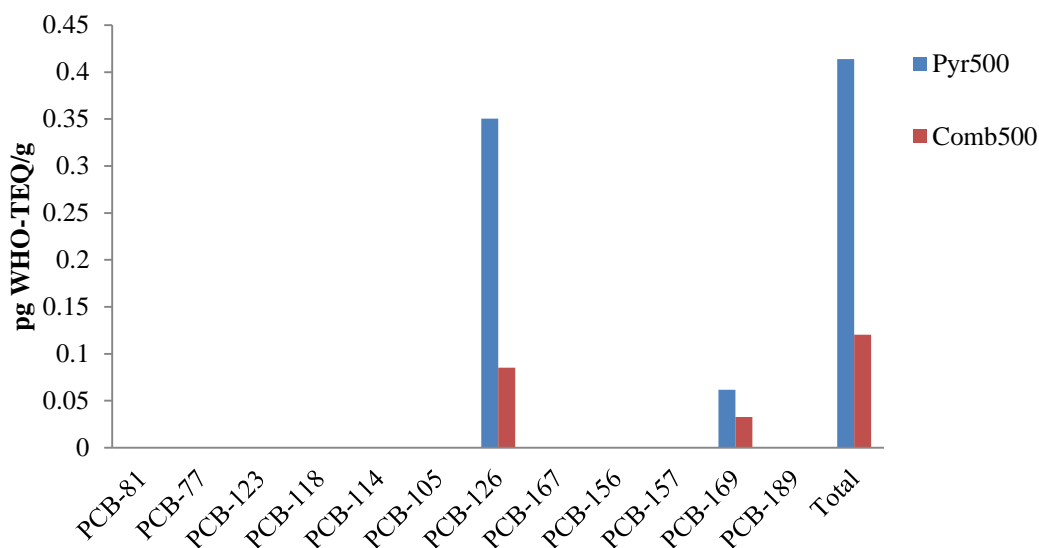
**Figure 1. Chlorobenzenes in pyrolysis and combustion.**

As to the results of chlorophenols, no emission of these compounds has been detected in pyrolysis being the total yield detected in combustion run 10.5 ppm. Figure 2 presents the yields for the different chlorophenol congeners. Mono-, di- and trichlorophenols appear in higher amounts.



**Figure 2. Chlorophenols in combustion run.**

The results of the PCB emissions at 500°C show that in both combustion and pyrolysis the main congeners are PCB-118, PCB-105 and PCB-77. Figure 3 shows the distribution of PCB congeners expressed as pg WHO-TEQ/kg. It can be seen that PCB-126 and PCB-169 are the compounds that contribute the most to the total toxicity in spite of not being among the congeners with highest emission levels, due to the relative high toxicity factors.



**Figure 3. TEQ-weighted PCBs emission profile from pyrolysis and combustion of WVO.**

Regarding PCDD/Fs, no significant difference is observed in total PCDD/F emissions between pyrolysis and combustion. The most abundant congeners are OCDD and OCDF in the two runs, and approximately both PCDDs and PCDFs count the same for the total amount.

The TEQ-weighted PCDD/F congener distribution is shown in Figure 4. The majority of the WHO-TEQ contribution comes from 1,2,3,7,8-PeCDD, 2,3,7,8-TCDD and 2,3,4,7,8-PeCDF. A similar trend was obtained by Conesa et al. <sup>4</sup> in the pyrolysis and combustion of meat and bone meals.

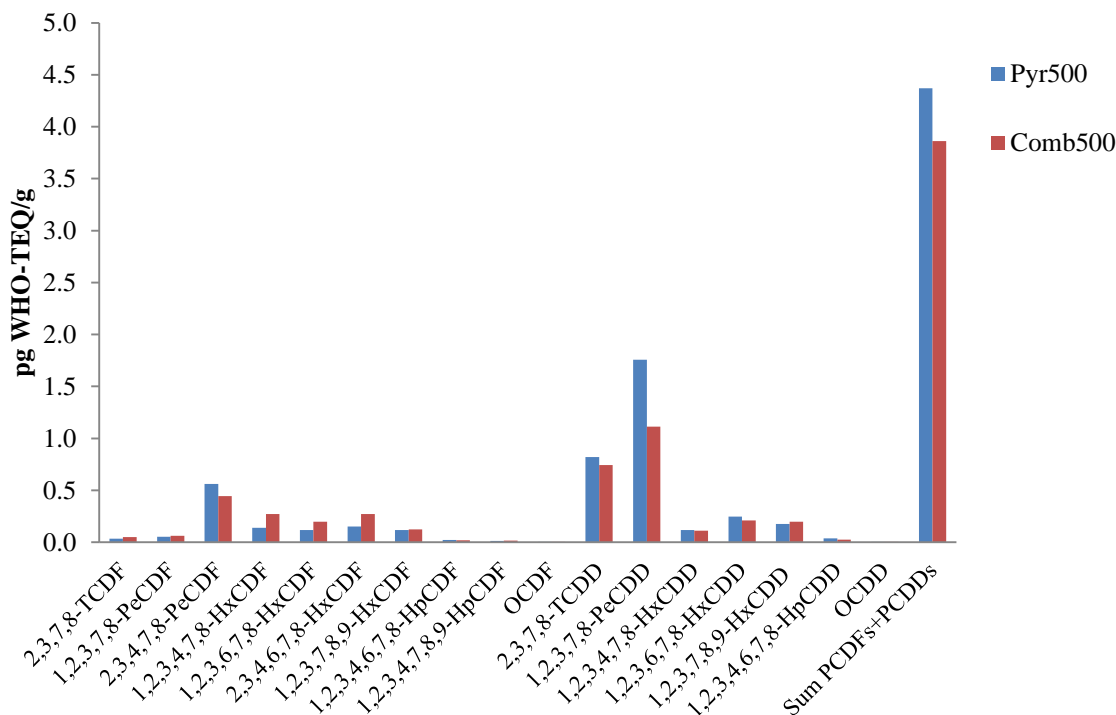


Figure 4. TEQ-weighted PCDD/F profiles from pyrolysis and combustion of WVO.

#### Acknowledgements

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