

Simultaneous analysis of PAH and oxy-PAH by gas chromatography-mass spectrometry

F. Viteri^{1,2}, R. Bilbao¹, A. Millera¹, M. U. Alzueta¹

1. Aragón Institute of Engineering Research (I3A), Department of Chemical and Environmental Engineering, University of Zaragoza, Río Ebro Campus, 50018 Zaragoza, Spain
2. Faculty of Engineering Sciences, Tecnológica Equinoccial University, 17-01-2764, Quito, Ecuador.

Introduction

Diesel engines are known to generate a high amount of pollutants emissions such as particulate matter, which consists mostly of carbonaceous soot. Associated to soot, many compounds forming the exhaust gases from the combustion of diesel fuel may be present. Among these, polycyclic aromatic hydrocarbons (PAH) are important pollutants that can even be adsorbed on the soot. In order to reduce soot emissions, oxygenated additives with different functional groups, such as alcohols, esters and ethers, have been proposed to be used as additives and blended with the diesel fuel. Some of these compounds may be produced through biorefinery processes, having thus a renewable character [1,2].

PAH have increased their importance along the past recent years because of their carcinogenic and mutagenic potential, and for this reason USA Environmental Protection Agency (EPA) defined 16 priority PAH, which are regulated by USA government policies [3]. Recently, the oxygenated derivatives of PAH (OPAH) have also considered to be taken into account since they have been found to be mutagenic in bacterial and human cells [4]. Some studies have measured PAH and OPAH in the airborne particles, in order to analyze the harmful potential of the outdoor in urban, industrial and traffic environments/areas [5].

In this context, our group aims to evaluate both the formation of PAH and OPAH generated during combustion processes, addressing the impact of the presence of oxygenated hydrocarbons on their concentration. In particular, the present study aims to identify and quantify PAH and OPAH of samples obtained from the pyrolysis of different oxygenated additives that could be blended with diesel fuel to reduce pollutants.

Methodology

The experiments are carried out under well laboratory conditions in a quartz flow reactor setup, in the 973-1473 K temperature range, by using different oxygenated compound inlet concentrations (approximately 90000 ppmv in carbon) and at atmospheric pressure.

A method by trapping the PAH and OPAH in two phases is considered: the first phase is found on the soot surface and stuck on the reactor walls, and the other, which corresponds to the gas phase, is retained by XAD-2 resin. The PAH and OPAH retained on the soot surface and the resin are subjected to Soxhlet extraction, using dichloromethane, and later concentrated by rotary evaporation. Finally, all the samples are analyzed by gas chromatography-mass spectrometry (GC/MS) with a selected ion monitoring mode (SIM), in order to increase the sensibility and the selectivity. The GC/MS procedure improves the

previous method developed in our research group [6], using an electron ionization, with an Agilent 7890A gas chromatograph coupled to a 5975C mass spectrometer [7].

The PAH measured are: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo (a) anthracene, chrysene, benzo (b) fluoranthene, benzo (k) fluoranthene, benzo (a) pyrene, dibenzo (a,h) anthracene, indeno (1,2,3-cd) pyrene and benzo (g,h,i) perylene. The OPAH measured are: 9-fluorenone, 9,10-anthraquinone, benzofluorenone, benzanthrone, benzo (a) anthracene-7,12-dione, naphthacene-5,12-dione, benzo (cd) pyrenone.

Results

The method has shown to exhibit a good efficiency for the identification and quantification of all the 16 PAH that were mentioned previously. Additionally, the initial tests on the analysis of the OPAH obtained in the pyrolysis of oxygenates, show a good isolation and resolution of the compounds identified. Further tests are being made in order to enhance the performance of the analysis of identification and quantification of OPAH.

Acknowledgements

The authors express their gratitude to MINECO and FEDER (Project CTQ2012-34423) and Aragón Government for financial support. Mr. F. Viteri acknowledges Ecuadorian “Secretaría Nacional de Educación Superior, Ciencia, Tecnología e Innovación” (SENESCYT), for the predoctoral grant awarded.

References

- [1] Román-Leshkov Y., Barrett C.J., Liu Z.Y., Dumesic J. A. Production of dimethylfuran for liquid fuels from biomass-derived carbohydrates. *Nature* 2007;447:982–986.
- [2] Al-Widyan M.I., Tashtoush G., Abu-Qudais M.. Utilization of ethyl ester of waste vegetable oils as fuel in diesel engines. *Fuel Process Technol* 2002;76:91–103.
- [3] U.S. Environmental Protection Agency (EPA). Health Assessment Document For Diesel Engine Exhaust. 2002.
- [4] Durant J.L., Busby W.F., Lafleur A.L., Penman B.W., Crespi C.L. Human cell mutagenicity of oxygenated, nitrated and unsubstituted polycyclic aromatic hydrocarbons associated with urban aerosols. *Mutat Res* 1996;371:123–157.
- [5] Sienna M. Oxygenated polycyclic aromatic hydrocarbons in urban air particulate matter. *Atmos Environ* 2006;40:2374–2384.
- [6] Sánchez N., Salafranca J., Callejas A., Millera Á., Bilbao R., Alzueta M. U. Quantification of polycyclic aromatic hydrocarbons (PAHs) found in gas and particle phases from pyrolytic processes using gas chromatography–mass spectrometry (GC–MS). *Fuel* 2013;107:246–253.
- [7] Viteri, F., Millera Á., Bilbao R., Alzueta M. U. Joint quantification of PAH and OPAH in gas and particle phases in the pyrolysis of oxygenated hydrocarbons. *In preparation* 2015.