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An experimental study of the influence of biofuel origin on particle-associated PAH emissions

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ABSTRACT

The chemical speciation of the 16 polycyclic aromatic hydrocarbons associated to the particulate matter of conventional diesel fuel, rapeseed methyl esters, waste cooking oil methyl esters, waste cooking oil ethyl esters and their conventional fuel blends has been carried out. The speciation of these individual compounds was made by a combination of thermal extraction, solid phase micro-extraction and GC/MS analysis. This PAH speciation method was applied to a real samples obtained from a diesel engine under two different operating modes, urban and extraurban modes. The purpose of this work was to study the relationship between the amount, type and carcinogenic potency of polycyclic aromatic hydrocarbons in engine emissions and the multi-component biodiesel fuel composition.

1. Introduction

The well-known mutagenic effects of soot particles are clearly associated with the presence of polycyclic aromatic hydrocarbons (PAHs) (De Kok et al., 2006) created during the incomplete combustion of the organic matter (Richter and Howard, 2000). Ultrafine particles, with higher amounts of PAHs, can penetrate deeply in the lungs and can be found in other organs (Kennedy, 2007), improving the PAHs availability for biological activity and therefore increasing their health risk.

The PAHs are present both in the particulate and gaseous emissions of the diesel engines and their distribution between both phases depends not only on their molecular weights (MWs), but also on the ambient temperature, PAH concentration and particle composition (Christensen, 2003; Westerholm et al., 1991). Although low MW PAHs are usually present in higher concentrations, the contribution of the particle-associated PAHs (higher MW) to the total carcinogenic potential is greater since this potential increases with the MW (Ravindra et al., 2008; Li et al., 2003). This is consistent with the higher contribution of the diesel particulate matter emissions (DPM), as compared to the components in the gaseous phase, to the immunotoxicity and cancer risks associated with diesel engine emissions (US EPA, 2002b).

There are two main mechanisms associated to PAHs emissions in diesel engines, survival of the PAHs originally present in the fuel (Collier et al., 1995; Mi et al., 2000), and combustion reactions in which PAHs are formed through pyrosynthesis of the fuel fragments (Kado et al., 2005; Rhead and Hardy, 2003). For the PAH survival route, the compound's basic structure is the same whilst for the pyrosynthesis route a new complex structure of fused rings is formed through combination of multiple products of the incomplete combustion (Rhead and Hardy, 2003; Topal et al., 2004). The former case is of special relevance for fuels without any aromatic content (Richter and Howard, 2000) in which intermediate species such as acrolein and cyclohexene can lead to the formation of the first aromatic ring (Knothe et al., 1997).

It is not simple to determine the influence of alternative fuels on PAHs emissions, since there is a lack of information about individual compounds (US EPA, 2002a) and few of the researches provide variability data (Krahl et al., 1996; Turrio-Baldassarri et al., 2004; US EPA, 2002a). However, most of the results available in the literature report reductions in the total PAH emissions with the use of biodiesel (Cardone et al., 2002; Krahl et al., 1996; Pinto et al., 2005; US EPA, 2002a), particularly in the amounts of the most carcinogenic compounds such as benzo(a)pyrene (Cardone et al., 2002). The decreases in PAH emissions can be as high as 80–90% for pure biodiesel (Lin et al., 2006; Sharp et al., 2000). Nevertheless, there are also authors who do not find significant differences between conventional fuel and biodiesel blends, (Durbin et al., 2000; Tang et al., 2007; Turrio-Baldassarri et al., 2004), or else

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report increases in the amount of the PAHs with the use of biodiesel (Kado et al., 1996; Kulkarni and Dalai, 2006).

Until now more than 32 PAHs have been identified in diesel engine emissions (US EPA, 2002b). However, the US Environmental Protection Agency (US EPA) has selected only 16 of these compounds as priority pollutants due to their higher carcinogenic potential. These compounds are naphthalene (NAPH), acenaphthylene (ACNY), acenaphthene (ACN), fluorene (FLUO), phenanthrene (PHEN), anthracene (ANTH), fluoranthene (FANTH), pyrene (PYR), benz(a)anthracene (B(a)A), chrysene (CHR) benzo(b) fluoranthene (B(b)F), benzo(k)fluoranthene (B(k)F), benzo(a)pyrene (B(a)P), dibenz(a,h)anthracene (DB(ah)A), indeno(1,2,3-cd) pyrene (I(123-cd)P) and benzo(g,h,i)perylene (B(ghi)P), and they have been the compounds chosen for analysis carried out in this work.

In this work we have used a recently developed method (Ballesteros et al., 2009) based on thermal extraction, solid phase micro-extraction (SPME) and gas chromatography–mass spectrometry (GC–MS) for the comparison of the DPM–PAHs emitted from different biodiesel fuels and their blends with conventional diesel fuel. The results obtained are useful to assess the influence of the vegetable oil origin (new or waste) and alcohol used for transesterification (methanol or ethanol) on the health effects of these fuels under different engine operating conditions. In addition to the results of speciated DPM–PAH compounds, data of gaseous NMHC (non-methane hydrocarbons), DPM and VOM (volatile organic matter) emissions and the values of dm (mean diameter) and opacity of the diesel particles are presented here. This information allows the comparison between DPM and PAHs content and other significant emission parameters.

2. Experimental equipment and procedures

2.1. Overview of the experimental set-up

A scheme of the engine, dynamometer and systems for on- and offline sampling and analysis of regulated and unregulated exhaust gas components is shown in Fig. 1.

Since emissions are strongly dependant on the exhaust gas recirculation (EGR) ratio, it is important to keep this parameter fixed when comparing different fuels. For this reason the engine EGR valve was driven by a stepper motor which allows to achieve the same EGR ratio for all the fuels tested. Herein EGR ratio was defined as the mass flow of the recirculating exhaust normalized by the total mass flow entering the cylinder. The EGR flow rate of the recirculating exhaust was calculated through a CO_2 balance in the engine.

Prior to test a new fuel, all lines were drained and then filled with the new fuel. Before beginning a new test, the sample lines were cleaned to remove deposits and hydrocarbons of previous runs. After this cleaning procedure, blank filters were collected and analyzed, showing no significant amount of contaminant. The engine was warmed with the new fuel for at least 1 h to purge any remains of the previously tested fuel from the engine fuel system. Likewise, each engine operating mode was tested for at least half an hour before sampling.

The duration of the engine tests for each mode was chosen so that three different particulate filters could accumulate a particulate mass of at least 1.3 mg each and six particle size distributions could be taken by using a Scanning Mobility Particle Sizer (SMPS). The time established for particle sample was held constant for all fuels, 30 min for the extraurban mode and 32 min for the urban mode.

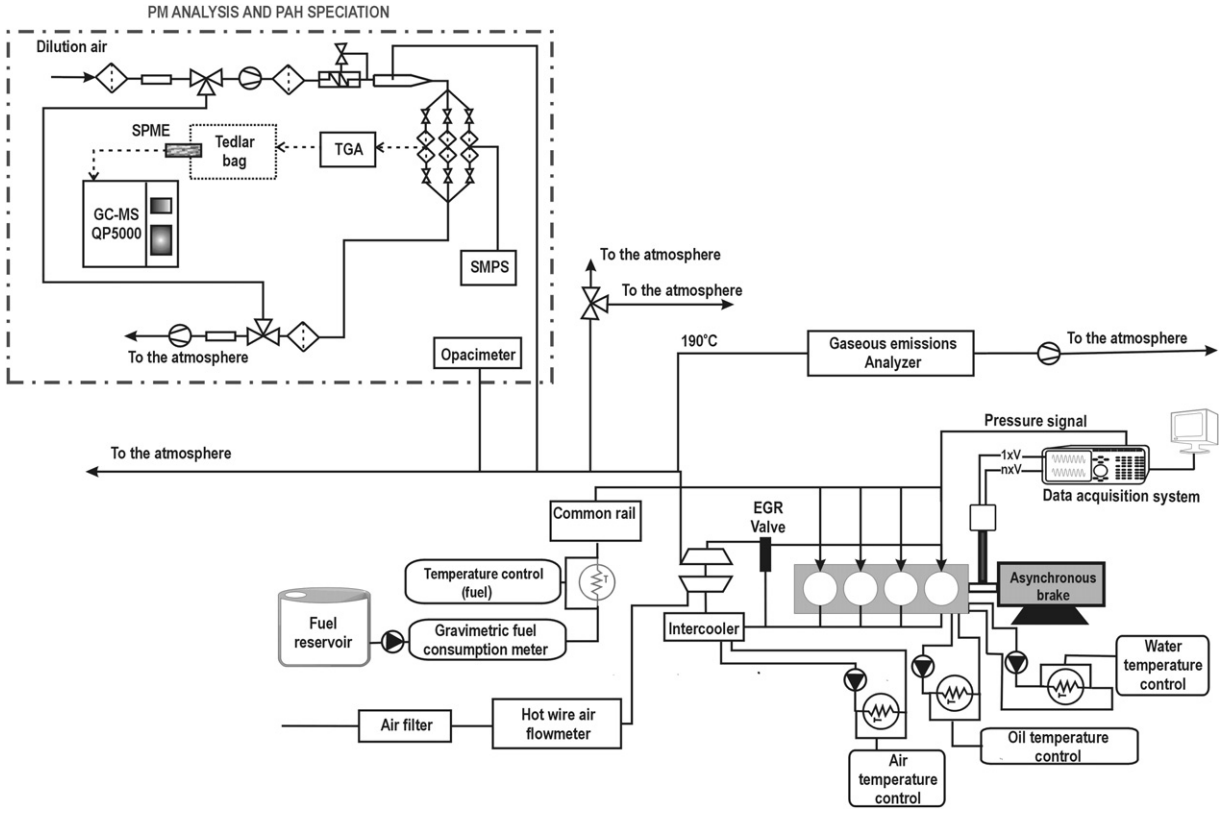

Fig. 1. Experimental set-up.