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Chemical characterization of biofuel exhaust emissions

Aleksandra Jedynska*, Peter C. Tromp, Marc M.G. Houtzager, Ingeborg M. Kooter

TNO, Netherlands Organization for Applied Scientific Research, Princetonlaan 6, PO Box 80015, 3508 TA Utrecht, The Netherlands

HIGHLIGHTS

- We tested different diesel and biodiesel blends in a truck engine.
- We report emissions of 108 individual components for all tested fuels.
- Biodiesel was associated with lower levels of emissions of most components.
- The majority of particle bound PAH were associated with the ultra-fine fraction.

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ABSTRACT

Use of biodiesel is increasing following implementation of various policy instruments and a surge in demand due to growing urbanized populations. A series of experiments to characterize the chemical composition of emissions generated during combustion of petro-diesel (B0), biodiesel blends (B5, B10, B20), biodiesel (B100) and pure plant oil were performed in a standard EURO III truck engine. In total 108 separate components of emissions from the various fuels were quantitatively assessed. Further, the size dependence of PAH emissions was investigated. It was found that biodiesel was associated with significantly lower levels of PM and CO emissions and reduced levels of components such as aldehydes, volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAH) and their derivatives, hopanes/steranes and elemental carbon/organic carbon (EC/OC). The majority of particle bound PAH were associated with the ultra-fine fraction (diameter range of 0.01–0.14 μm). The use of a diesel particulate filter reduced B0 emissions to levels of B100. While our study was conducted under ideal controlled conditions, our data support the widely held view that biodiesel emissions have a different chemical composition than emissions from petro-diesel. The consequences of this in terms of health and environmental impact should be assessed in wider studies.

1. Introduction

Biodiesel is the most common renewable fuel available in Europe and currently accounts for about 82% of total biofuel production (Yusuf et al., 2011). Although the use of biofuels still involves a burning process that produces emissions (in the same way as petroleum-based diesel), biodiesel is widely regarded to be associated with lower levels of emissions of components such as carbon dioxide (CO_2) and particulate matter (PM) (Atabani et al., 2012; Demirbas, 2007; Yusuf et al., 2011). Many studies have previously been published that describe the composition and levels of primary regulated components in exhaust gases from biodiesel (Dorado, 2003; Geyer et al., 1984; Schumacher et al., 1996; Verbeek et al., 2008). Such components include CO_2, PM, nitrous compounds (NOx), carbon monoxide (CO), and total hydrocarbon (THC) emissions. Currently however, the effect of the biofuel burning process on so-called unregulated emissions remains much less clear. Previously published studies that have focused on these components give a very variable impression of what emissions are truly associated with biodiesel use (Di et al., 2009; Fontaras et al., 2010; Gangwar et al., 2011; Ge et al., 2007; Heikkilä et al., 2012; Karavalakis et al., 2010a, 2010b, 2009; Song et al., 2011; Tan et al., 2009; Topinka et al., 2012; Tsai et al., 2010). Such components include aldehydes, volatile organic compounds (VOC) and polycyclic aromatic hydrocarbons (PAH) and their oxy- and nitro-derivatives. One particular aspect that has also largely been ignored (in previous studies) is the association of specific components of exhaust fumes with soot particles of different sizes.

We (Kooter et al., 2011) and others (Gaffney and Marley, 2009)

* Corresponding author.
E-mail address: aleksandra.jedynska@tno.nl (A. Jedynska).

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have previously called for biofuel exhaust gas emission components to be investigated more thoroughly. Apart from environmental concerns, one of the major reasons for investigating the chemical composition of exhaust gases from biodiesel is to understand more fully any potential health risks associated with biodiesel use. We have previously reported the results of an investigation into the toxicological characteristics of diesel engine emissions (Kooter et al., 2011). Part of that report included a limited analysis of the chemical composition of exhaust gas generated from various compositions of (bio-)diesel. Here we describe the full chemical characterization of biodiesel exhaust gas emissions.

The specific aims of the study were threefold: 1) more fully characterize the chemical components present in emissions generated by a diesel engine running diesel, diesel/biodiesel blends, pure biodiesel and pure plant oil; 2) establish the distribution of chemical components among ultra-fine, fine and course soot particle fractions in exhaust gas emissions; and 3) more fully establish the effect of a diesel particulate filter on the chemical profile of exhaust gas generated from diesel fuel.

2. Materials and methods

2.1. Test engine and measurement program

Full experimental and methodological details have previously been published (Kooter et al., 2011). Briefly, exhaust gas emissions from different types of diesel, biodiesel and pure plant oil were generated by a six cylinder Euro III heavy-duty truck engine (DAF XE355). The engine had a cylinder displacement of 12 L, 355 kW power output and was not initially fitted with any type of emission control device. All experiments were conducted using the European Transient Cycle (ETC, EC directive 2005/78/EC) with the engine mounted on a transient engine dynamometer at the TNO powertrain test center (Helmond, The Netherlands) (Fig. 1). All experiments were conducted during October and November 2008.

The chemical characteristics of exhaust gas emissions from the following fuels were compared: conventional diesel (B0, EN590), 100% biodiesel (B100, EN14214), mixtures of biodiesel and conventional diesel (5% (B5), 10% (B10) and 20% (B20) biodiesel by volume), and pure plant oil (PPO, DIN 51605). The specifications of the used fuels are presented in Supplementary Materials Tables S1 – S3. In addition, the application of a continuously regenerating, wall flow, ceramic, monolith retrofit diesel particulate filter (DPF) was tested with conventional diesel (B0 + DPF).

In expectation of low concentrations of certain components of the exhaust gas emissions, a minimum of three ETC tests per fuel were performed to generate a sample. For the sampling of PAH and their derivatives, hopanes/steranes and EC/OC, six ETC tests per fuel were used to generate samples from B100, PPO and B0 + DPF. Each fuel was sampled twice, except for B0, which was sampled four times. Two samples of B100 and B0 + DPF were pooled to increase the chance for the components detection. To determine background (environmental) concentrations of potential chemical components of the fuels, three experiments were run in exactly the same way but without the engine running. These background measurements were averaged and used to correct the generated experimental data.

2.2. Collection of emission samples

The sampling methods used to collect and analyze samples of regulated and unregulated components of exhaust gas emissions from diesel and biodiesel were previously published (Kooter et al., 2011). Briefly, a two-stage double-dilution tunnel with constant volume sampling (CVS, Horiba) was employed. Sampling points were used to collect and analyze various components of emissions. In the first stage the following components were sampled: carbon monoxide (CO), carbon dioxide (CO_2), total hydrocarbons (THC), nitrogen oxides (NOx), elemental carbon/organic carbon (EC/OC), aldehydes, and volatile organic hydrocarbons (VOCs) in the ranges of $C_1 - C_5$ and $C_6 - C_{12}$. An electronic low-pressure impactor (ELPI) and Berner low-pressure impactor were also used for fractionation of exhaust emissions according to particle size, number and mass (more details in Supplementary Materials). Particle measurements were performed at an exhaust gas temperature of 51.7 °C according to European Directives 2005/78/EC and 2005/55/EC. All sampling tubing and sampling devices were made of electrically conductive material (conductive silicone rubber and stainless steel) and were electrically grounded to prevent electrostatic effects and to minimize particle loss. In addition, in the ELPI sintered and oiled plates were used.

At the second dilution stage the following components were sampled: regulated particulate matter (PM), polycyclic aromatic hydrocarbons (PAH), nitro-polycyclic aromatic hydrocarbons (nitro-PAH), oxygenated-polycyclic aromatic hydrocarbons (oxy-PAH), hopanes and steranes. Specific details of sampling

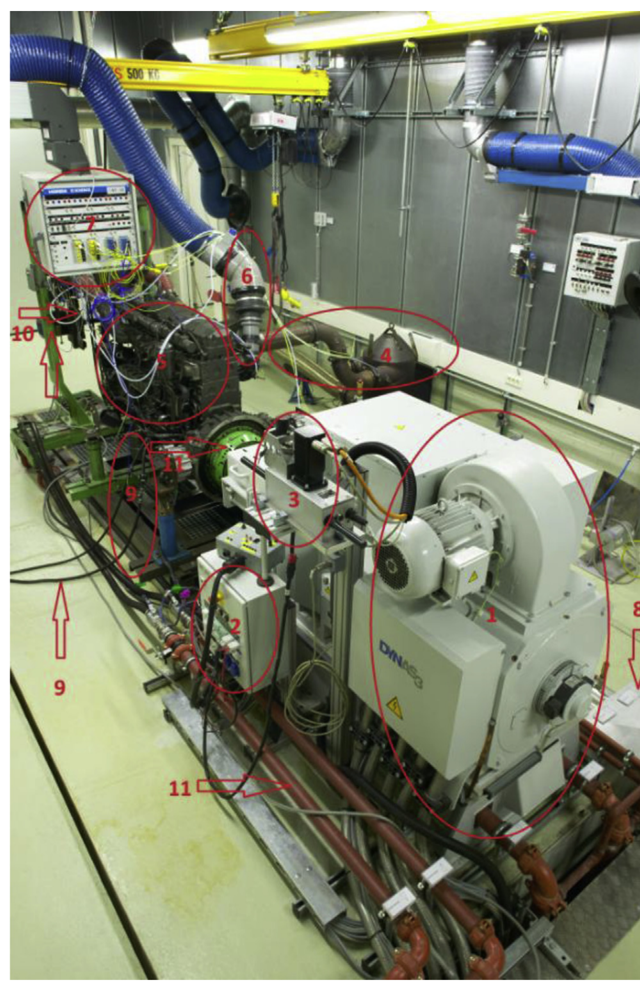

Fig. 1. Heavy duty engine in the experimental setup. 1: dynamic dynamometer for measuring and controlling and control the speed of the engine's torque; 2: power supply of the engine; 3: throttle actuator,4: exhaust pipe with muffler; 5: the EUROIII heavy duty diesel engine; 6: inlet of conditioned air; 7: temperature and pressure monitoring; 8: engine cooling tubes; 9: fuel connections; 10: intercooler of the engine; 11: cooling water pipes for the intercooler (photo: Johan Aarssen fotografie).