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Polycyclic aromatic hydrocarbons (PAHs) in exhaust emissions from diesel engines powered by rapeseed oil methylester and heated non-esterified rapeseed oil

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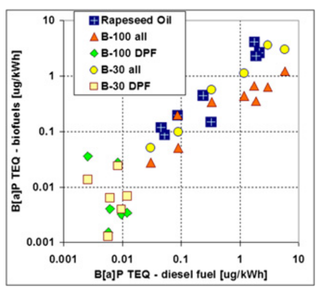
HIGHLIGHTS

- ► Emissions of PAHs from four diesel engines examined at different labs.
- ► Consistent results with different analytical methods and toxic equivalency factors.
- ► Biodiesel and rapeseed oil reduce lighter PAH, increase heavier carcinogenic PAHs.
- ► Biodiesel PAH reduction lower on particle filters without catalyst.

GRAPHICAL ABSTRACT



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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) of exhaust emissions were studied in four direct-injection turbocharged four-cylinder diesel engines, with power ratings of 90–136 kW. The engines were operated on biodiesel (B-100), a blend of 30% biodiesel in diesel fuel (B-30), and heated rapeseed oil (RO) in two independent laboratories. Diesel particle filters (DPF) and selective catalytic reduction (SCR) systems were used with B-30 and B-100. Concentrations of individual PAHs sampled in different substrates (quartz, borosilicate fiber and fluorocarbon membrane filters, polyurethane foam) were analyzed using different methods. Benzo[a]pyrene toxic equivalents (BaP TEQ) were calculated using different sets of toxic equivalency factors (TEF). Operation on B-100 without aftertreatment devices, compared to diesel fuel, yielded a mean reduction in PAHs of 73%, consistent across engines and among TEF used. A lower PAH reduction was obtained using B-30. The BaP TEQ reductions on DPF were 91–99% using B-100, for one non-catalyzed DPF, and over 99% in all other cases. The BaP TEQ for heated RO were higher than those for B-100 and one half lower to over twice as high as that of diesel fuel. B-100 and RO samples featured, compared to diesel fuel, a relatively high share of higher molecular weight PAH and a relatively low share of lighter PAHs. Using different sets of TEF or different detection methods did not consistently affect the observed effect of fuels on BaP TEQ. The compilation of multiple tests was helpful for

Abbreviations: BaP, Benzo[a]pyrene; cDPF, Catalyzed diesel particle filter; DOC, Diesel oxidation catalyst; DPF, Diesel particle filter; ESC, Engine Steady Cycle; HPLC, High Performance Liquid Chromatography; PAHs, Polycyclic aromatic hydrocarbons; SCR, Selective catalytic reduction; TEF, Toxicity equivalency factor; TEQ, Toxicity equivalent; WHSC, World Harmonized Steady Cycle.

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discerning emerging patterns. The collection of milligrams of particulate matter per sample was generally needed for quantification of all individual PAHs.

1. Introduction

Non-esterified vegetable oils, chemically, n-alkyl-triglycerols of fatty acids, are typically used for the production of biodiesel (also FAME – fatty acid methylesters). Neat biodiesel and its blends with diesel fuel are popular alternative fuels for compression ignition (diesel) engines (Szybist et al., 2007; Demirbas, 2007; Knothe, 2010). Non-esterified oils have historically been used directly as fuel (Knothe et al., 1997; Knothe, 2001; Ramadhas et al., 2004), but such use has often been problematic, primarily due to high viscosity of vegetable oils. The majority of the engines powered by vegetable oil use an additional heated fueling system for vegetable oils, with diesel fuel used to start and warm up the engine, and again to flush the fuel system prior to engine shutdown.

As engines are one of the principal sources of air pollution in most urban areas, the effects of new fuels on exhaust emissions are of concern. Diesel engines emit particles predominantly in the tens of nanometers (nm) (Kittelson, 1998), which readily deposit in lungs (Gerde et al., 2001; Gehr et al., 2006). Particles in lower tens of nm and smaller can penetrate through cell membranes into the blood, and have a wide and detrimental effect on human health (Künzli et al., 2000). Proximity to sources of internal combustion engine exhaust has been associated with increased risks of various chronic health problems (Lewtas, 2007; McEntee and Ogneva-Himmelberger, 2008; Balmes et al., 2009). One of the groups of compounds of concern is polycyclic aromatic hydrocarbons (PAHs), as reviewed in (US EPA, 1993; Larsen and Larsen, 1998; IARC, 2010). Reviews of the effect of biodiesel on PAH emissions state that the reported effects are often contradictory (Karavalakis et al., 2010), data are scarce, have low repeatability and are “often questioned by the authors themselves” (Lapuerta et al., 2008). Compared to diesel operation, Zou and Atkinson (2003) found that methylester of canola oil yielded a reduction of only lighter, less toxic PAHs, while Karavalakis et al. (2010) reports an increase in lighter PAHs. The effects of non-esterified oils on PAH range from a decrease (Kalam et al., 2008; Abbass et al., 1990) to an increase (Krahl et al., 1996; Lea-Langton, 2008). The effects of heated vegetable oil operation on emissions were dependent on engine operating conditions (Krahl et al., 1996; Czerwinski et al., 2008; Vojtisek-Lom et al., 2009).

The goal of this work was to elucidate the effects of fueling diesel engines with rapeseed oil methylester (biodiesel) and heated non-esterified rapeseed oil on the emissions of polycyclic (polynuclear) aromatic hydrocarbons (PAH). To amass a sufficient pool of data, the experimental work was carried out on four contemporary diesel engines; non-road engines, Zetor and Liebherr with inline pump and unit injectors, respectively, and on-road vehicle engines Cummins and Iveco with electronically controlled Common Rail fuel injection systems, operated at various loads at two different engine test facilities, with different sampling approaches and sampling media used. The concentrations of PAHs were analyzed in three independent laboratories using different analytical methods.

2. Materials and methods

2.1. Engines, exhaust aftertreatment, fuels and lubricating oils

The parameters of four engines are listed in Table 1. The Zetor 1505 and Cummins ISBe4 engines were tested at the Internal Combustion Engine Laboratory at the Technical University of Liberec (TUL), Czech Republic. The Iveco and Liebherr engines were tested at the Laboratory for IC Engines and Exhaust Emission Control (AFHB) at the Bern University of Applied Sciences, Biel, Switzerland. In addition to tests with no exhaust aftertreatment, the Iveco engine was operated with a selective catalytic reduction catalyst (SCR) for NO_x reduction, and with a diesel particle filter (DPF) combined with SCR. The Liebherr engine was also operated with a diesel oxidation catalyst (DOC) followed by a DPF with catalytic coating (cDPF), and with a passive DPF with no catalytic coating. The tests were performed using European highway-grade diesel fuel (EN 590) and commercial rapeseed oil methylester (EN 14214). A mineral-based lubricating oil (M7-ADSIII, Paramo, Pardubice, Czech Republic) was used for all Cummins engines and the first set of Zetor engine tests (TUL-1). A low-ash ester-based biodegradable lubricating oil (Plantomot 5W-40, Fuchs Oil, Brno, Czech Republic) was used for the second (TUL-2) and third (TUL-3) sets of Zetor engine tests. The Zetor and Cummins engines which were operated on non-esterified fuel-grade (DIN 51605) rapeseed oil (FabioProduct, Holín, Czech Republic) were equipped with a dual-fuel system which allows alternate operation on diesel fuel or heated vegetable oil (Vojtisek-Lom et al., 2012).

All engines were operated in steady-state modes, with details of each test set given in Table 2. For the Zetor and Cummins engines, operating modes from ISO-8178, schedules C-1 and C-2, non-road tests, and from ESC (Engine Steady State Cycle) and WHSC (World Harmonized Steady-state Cycle) were used, with durations of each point adjusted to allow for continuous sampling. The Iveco engine was operated at 2200 rpm at 10% and 100% (full) load. The Liebherr engine was operated at 900 rpm and 315 Nm (30 kW) and at 1100 rpm and 100% load (nominally 480 Nm, 55 kW).

2.2. Exhaust sampling

For the first two sets of Zetor engine, exhaust from an improvised full-flow dilution tunnel (TUL-1) and raw exhaust (TUL-2, 2.4–3.7 m^3 per sample) were sampled on 47 mm diameter cartridges containing polyurethane foam (PUF), a membrane filter,

Table 1
Engine parameters.

Engine	Manufacturer	Emissions category	Fueling system	Swept volume [dm^3]	Rated power
Zetor 1505	Zetor a.s., Brno, Czech Republic	EU non-road Stage III-A	Inline pump Motorpal	4.16	90 kW @ 2200 rpm
Cummins ISBe4	Cummins Ltd., Darlington, England	Euro 4	Common Rail Bosch 2nd gen	4.5	136 kW @ 2100–2700 rpm
Iveco F1C	Iveco, Torino, Italy	Euro 3	Common Rail Bosch 1600 bar	3.0	100 kW @ 3500 rpm
Liebherr D934 S	Liebherr, Bulle, Switzerland	EU non-road Stage III-A	Unit injectors Bosch	6.36	111 kW @ 2000 rpm