Fuel 103 (2013) 414–420

Contents lists available at SciVerse ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Exhaust emissions and mutagenic effects of diesel fuel, biodiesel and biodiesel blends

Olaf Schröder [a,*], Jürgen Bünger [b,c], Axel Munack [a], Gerhard Knothe [d], Jürgen Krahl [e]

[a] Johann Heinrich von Thünen-Institut, Federal Research Institute for Rural Areas, Forestry and Fisheries, 38116 Braunschweig, Germany
[b] BGFA – Research Institute of Occupational Medicine, German Social Accident Insurance, University of Bochum, 44789 Bochum, Germany
[c] Institute of Occupational and Social Medicine, Georg-August-University of Göttingen, 37073 Göttingen, Germany
[d] National Center for Agricultural Utilization Research, United States Department of Agriculture, 1815 N. University St., Peoria, IL 61604, USA
[e] Coburg University of Applied Sciences and Arts, 96406 Coburg, Germany

HIGHLIGHTS

- We run three diesel engines (Euro 0, III and IV) using biodiesel blends.
- The influence on the exhaust emissions and mutagenic effects were measured.
- Regulated exhaust emissions change approximately linearly with the blend.
- Blends with 20% biodiesel shows a maximum of mutagenic effects and change nonlinear with the blend.

ARTICLE INFO

Article history:
Received 12 March 2012
Received in revised form 25 August 2012
Accepted 28 August 2012
Available online 11 September 2012

Keywords:
Biodiesel
B20
Diesel engine exhaust gas
Mutagenic effect
Exhaust gas emissions

ABSTRACT

The replacement of petroleum-derived fuels by renewable biogenic fuels has become of worldwide interest with the environmental effects being scientifically investigated. Biodiesel has been proven to be a suitable alternative to petrodiesel and blending up to 20% biodiesel with petrodiesel is policy promoted in the USA and the EU.

To investigate the influence of blends on the exhaust emissions and possible health effects, we performed a series of studies with several engines (Euro 0, III and IV) using blends of rapeseed-derived biodiesel and petrodiesel. Regulated and non-regulated exhaust compounds were measured and their mutagenic effects were determined using the Bacterial Reverse Mutation Assay (Ames-Test) according to OECD Guideline 471.

Exhaust emissions of blends were approximately linearly dependent on the blend composition, particularly when considering regulated emissions. However, a negative effect of blends was observed with respect to mutagenicity of the exhaust emissions. In detail, an increase of the mutagenic potential was found for blends with the maximum observed for B20. From this point of view, B20 must be considered as a critical blend when petrodiesel and biodiesel are used as binary mixtures.

1. Introduction

Biodiesel can be used as a neat fuel (B100) or in any blend ratio with petrodiesel. The most popular biodiesel blend in the USA is B20 (20% biodiesel, 80% diesel fuel), which can be used for Energy Policy Act of 1992 (EPAct) compliance. In the European Union, the use of biofuel blends is recommended and was introduced by federal regulations in several countries. In Germany, biodiesel is currently blended as B7 (7% biodiesel). Actually, B7 plus three percent hydrotreated vegetable oil (HVO) as well is intended to become possible in Germany.

Biodiesel reduces most exhaust emissions when used in unmodified diesel engines [1–3]. The amount of reduction depends on the blend level. B100 produced from rapeseed oil or soybean oil reduces life cycle CO_2 emissions by 50–75% compared to petrodiesel. This effect is linear to the blend level, leading to life cycle CO_2 emissions reduced by 2.5–3.75% per 5% increase of biodiesel blending. Low-level blends induce small reductions in emissions of hydrocarbons, carbon monoxide, particulate matter, and air toxins as well. However, nitrogen oxides (NO_X) contributing to smog formation may increase slightly when biodiesel is used. Numbers vary, however B20 is believed to increase NO_X by 2–4%. Several biodiesel researchers are working on fuel additives to address this problem. For blend levels of $\leqslant$5%, the NO_X increase is negligible.

Long-term occupational diesel engine emissions (DEE) exposure was associated with the risk of lung cancer in a pooled analysis of

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* Corresponding author.
E-mail address: olaf.schroeder@vti.bund.de (O. Schröder).

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http://dx.doi.org/10.1016/j.fuel.2012.08.050

11 population-based European and Canadian case-control studies which covered the years from the 1950–1980s in Olsson et al. [4]. Whereas previous studies showed rather moderately increased lung cancer risk, a very recent "nested case control study" revealed dose dependent increased odd ratios up to 7.30 (95% confidence interval (CI) = 1.46–36.57) for DEE exposed "non metal miners" which were exposed towards 304 μg/m^3 y or more [5]. This study was based on a cohort study which investigated 12,315 workers exposed to diesel exhaust at eight US non-metal mining facilities. Hazard ratios for lung cancer mortality up to 5.01 (95% CI = 1.97–12.76) were seen in this cohort [6]. These results caused the International Agency for Research on Cancer (IARC) to change the classification of DEE from "probably carcinogenic to humans" (group 2A) into "carcinogenic to humans" (group 1) in June 2012 [7]. The epidemiological evidence is supported by long-term inhalation studies in the rat [8–10] and genotoxic and inflammatory properties of DEE components [7]. Carcinogenicity of DEE from combustion of common petrodiesel was ascribed to chronic inflammatory effects of diesel particulate matter [11–15] and to adherent polycyclic aromatic hydrocarbons (PAH). Corresponding to the strong genotoxicity of some PAH, extracts of diesel particulate matter show mutagenicity in the bacterial reverse mutation assay [16–20].

Using biodiesel instead of petrodiesel, a decreasing mutagenicity was found in several studies [21,22,6]. Only few publications regarding the health effects of DEE from blends are were found. First comparative investigations on DF, RME, and blends thereof were conducted by Grägg [23]. Blends of MK1 and RME (B5 and B30) produced a stronger mutagenicity than could be expected from the results for the pure fuels in the Ames test. Using rape seed ethyl ester (REE) as biofuel, Kado et al. [24] found also less mutagenicity (Ames test) for REE than for DF. The highest mutagenicity in this test was found for B20. The health effects on human cells were investigated by Ackland et al. [25] and Liu et al. [26]. They also found stronger health effects using blends than expected from pure fuels.

2. Materials and methods

2.1. Engine and test procedures

Studies were carried out at the emissions test facility of the Institute for Agricultural Technology and Biosystems Engineering at the Federal Research Institute for Rural Areas, Forestry and Fisheries (vTI) in Braunschweig and at the Coburg University of Applied Sciences, Germany. Three different engines were used:

At the Institute for Agricultural Technology and Biosystems Engineering, a Mercedes-Benz Euro III engine OM 906 LA with turbocharger and intercooler (Table 1) was coupled to a Froude Consine eddy-current brake. The engine had no exhaust gas aftertreatment. Regulated emissions were measured in accordance with the 13-mode European Stationary Cycle (ESC). Particulate material for the mutagenic test was sampled continuously from minute 3 to minute 28 during the ESC test.

A Euro IV engine MAN D08 36 LFL51 with turbocharger, intercooler and exhaust-gas recirculation (Table 2) was coupled to a dynamometer from AVL, Graz, Austria. For exhaust aftertreatment a continuously operating particle filter, a PM-Kat®, was attached. This Filter, added to a stainless steel muffler, works without plugging and is maintenance free. It does not need any additional lubricants and should reduce particulate matter by 60%. The PM-Kat® incorporates an oxidation catalyst, which should eliminate hydrocarbons. The test procedure was the European Transient Cycle (ETC) for mutagenic tests and the ESC for determination of regulated emissions. The sampling procedure for mutagenicity was carried out over the full test cycle with a constant flow rate of 25 L/min out of the raw exhaust.

Table 1
Technical data of Mercedes engine OM 906 LA.

Piston stroke	130 mm
Bore of cylinder	102 mm
Number of cylinders	6
Stroke volume	6370 cm^3
Rated speed	2300 min^{-1}
Rated power	205 kW
Maximum torque	1100 N m at 1300 min^{-1}
Compression ratio	17.4

Table 2
Technical data of MAN engine D08 36 LFL51.

Piston stroke	125 mm
Bore of cylinder	108 mm
Number of cylinders	6
Stroke volume	6871 cm^3
Rated speed	2300 min^{-1}
Rated power	206 kW
Maximum torque	1100 N m at 1200–1800 min^{-1}
Compression ratio	18.0

At Coburg University of Applied Sciences a one-cylinder test engine 502.019 from AVL (Table 3) was used. The engine had no exhaust gas aftertreatment. Particles for mutagenic tests were sampled at rated power only.

2.2. Sampling of regulated compounds

The regulated compounds of the exhaust gas were determined for the OM 906 engine and the MAN engine in the same way. Carbon monoxide (CO), hydrocarbons (HCs) and nitrogen oxides (NO_X) were sampled each second from the raw exhaust gas stream and determined with commercial gas analyzers. Hydrocarbons (HCs) were determined with a gas analyzer RS 55-T (Ratfisch, Germany). Carbon monoxide (CO) was measured by means of an analyzer Multor 710 (Maihak, Germany) and nitrogen oxides (NO_X) were analyzed with a CLD 700 EL ht chemical luminescence detector (Eco Physics, Germany).

All particle measurements were accomplished after dilution of raw exhaust gas in a dilution tunnel. A dilution factor of about 10 is applied for determination of particle mass and particle number measurements. Dilution factors are calculated from separate recordings of CO_2 contents in fresh air and diluted exhaust gas. Particle mass was determined gravimetrically after sampling on Teflon coated glass fiber filters (T60A20, Pallflex, diam. 70 mm, Pallflex Products Corp., Putnam, CT, USA), with sampling intervals according to individual weighting factors of each engine mode. Weights of fresh and sampled filters were determined to an accuracy of ±1 μg by means of a microbalance M5P (Sartorius, Göttingen, Germany) always preceded by at least 24 h of conditioning in a climate chamber held at 22 °C and 45% relative humidity.

Table 3
Technical data of AVL engine 502.019.

Piston stroke	120 mm
Bore of cylinder	125 mm
Number of cylinders	1
Stroke volume	1472 cm^3
Rated speed	2000 min^{-1}
Rated power	8.9 kW
Maximum torque	42.4 N m
Compression ratio	16.0