Influence of the fatty acid spectrum of vegetable oil methyl esters as pure fuel and blends on the emissions from diesel engines

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Abstract

Biodiesel (in Germany usually rapeseed oil methyl ester, RME) is used as a neat fuel as well as in blends with mineral diesel fuel (DF). Thus, in 2008 in Germany a total of about 2.7 million tons (about 3.1 billion litres) of biodiesel were sold, of which 41 percent was used as a neat fuel and 59 percent in blends. Since then, because of the tax regulations, the proportion of neat fuel in the total biodiesel sales fell to below 10%. Currently, a maximum of 7 percent biodiesel in diesel fuel is allowed (B7 Blend). The quality requirements for B7 are described in DIN 51628. Because of the limited availability of fossil resources, an increase of biogenic compounds in fuels is desired. To achieve this goal, next to rapeseed oil, other sustainably produced vegetable oils can be used as raw materials. These raw materials influence the fuel properties as well as the emissions. For blends, the emissions are not necessarily a reflection of the percentage emissions of the underlying pure fuels.

To investigate the environmental impact of the exhaust gas, it is necessary to determinate next to the regulated exhaust gas components (nitrogen oxides, particulate matter, carbon monoxide and hydrocarbons) further non-regulated components. In detail, particle size distribution, emissions of polycyclic aromatic hydrocarbons, and mutagenicity in the Ames test are of special interest. These emissions can not be derived from the regulated components.

In this paper emission measurements on a Euro III engine OM 906 of Mercedes-Benz are presented. As fuel vegetable oil methyl esters from various sources (rapeseed oil, soybean oil, palm oil, coconut oil and linseed oil) and reference diesel fuel were used as well as blends of the vegetable oil methyl esters with diesel fuel.

The carbon monoxide and hydrocarbon emissions of the tested methyl esters show advantages over DF. The particle mass emissions of methyl esters were likewise lower than those of DF. Linseed oil methyl ester showed the highest particle mass emissions of the methyl esters. A disadvantage is the use of biodiesel with respect to emissions of nitrogen oxides. They increased depending on the type of methyl ester by 10% to 30%.
Emissions of polycyclic aromatic hydrocarbons (PAHs) and the results of mutagenicity tests correlate with those of the PM measurements, at which for palm oil methyl ester next to coconut oil methyl ester the lowest emissions were detected. From these results one can formulate a clear link between the iodine number of the ester and the emission behaviour. For blends of biodiesel and diesel fuel, emissions changed linearly with the proportion of biodiesel. However, especially in the non-regulated exhaust gas components, some deviations from this linear trend were detected.

MATERIALS AND METHODS

Engine and Test cycle

Engine tests were carried out at the emission test stand of the Institute of Agricultural Technology and Biosystems Engineering at the Johann Heinrich von Thünen-Institut in Braunschweig. Emission tests were achieved, using a six-cylinder (6370 cm^3) Mercedes-Benz engine OM 906 LA with turbocharger and intercooler. The engine has a rated power of 205 kW and a maximum torque of 1100 Nm at 1300 min^{-1}. It is certified to the Euro III exhaust gas standard.
Exact engine load during test runs was accomplished by crank shaft coupling to a Froude Consine eddy-current brake. Engine test runs were in accordance with the guideline 2005/55/EG of the European Union in the European Stationary Cycle (ESC). This cycle starts with 4 minutes of idle, followed by 12 modes of 2 minutes duration.
Sampling of the limited compounds and particle size distribution was achieved during the last minute of each mode. In contrast, the sampling material to determine PAH emissions and mutagenic effects was started after two minutes and was running continuously with a constant volume flow of 25 l/min till the end of the ESC cycle after 28 minutes. Due to this sampling procedure, also transient parts of the test were sampled and the weighting of the modes was moved to idle and light load modes.

Fuels

Diesel fuel and 5 fatty acid methyl ethers were used. The reference DF corresponded to the fuel standard DIN EN 590. The methyl esters originated from coconut oil, palm oil, rapeseed

oil, soy bean oil, and linseed oil. They differed in the iodine number and the cold filter plugging point. The iodine number ranged from 26 g iodine/100 g for coconut oil methyl ester to 175 g iodine/100 g for linseed oil methyl ester. The rage of the CFPP was from +1 °C (PME) to -17 °C (RME). The predominant chain length of the fatty acids was C18 for RME, SME, and LME. PME had a high amount of C16 chains, CME of C12.

RME met the DIN EN 14214 for biodiesel. CME had a lower viscosity (2.86 mm^2/s) and a higher sulphur content (21 ppm) than required by the norm. Also the acid number of CME and PME (0.56 and 0.79 mg KOH/g) exceeded the limit of the norm. The iodine number of SME (129 g idine/100 g) and LME (175 g iodine/100 g) and the oxidation stability of these esters didn't meet the norm, too.

Analytical Methods

Hydrocarbons (HC) were determined with a gas analyzer RS 55-T (Ratfisch, Poing, Germany), (FID). Carbon monoxide (CO) was measured by means of an analyzer BA 5000 (Bühler, Reute, Germany). Nitrogen oxides (NO_x) were analyzed with a CLD 700 EL ht chemical luminescence detector (Eco Physics, Munich, Germany).

Particulate matter (PM) was measured by use of a part-stream dilution tunnel. A dilution factor of about 10 was applied for determination. Dilution factors were 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.

For the determination of mutagenic effects and PAH, particulate matter was collected from the undiluted exhaust stream onto a glass fiber filter coated with PTFE (Teflon) (T60 A20, Pallflex Products Corp., Putnam, CT, USA). According to VDI-guideline 3872 part 1 the exhaust gas phase was cooled using an intensive cooler (Schott, Mainz, Germany) and condensates were collected separately. Further condensed compounds were desorbed from the cooler with 100 ml methanol and added to the condensates.

Each fuel was tested three times. The filters were conditioned (22 °C, rel. humidity 45%), weighed before and after sampling to determine the total particulate matter, and stored at -18 °C.

To determine the mutagenicity, extraction of the soluble organic fraction (SOF) from the filters was performed with 150 ml dichloromethane in a Soxhlet apparatus (Brand, Wertheim, Germany) for 12 h in the dark (cycle time 20 min). The extracts as well as the condensates were concentrated by rotary evaporation and dried under a stream of nitrogen. They were redissolved in 4 ml dimethyl sulfoxide immediately before use.

Filters and condensates of PAH samples were extracted with toluene. The amount of PAH in the extracts was determined with HPLC after enrichment with donor-acceptor complex chromatography (DACC) [1].

Results

The carbon monoxide and hydrocarbon emissions of the tested methyl esters show advantages over DF. While the carbon monoxide emissions of the tested methyl esters show no differences, the hydrocarbon emissions of CME shows the highest value, LME and RME lowest emissions. This result corresponds to the chain length of the fatty acid methyl esters. The particle mass emissions of methyl esters were likewise lower than those of DF. Linseed oil methyl ester showed the highest particle mass emissions of the methyl esters (figure 1).

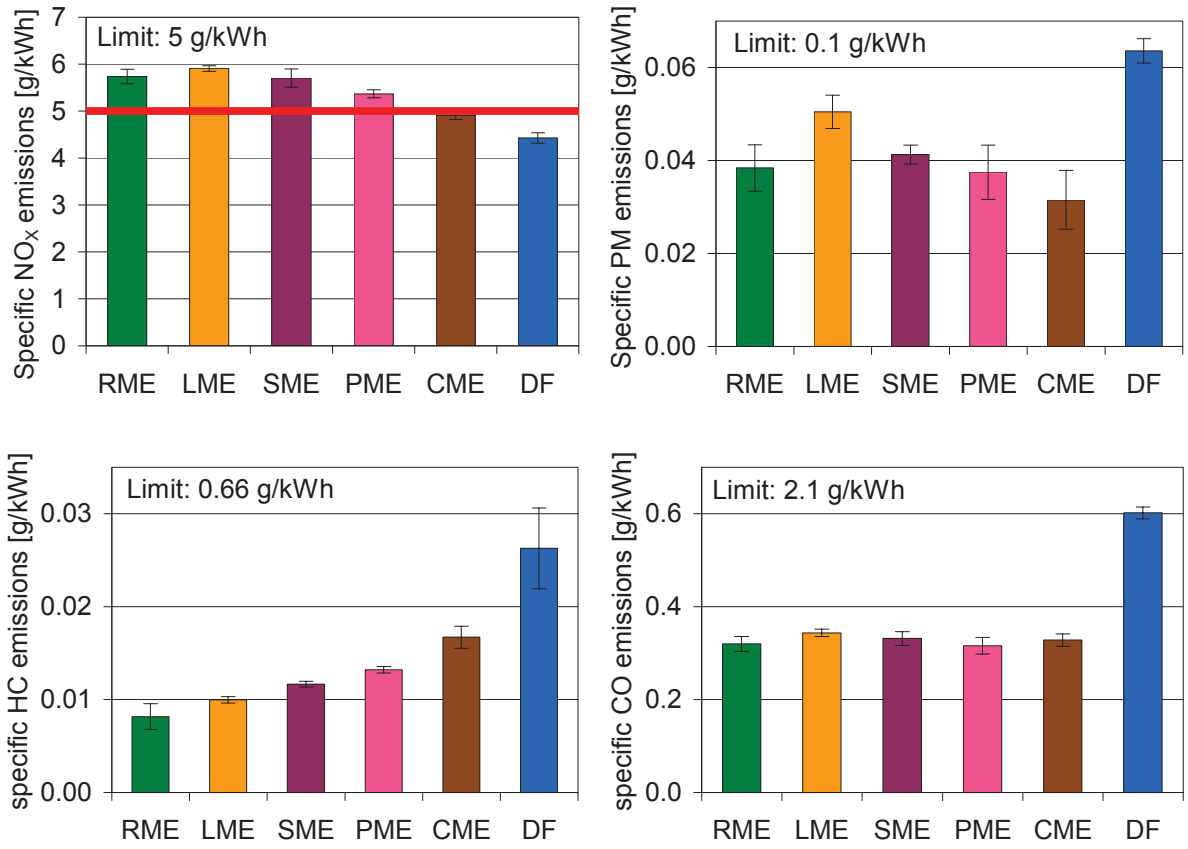

Fig. 1: Regulated emissions of the Mercedes OM 906 engine and Euro III limits, ESC test .

The emissions of nitrogen oxides increased using FAME instead of diesel fuel. With exception of coconut oil methyl ester, all other methyl esters exceeded the Euro III limit of 5 g/kWh. Linseed oil methyl ester showed the highest emissions. For coconut oil methyl ester and palm oil methyl ester the increase was more moderate (figure 1).

To test the mutagenic potential of the fuels, two Ames-tests were performed. As the biological fitness of the Salmonella bacteria can differ from test to test, in both tests diesel fuel was used as reference. In the first test RME, SME, PME, and CME were compared to diesel fuel. All methyl esters of the first test showed a lower mutagenic response than diesel fuel. Coconut oil methyl ester had the lowest mutagenicity of the esters. In the second test LME and diesel fuel were tested. In this test the mutagenic effect of LME exceeded the effect of diesel fuel by 80% (figure 2).

The sampling of PAH was identical to those of mutagenicity. Diesel fuel emitted more than five times more PAH than the methyl esters. From the methyl esters SME emitted most PAH. RME and LME emitted two-thirds, PME and CME only one-third of the PAH amount from SME. If PAH with four or more rings were considered, LME had the highest emissions. These emissions decreased sequentially for SME, RME, PME, and CME. This series corresponds nicely to the iodine number (figure 3).

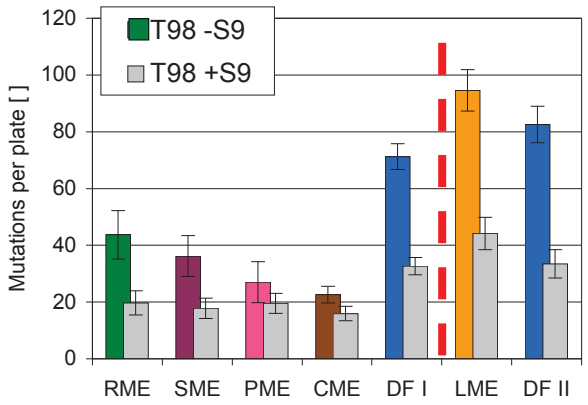

Fig. 2: Means and standard deviations of triplicate mutagenicity tests of DF and methyl esters using tester strain TA98 with (+S9) and without (-S9) metabolic activation by rat liver enzymes, OM 906, ESC.

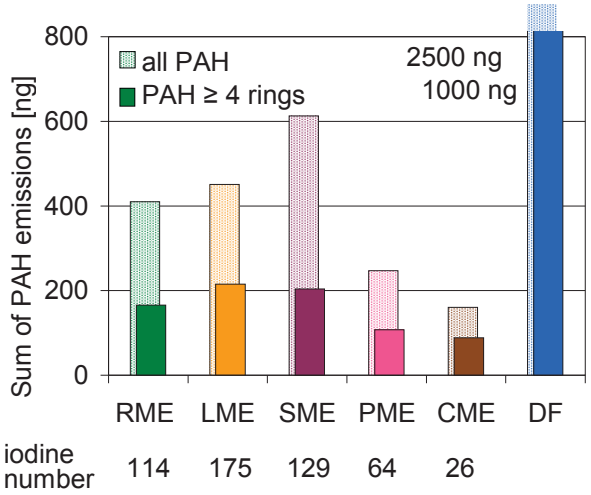

Fig. 3: Sum of all PAH emissions and PAH with four or more rings of DF and methyl esters, OM 906, ESC and iodine number of the methyl esters.

If fatty acid methyl esters were blended to diesel fuel, most of the emissions of the blend changed linearly with the ester content. However, some emissions showed a non-linear trend. It was found that RME blended to diesel fuel had a maximum of the mutagenic effect at 20% RME [2]. This effect was not found by blending SME to diesel fuel (figure 4). Using PME, a maximum of mutagenicity was found at 10% of methyl ester (figure 5). These effects may originate from the formation of fatty acid oligomers and the solubility of those oligomers in the blend [3].

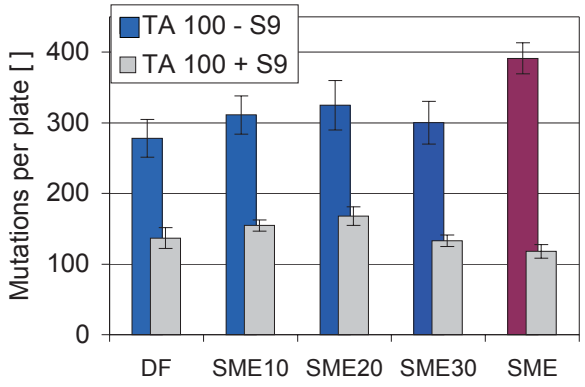

Fig. 4: Means and standard deviations of triplicate mutagenicity tests of 10%, 20%, and 30% blends of SME using tester strain TA100 with (+S9) and without (-S9) metabolic activation by rat liver enzymes, OM 906, ESC.

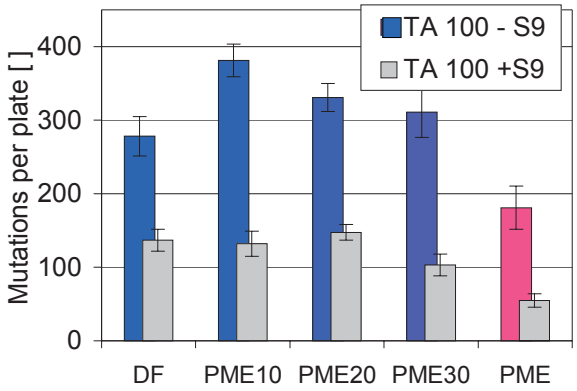

Fig. 5: Means and standard deviations of triplicate mutagenicity tests of 10%, 20%, and 30% blends of PME using tester strain TA100 with (+S9) and without (-S9) metabolic activation by rat liver enzymes, OM 906, ESC.

[1] Munack, A., Pabst, C., Ruschel, Y.,Schaak, J., Schmidt, L., Schröder, O., Bünger, J., Krahl, J.: Untersuchung von nicht limitierten Emissionen eines Nutzfahrzeugmotors mit verschiedenen Biodieselblends. Final Report, Johann Heinrich von Thünen-Institut (vTI), Braunschweig, 2011, 114 p

[2] Krahl, J., Munack, A., Ruschel, Y., Schröder, O., Bünger, J.: Gas Emissions and Mutagenic Effects of Diesel Fuel, Biodiesel and Biodiesel Blends. SAE Paper 2008-01-2508, 2008

[3] Fang, H.L,, McCormick, R.L.: Spectroscopic Study of Biodiesel Degradation Pathways. SAE Technical Paper 2006-01-3300, 2006