Emissions from diesel engines using fatty acid methyl esters from different vegetable oils as blends and pure fuel

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Abstract. Biodiesel is used as a neat fuel as well as in blends with mineral diesel fuel. 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. To investigate the environmental impact of the exhaust gas, it is necessary to determine regulated and non-regulated exhaust gas components. In detail, emissions of aldehydes and polycyclic aromatic hydrocarbons (PAH), as well as mutagenicity in the Ames test are of special interest. 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 and reference diesel fuel were used as well as blends of the vegetable oil methyl esters with diesel fuel. PAH were sampled according to VDI Guideline 3872. The sampling procedure of carbonyls was accomplished using DNPH cartridges coupled with potassium iodide cartridges. 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, only linseed oil methyl ester showed higher particle mass emissions. 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.

1. Introduction
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. In 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 determine next to the regulated exhaust gas components (nitrogen oxides, particulate matter, carbon monoxide and hydrocarbons) further non-regulated components. In detail, emissions of aldehydes and polycyclic aromatic hydrocarbons (PAH), as well as mutagenicity in the Ames test are of special interest. These emissions can not be derived from the regulated components.

2. Materials and Methods

2.1. 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 cm³) 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 each. Figure 1 shows the courses of speed and torque of the ESC test.

![Figure 1. Speed and torque during the 13-mode ESC test.](image)

Sampling of the limited compounds, aldehydes, and particle size distribution was achieved during the last minute of each mode of the ESC test. In contrast, the sampling of the 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 (figure 1).
2.2. Fuels

Diesel fuel and 5 fatty acid methyl esters (FAME) were used. Their physicochemical properties are listed in table 1. 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 mm²/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 iodine/100 g) and LME (175 g iodine/100 g) and the oxidation stability of these esters didn’t meet the norm, too.

Table 1. Physico-chemical properties of the fuels.

|                         | Limits | RME | LME | SME | PME | CME | DF |
|-------------------------|--------|-----|-----|-----|-----|-----|-----|
| Density (15°C) [g/L]    | min.   | 875 | 890.6 | 886.4 | 876.6 | 872.9 | 820 | 845 | 833.8 |
|                         | max.   | 900 | 883 | 890.6 | 886.4 | 876.6 | 872.9 | 845 | 833.8 |
| Kin. viscosity (40°C) [mm²/s] |       | 3.5 | 4.42 | 3.78 | 4.297 | 4.678 | 2.86 | 4.5 | 3.20 |
| Flashpoint [°C]         |        | 120 | 176 | 186.5 | 168 | 162 | 124 | 55 | 75 |
| C.F.P.P. [°C]           |        | -0/-10/-20 | -21 | -8 | -7 | +1 | -10 | -0/-10/-20 | -27 |
| Total sulphur [mg/kg]   | -      | 10.0 | 1.5 | 1.1 | 1.7 | <1 | 21 | - | 10 <1 |
| Ash content [w/w %]     | -      | 0.02 | <0.001 | <0.01 | <0.01 | <0.01 | <0.01 | 0.01 | 0.001 |
| Carbon residue [w/w %]  | -      | 0.3 | 0.06 | 0.05 | 0.19 | 0.15 | <0.01 | - | 0.30 | 0.01 |
| Cetane number [-]       |        | 51 | 51.3 | 48.8 | 51.1 | 65.9 | 59.9 | 49 | 53.2 |
| Water content [mg/kg]   | -      | 500 | 146 | 126 | 521 | 420 | 298 | - | 200 | 20 |
| Copper corrosion [-]    | -      | 1 | 1 | 1 | 1 | 1 | 1 | - | 1 | 1 |
| Acid number [mg KOH/g]  | -      | 0.5 | 0.04 | 0.066 | 0.135 | 0.793 | 0.557 | - | - |
| Iodine number [g/100 g] |        | 120 | 114 | 175 | 129 | 64 | 26 | - | - |
| Polycyclics [w/w %]     | -      | - | - | - | - | - | 4.3 | - | 4.4 |

2.3. Analytical Methods for Exhaust Gas Components

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 (NOₓ) 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 CO₂ 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 MSP (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) (T60A20, 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].

2.4. Determination of aldehydes
To determine aldehydes from exhaust gas the DNPH method was used. In this method 2,4-dinitrophenylhydrazine reacts with the aldehydes to the corresponding hydrazones (1). These hydrazones were detected and quantified by HPLC[3].

\[
\begin{align*}
\text{R}_1\text{C} = \text{O} + \text{HNNNO}_2 \xrightarrow{\text{H}^+} \text{R}_1\text{C} = \text{N} = \text{N}\text{NO}_2 + \text{H}_2\text{O} \\
\text{R}_1 \text{ and R}_2 = \text{H or hydrocarbon chain}
\end{align*}
\] (1)

For sampling the aldehydes DNPH-Silica cartridges (Waters, Milford, USA) were used. These cartridges consist of silica coated, acidified DNPH (particle size between 0.5 to 1.0 mm). A sample flow of 0.5 L/min of raw exhaust gas was led over the cartridges, after cooling the exhaust gas to approximately 60 °C. The sampling time at the end of each load mode of the ESC test was calculated from flow rate of the exhaust gas and the weighting factor of each load mode.

After the test, the cartridges were washed with acetonitrile in a 2 mL volumetric flask. The flow rate was lower than 3 mL/min.

In first tests all DNPH was consumed and only a small amount of hydrazones was detectable by HPLC. The reason for the loss can be the reaction of nitrogen dioxide with DNPH [2]. This reaction can also be used to detect the nitrogen dioxide concentration in the exhaust gas quantitatively[4]. At too high concentration of nitrogen oxide in a DNPH solution, however, the freshly formed hydrazones can decompose. To avoid this undesired reaction, a potassium iodide cartridge was placed before the DNPH cartridge. So the nitrogen dioxide is reduced by potassium iodide and cannot interfere with DNPH or hydrazones anymore.

A closer look at different sampling times at constant engine load indicates that the loss of DNPH is primarily responsible for the low aldehyde values (figure 2). With DNPH overshoot nitrogen dioxides from the exhaust gas react with DNPH first. If all DNPH is spent, freshly formed hydrazones react with nitrogen dioxide. At 1.5 and 5 minutes DNPH is still available. The concentrations of formaldehyde and acetaldehyde are comparable with and without KI cartridge - even at 5 minutes, when all DNPH is nearly consumed. At 15 minutes all DNPH is consumed without KI cartridge. The
significant impact of the KI cartridge becomes clear: With KI cartridge formaldehyde shows a constant increase. However, at the end the acetaldehyde gradient was lower than expected.

![Graph](image.png)

**Figure 2.** Relative DNPH concentration (upper part) and relative formaldehyde and acetaldehyde concentrations (lower part) with and without KI cartridge at different sampling times.

### 3. 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 3).

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 3).
Figure 3. Regulated emissions of the Mercedes OM 906 engine and Euro III limits, ESC test.

Figure 4. 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.

Figure 5. 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.

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 4).

The sampling of PAH was identical to that one applied for sampling for mutagenicity testing. 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 5).

Aldehyde emissions of diesel fuel, linseed oil methyl ester and rape seed oil methyl ester are presented in figure 6. Formaldehyde and acetaldehyde contribute 85% to the total aldehyde emissions. Only acetaldehyde, butyraldehyde, and benzaldehyde were less emitted using methyl esters. But due to the high impact of formaldehyde to total emissions no advantage for any of the biofuels was found. Discordant results were reported by several authors[5],[6],[7], who found an increase of aldehydes emissions using fatty acid methyl esters. On the other hand, Sharp et al.[8] found a substantial reduction in aldehyde emissions with SME.

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[9]. This effect was not found by blending SME to diesel fuel (figure 7). Only a small non significant local maximum was detected at 20% SME. In this test the exhaust from pure SME showed the highest mutagenic potential. Using PME, a maximum of mutagenicity was found at 10% of methyl ester (figure 8). A maximum of PAH emissions was found for a 10% blend with PME by Lin at al.[10], too.

Fang and McCormick[11] found a maximum of deposits in 20% blends that could be oligomers from biodiesel. These deposits can be re-dissolved in blends with a higher percentage of biodiesel. It can be assumed that these biodiesel oligomers may have a higher boiling point than biodiesel or may even boil under decomposition like neat vegetable oil. According to the hypotheses regarding the high
mutagenicity of neat vegetable oil\cite{12}, possibly B20 exhaust could be more mutagenic because of a maximum of insoluble oligomer formation leading to a maximum of pyrolysis products in the exhaust.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure7.png}
\caption{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.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure8.png}
\caption{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.}
\end{figure}

4. Conclusion
Regulated and non regulated emissions of a Euro III diesel engine OM 906 were measured. 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 versus DF. The particle mass emissions of methyl esters were likewise lower than those of DF, only linseed oil methyl ester showed higher particle mass emissions. A disadvantage of all tested biodiesel fuels was the increase of nitrogen oxides. This varied depending on the methyl ester from 10\% to 30\%.

Aldehyde emissions were tested for rapeseed oil methyl ester, linseed oil methyl ester, and diesel fuel. To optimize the analytical procedure and to avoid measuring errors, potassium iodide cartridges were used during the sampling to suppress the side reaction from nitrogen oxides. The aldehyde emissions didn’t vary significantly between all fuels.

The Ames tests showed the lowest mutagenicity for palm oil methyl ester next to coconut oil methyl ester. The low numbers of double bounds, which are indicated by the low iodine numbers of these esters, seem to be responsible for this result.

For blends of biodiesel and diesel fuel, emissions changed linearly with the biodiesel percentage. However, especially for non-regulated emissions, some deviations from this linear trend were detected. For PME blends a maximum of mutagenicity in the range of B10 was observed.

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