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Comparison of Relevant Exhaust Gas Emissions from Biodiesel and Fossil Diesel Fuel

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Abstract
Fossil diesel fuel and rape seed oil methylester are compared with regard to exhaust gas emissions and effects of these emissions on human health and the environment. Tests were carried out using an agricultural tractor and a test engine. The aspects treated are: use of blends, particle sizes, mutagenic potency of the particulate matter, and ozone precursors. Whereas slight disadvantages of biodiesel were found concerning NO_X and ozone precursors, a significant soot reduction was observed that is connected with a lower mutagenic potency of the particulate matter.

Keywords
Diesel fuel, Biodiesel, Blends, RME, Emissions, Particle size, Mutagenicity, Ozone precursors

1. Introduction

Biodiesel, in Germany mainly rape seed oil methylester (RME), has been considered as alternative fuel that can be used in many conventional diesel engines. However, even the combustion of green fuels leads to the emission of gaseous hazardous compounds and particulate matter that may effect human health.

In particular, diesel engine exhaust (DEE) has been classified carcinogenic to experimental animals and as a probable carcinogenic agent to humans by the International Agency for Research on Cancer (1989). Several studies reported a relative risk of approximately 1.5 for lung cancer by DEE after a long-term exposure, cf. Mauderly (1994). The carcinogenic effect of diesel exhaust exposure is mainly ascribed to the inhalation of soot particles, as Scheepers and Bos (1992) reported. Huisingh et al. (1978) pointed out, that many known or suspected mutagens and carcinogens, e. g. polycyclic aromatic compounds (PAC), are adsorbed onto the surfaces of carbon cores of DEE particulate matter as organic phase. Due to their median dynamic diameter of 0.1 to 0.3µm the particles are readily inhaled and about 10% are deposited in the alveolar region of the lung, cf. Scheepers and Bos (1992).

Therefore one focus of interest was the comparison of the particulate matter emissions from fossil diesel fuel (DF) to those from biodiesel not only with regard to the overall emitted masses, but also to particle masses and particle numbers in different size fractions. In order to estimate the physiological effects of DF and RME particulate matters, their mutagenic potencies were determined.

Moreover it was studied, in which degree biodiesel exhaust gases influence the tropospheric ozone formation relative to DF.

2. Experimental

All investigations were carried out using an agricultural tractor and a test engine.

2.1 Analytical equipment

All *gaseous regulated compounds* were taken directly from the undiluted exhaust gas stream and were measured using customary analyzers. The *particulate matter* was sampled from a doubly isokinetic dilution tunnel and collected on PTFE coated glass fiber filters. Organically soluble matter was determined by heating the filters for 24 hours at 220°C. Tests revealed that this method gives comparable results to six hours soxhlet extraction with dichloromethane. *Aldehydes* were quantified by the 2,4-dinitrophenyle (DNPH) derivatisation method with HPLC detection. For this an exhaust gas sample was led through a set of impingers filled with acetonitrile/DNPH solution. *Alkenes and alkynes* were determined by GC/MS with deep temperature enrichment. *Methane and nitrous oxide* were measured by high resolution FTIR with a long path gas cell. Analyses of spectra were performed by fitting sets of calibration spectra. Besides methane and nitrous oxide, *nitrogen oxide* and *nitrogen dioxide* were determined, too. The results of NO_x determination by FTIR agree with those of the chemiluminescence detector. *Benzene* was determined by GC with a flame ionization detector (FID). For the *particulate matter* analyses a Scanning Mobility Particle Sizer (SMPS) model 3934 with a Condensation Particle Counter (CPC) Model 3010 from TSI Company was used; details about the underlying on-line measuring principles can be found in the article by Bischof and Horn (1999). The SMPS system separates particles in a range from 7 to 300 nm. Over this range particles were divided in more than 100 different sizes by electrostatic mobility.

2.2 Engines

As test engine a Farymann engine type 18 D, an air cooled 4.2 kW one cylinder four-stroke diesel engine with direct injection, was chosen. This engine can be handled and controlled easily. All tests were carried out with and without oxidation catalytic converter. Because of the advantages of the convenient Farymann engine, it was chosen for the extended serial investigations with different blends. Additionally a Fendt tractor type 306 LSA with direct injection 52 kW, four cylinder diesel engine (type MWM D 226.4.2) was tested. It was equipped with a special oxidation catalytic converter for biodiesel (Oberland Mangold, Germany). The tractor was used for the investigation of ozone precursors and particulate matter emissions.

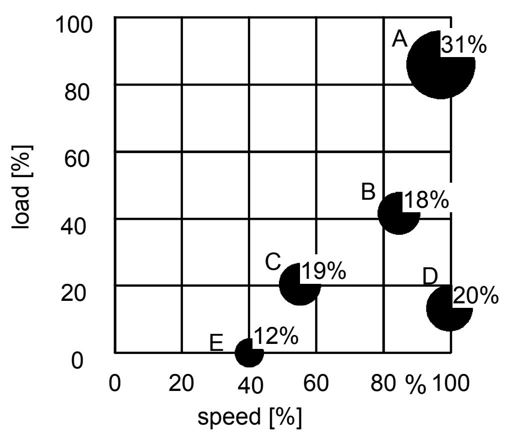

Figure 1: Modes of the agricultural 5-mode test

2.3 Engine test procedures

As engine test procedure, the German agricultural 5-mode test was chosen. This cycle has no legislative foundation, but simulates the typical load of agricultural tractors in Germany, as evaluated by Welschof (1981), see fig. 1.

2.4 Fuels

RME was delivered by Oelmühle Leer Connemann Company, Leer, Germany, and 370 ppm sulfur DF by German Shell, Hamburg, Germany. In Germany biodiesel has to meet the standard DIN E 51606.

3. Results and discussion

3.1 Blends from RME and DF

Since non-fleet vehicles are often alternately fueled with RME or DF, the regulated and some important non-regulated exhaust gas compounds (e.g. benzene and aldehydes) were determined using different blends from both fuels. It was the goal to detect any positive or negative disproportionate effects depending on special blends.

Concerning the *gaseous regulated compounds*, the following results were obtained: Without a catalytic converter a decline in HC is observed with increasing RME percentage. In contrast CO emissions increase. The catalytic converter reduces the emissions of hydrocarbons as well as the emissions of carbon monoxide. The efficiency of the catalytic converter depends on the blend; in contrast to the above mentioned increase of CO with increasing content of RME, by use of the catalytic converter a slight decrease is observed. The results are shown in fig. 2a.

With and without catalytic converter the *particulate matter* (PM) increases nonlinearly with the RME percentage. However, this nonlinearity appears only in mode C, whereas all other modes show a linear dependency. Details are reported by Schröder et al. (1998). As expected, due to the well known reduction of soot by RME - Krahl et al. (1996b) -, the organically insoluble matter decreases with higher percentage of RME. This effect is linear with the blend.

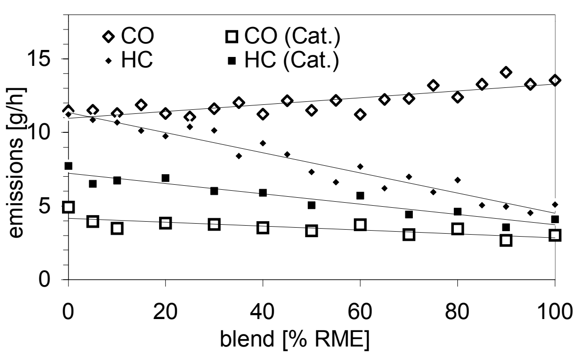

Figure 2a: Regulated compounds HC and CO; Farymann test engine with and without catalytic converter, 5-mode test

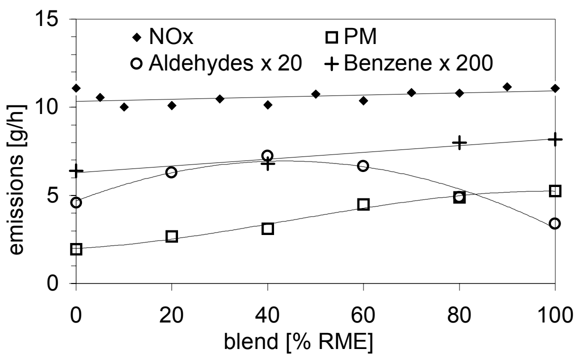

Figure 2b: NO_X, PM, aldehydes, and benzene; Farymann test engine with catalytic converter, 5-mode test

Concerning the emissions of NO_x, there is almost no influence of the catalytic converter. The emissions slightly increase with increasing RME content. There is no difference in *nitrous oxide* emissions relative to the fuel. However, the catalytic converter leads, summed up over the whole test cycle, to a duplication of the emissions.

This Farymann engine shows a nonlinear dependency of *aldehydes* emissions with the blend. A maximum can be observed at 40% of RME. In case of this test engine RME leads to less emissions than DF. This does not correlate with usually found results. In the average of published investigations RME leads to an increase of the aldehydes' emissions versus DF to approximately 120 %, cf. Krahl et al. (1996b). Also the Fendt tractor emits more aldehydes running on RME than on DF (fig. 5a). More research is needed to explain why this Farymann engine exhibits such a positive tendency for RME. Without the catalytic converter the emissions are 2- to 4-fold higher, whereby a nonlinear trend is observed with a slight minimum at 50% (not shown).

Benzene emissions increase with the percentage of RME, although in contrast to diesel fuel RME does not contain any benzene. This indicates that the benzene content of fuels is not necessarily the main source for benzene in exhaust gas emissions. The catalytic converter reduces the emission by one third.

The above addressed results concerning non-regulated compounds after catalytic conversion of the exhaust gas are shown in detail in fig. 2b (observe the different scales for aldehydes and benzene!). Summing up, no optimal blend was found for the measured compounds. The well known advantages and disadvantages of RME change mainly linearly with the blend. Only particulate matter and aldehydes show nonlinear trends. The dependency of the catalytic conversion ratio on blends indicates that the adaptation of fuels (blends) to the exhaust gas treatment may be a useful way to reduce emissions. In all, no specific blend can be recommended to minimize emissions. On the other hand there exists no blend with distinct negative effects on the exhaust gas composition.

3.2 Particle size distributions

Up to the present time particulate matter (PM) mass has been the regulated value. Recently, particle size distributions, showing particle *masses* or particle *numbers* in different size fractions have been recognized as more important than the overall mass. These distributions will be referenced as particle *mass* distribution (PMD) or particle *number* distribution (PND), respectively. Small particles reach pulmonary alveoli and are deposited there, while larger particles are deposited in the upper airways and eliminated by the ciliated epithelium of the airways. Especially ultrafine particles (< 100 nm) are considered as critical to human health (Heinrich, 1998). Therefore, an

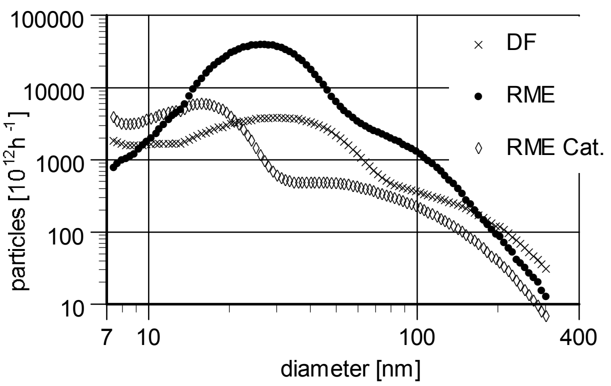

Figure 3: Particle number distribution (PND) of RME, DF, and RME with catalytic converter; Fendt tractor, 5-mode test

SMPS system was used to measure the PND. Experiments were carried out on the Fendt tractor.

In fig. 3 the particle number distribution in dependence of the particle size for RME, DF and RME with catalytic converter is presented as weighted result of the 5-mode test. The maximum of the PND is at 30 nm for diesel fuel. A shift to slightly smaller particle sizes is observed for RME (maximum at 27 nm). Moreover, the particle number for RME is higher in the whole range. The catalytic converter reduces the particle number and the maximum of the PND (maximum at 16 nm).

Besides the weighted result of the 5-mode test, also each single mode was considered separately. In modes A and E (not shown) the shapes of the particle number distributions are comparable; however, in mode E much more particles are emitted. The absolute particle numbers of RME and DF are similar in mode A, whereas RME emits more particles than DF in mode E. The catalytic converter reduces the particle numbers in both modes. The maxima are at 100 nm (mode A, DF and RME), 65 nm (mode A, RME with catalytic converter), and 40 nm (mode E). The catalytic converter leads to a shift to smaller particles, which is more distinct in modes B, C, D. This indicates that the small to medium size particles may be liquid, most probably unburned fuel that is easily eliminated or – at least – reduced in size by the catalytic converter. In contrast, the larger particles may have a solid core that cannot be oxidized. These theoretical considerations match with results of measurements by Schröder et al. (1999) with an impactor, were the smaller particles were eliminated well by the catalytic converter. Impactors measure the PMD; a reliable correlation between PMD and PND has not been obtained yet.

3.3 Mutagenic effects of particulate matter

For evaluation of pollutants, biological effects are the basic value. Therefore diesel engine exhausts from RME and DF were tested on mutagenic activity. Organic extracts of filter collected particulate from DEE act as mutagens in bacterial and mammalian in vitro assays. Most investigations were performed using the Salmonella typhimurium/mammalian microsome assay developed by Ames et al. (1975).

This test detects mutagenic properties of a wide spectrum of chemicals by reverse mutations of a series of Salmonella typhimurium tester strains, bearing mutations in the histidine operon. This results in a histidine requirement of the tester strains in contrast to wild-type Salmonella typhimurium. The Ames test is worldwide the most frequently used test system to investigate mutagenicity of complex mixtures like combustion products. According to the criteria given by Ames et al. (1975), results were considered positive if the number of revertants on the plates containing the test concentrations was double the spontaneous reversion rate and a reproducible dose/response relationship was observed. The analytical procedure was investigated more extensively by Krahl et al. (1999). For the investigations the Farymann test engine was chosen.

The collected masses of particulate matter differed widely depending on the engine loads and the fuels. In most tests the collected masses from RME exhaust were higher than from DF. Higher percentages of the sampled masses were organically extractable from the filters for RME than from those used for DF. It seems likely that this observation is due to a smaller content of soot in biodiesel exhausts, as shown before in Krahl et al. (1996a) and (1996b).

In the tester strain TA98 a significant increase of spontaneous mutations was obtained for both fuels. However, for DF the revertant frequencies were 2- to 8-fold higher compared to RME (fig. 4). Revertant frequency was also significantly elevated in the tester strain TA100 and the mutations using DF were 2- to 3-fold higher than for RME. Testing with activated liver S9-fraction slightly decreased the number of revertants in most experiments.

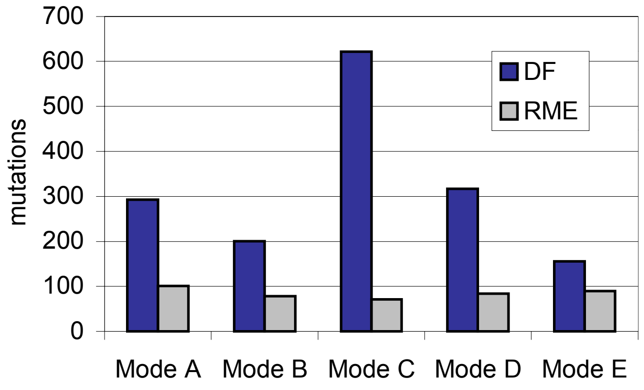

Figure 4: Number of mutations per plate from extracts of RME exhaust particles on tester strain TA98 compared to DF in the (number of spontaneous mutations = 32 per plate); Farymann test engine, 5-mode test

These results indicate a lower mutagenic potency of PM from RME compared to DF. This is probably due to the lower content of PAH and soot in the exhaust, although the emitted masses from RME are higher at most load modes. Testing with activated rat liver enzymes led to a slight detoxification of the extracts.

3.4 Ozone precursors

In summer ozone becomes one of the most important air pollutants. Especially in urban areas traffic contributes to ozone formation, because the photochemical reaction of exhaust gas compounds like volatile organic compounds (VOC) leads in presence of nitrogen oxides and sunlight to ozone.

As seen above, hydrocarbons are reduced by the use of RME whereas nitrogen oxides and, in the majority of cases, aldehydes increase. These contrary tendencies do not allow a theoretical comparison of the ozone forming potencies of RME and DF, cf. Krahl et al. (1996c). Therefore it was an important task to compare the emissions of ozone precursors in the exhaust gases of both fuels.

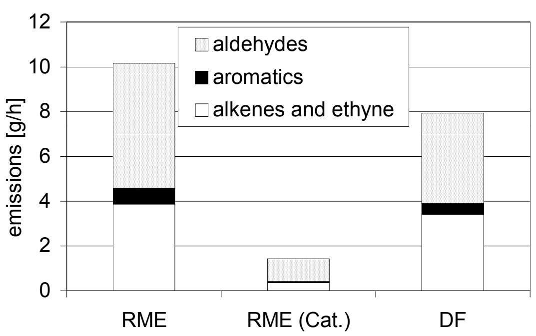

Figure 5a: Emissions of ozone precursors; Fendt tractor; 5-mode test

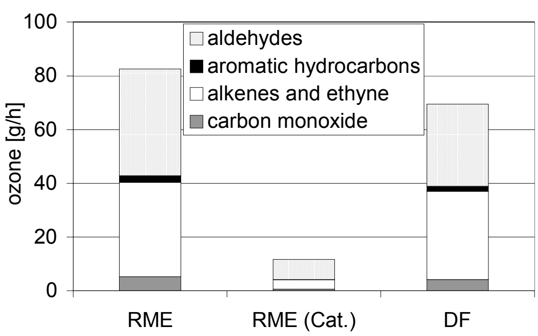

Figure 5b: Calculated ozone forming potentials; Fendt tractor; 5-mode test

The used GC/MS system is able to detect hydrocarbons in concentrations of several magnitudes. The limit of detection is in the ppt range. A detailed description of the sampling procedures is given by Schröder et al. (1999). The total emissions of individual hydrocarbons are shown in fig. 5a. Due to the large number of compounds, aldehydes, aromatics, and alkenes including ethyne are shown as groups.

It was found that the compounds with few carbon atoms dominate the emissions and that DF exhaust contains less ethene and ethyne than RME exhaust. On the other hand DF leads to higher propene emissions. Currently no explanation is available for these observations. In the 5-mode test RME raises the emissions of ozone precursors by approximately 20 %. The catalytic converter reduces the emissions as expected. To estimate the ozone forming potential of the emissions the concept of the specific maximal incremental reactivity (MIR) of single compounds is useful. The MIR values were taken from Carter (2000). A comparison between emissions and their ozone forming potentials makes obvious that alkenes and aldehydes have the most relevant impact to ozone formation, while the aromatics have a lower percentage (fig. 5b). The MIR value of carbon monoxide (0.07 grams ozone per gram component) is over 100 times smaller than the MIR value of ethene (9.97 grams ozone per gram component) or formaldehyde (9.12 grams ozone per gram component). But due to the high emitted mass of CO, its ozone forming potential has to be taken into account, too.

4. Conclusions

It was the goal to compare fossil diesel fuel and rape seed oil methylester (RME) with regard to exhaust gas emissions and the effects of these emissions on human health and the environment. Tests were carried out using an agricultural tractor and a test engine. Several aspects were of special interest; these were: use of blends, particle numbers in dependence of size, mutagenic potency of the particulate matter, and ozone precursors.

Overall, RME leads to negative and positive effects that cannot be avoided or promoted by blends. On the one hand there seems to be a slight disadvantage due to NO_X and ozone precursors. On the other hand a significant soot reduction is obvious that is connected with a lower mutagenic potency of the particulate matter.

Future research on particle size distributions (where both particle masses and particle numbers in different size fractions are considered) may reveal additional effects of RME on human health and the environment that will help to use biodiesel more efficiently.

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