Comparison of biodiesel with different diesel fuels regarding exhaust gas emissions and health effects

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ABSTRACT

The more stringent regulations for diesel engine emissions lead to the requirement that both fuels and engines must be developed jointly. In the future, so-called designer fuels will help to achieve the stringent limits. In our research, conventional diesel fuel, biodiesel, Swedish low sulfur diesel fuel MK1 and a specially designed diesel fuel were compared using a DaimlerChrysler diesel engine, running the modes of the ECE-R 49 test cycle. The results for regulated and non-regulated gaseous emissions, particulate matter size distributions as well as mutagenic effects of particle extracts are reported.

INTRODUCTION

Two years ago, results of a study carried out at Chalmers University, Gothenburg, Sweden, were intensively discussed in the public. In this study (Pedersen et al., 1999) the authors – belonging to the group of Olsson – claimed that they had found up to tenfold higher emission rates of benzene and ozone precursors when using biodiesel (rapeseed oil methylester) compared to Swedish diesel fuel MK1.
The experiments were carried out in a very small reactor that was heated to 550 °C and fed with a constant air stream into which the fuels were injected. The exhaust gas analysis was carried out by GC/MS. In their conclusion, the authors stated that "Hitherto, the disadvantages of renewable products have been neglected in research and development. The advantages of renewable products are advocated strongly by their proponents urging for a quick and subsidized market introduction." (Pedersen et al., 1999).
Many researchers in Europe and the U.S. were skeptical concerning a transfer of the results obtained in this small reactor to the real combustion in a diesel engine. Needless to say the temperature, pressure, and droplet size are not comparable, which should result in different chemical reaction pathways. However, nowhere in the world experiments had been carried out with the aim to compare the emissions of biodiesel and Swedish diesel fuel MK1 from real diesel engine combustion.
This was the motivation to compare, in a dedicated research project, different fuels regarding their exhaust emissions from a modern DaimlerChrysler diesel engine. Since diesel engine particles are likely to pose a lung cancer hazard to humans (USEPA 2002), the determination of mutagenic potentials of particulate matter was carried out to estimate possible carcinogenic health effects.

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MATERIALS AND METHODS

FUELS

In order to evaluate the emissions on a broad basis, four different fuels were considered:

- Swedish low sulfur diesel fuel **MK1**, according to the Swedish standard SS 15 54 35, obtained from Saybolt Sweden AB, Gothenburg, Sweden,
- German biodiesel (rapeseed oil methylester; **RME**), according to German standard E DIN 51606, obtained from Oelmühle Leer Connemann GmbH & Co,
- fossil diesel fuel (**DF**) according to the European standard DIN EN 590, obtained from Louis Dreyfus & Cie Mineralöl GmbH, Hanover, Germany,
- a low sulfur diesel fuel with high aromatic compounds content and flatter boiling characteristics, according to the European standard DIN EN 590, obtained from Röling System Logistic Service GmbH, Buchholz, Germany. This diesel fuel is referred to as **DF05**.

Characteristics of the four fuels are compiled in Table 1.

Table 1. Characteristics of the four diesel fuels used in the experiments.

	MK1 according to SS 15 54 35	**MK1**	RME according to E DIN 51606	**RME**	DF according to DIN EN 590	**DF**	**DF05**
density (15°C) [g/L]	805-820	813.2	875-900	883	820-845	825.1	827.1
kin. viscosity (40°C) [mm_/s]	min. 1.7	1.902	3.5-5.0	4.5	2-4.5	2.373	2.233
flashpoint [°C]	min. 60	n.d.	min. 110	>150	> 55	62.5	73.0
C.F.P.P. [°C]	max. -32	<-37	max. -20	-20	max. -20	-27	-23
total sulfur [mg/kg]	max. 10	<5	max. 100	<10	max. 50	41	<10
carbon residue [w/w %]	max. 0.2	n.d.	max. 0.05	<0.05	max. 0.30	<0.05	0.17
cetane number [-]	-	n.d.	min. 49	>55	min. 51	53.6	65.1
water content [mg/kg]	-	n.d.	max. 300	180	max. 200	20	65
particulate content [mg/kg]	-	n.d.	max. 20	<20	max. 24	n.d.	6
copper corrosion [-]	max. 1	n.d.	max. 1	1	max. 1	1	1
acid number [mg KOH/g]	-	n.d.	max. 0.5	0.145	max. 0.5	<0.05	n.d.

n.d. = not detected

ENGINE AND OPERATING CONDITIONS

A modern DaimlerChrysler diesel engine, type OM 904 LA with turbocharger and charge-air cooling, was used as the test engine. This engine is normally installed in light-duty transport vehicles. Technical data of this engine are given in Table 2.
The test modes applied were chosen according to the ECE-R 49 test with 13 modes for load and number of revolutions, cf. figure 1.

Table 2. Technical data of the used engine Mercedes-Benz OM 904 LA.

Stroke of cylinder	130 mm
Bore of cylinder	102 mm
Number of cylinders	4
Stroke volume	4250 cm_
Normal rate of revolutions	2300 min^{-1}
Rated power	125 kW
Maximum torque	635 Nm at 1380 min^{-1}
Compression ratio	17.4

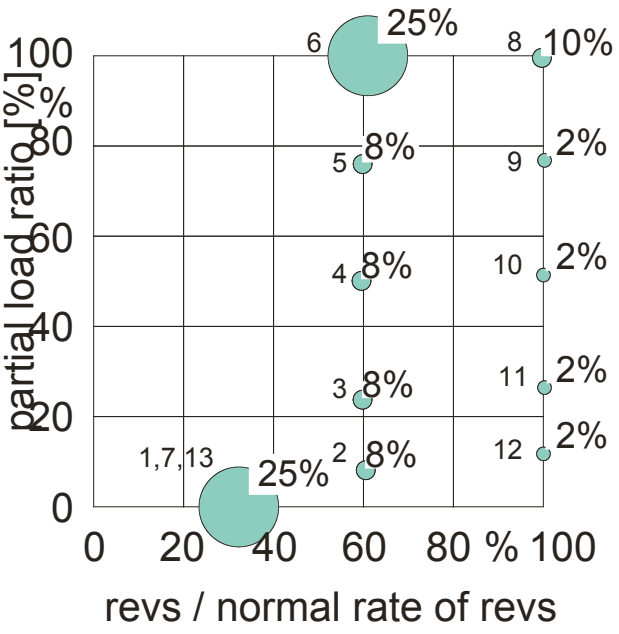

Figure 1. Operating points for the engine according to the ECE-R 49 13-mode test.

ANALYTICAL EQUIPMENT

Figure 2 shows that part of our emission test stand equipment that was used in the project. The equipment for measurement of the regulated exhaust gases consisted of:

- CO: Multor 710 (Maihak),
- HC: RS 55-T (Ratfisch),
- NO_X CLD 700 EL ht (Eco Physics),
- PM: Sampling is performed after passing a double iso-kinetic part steam dilution tunnel.
  PTFE coated glass fibre filters T60A20 (Pallflex Products Corp.) are used and weighed by μg-balance M5P (Sartorius).

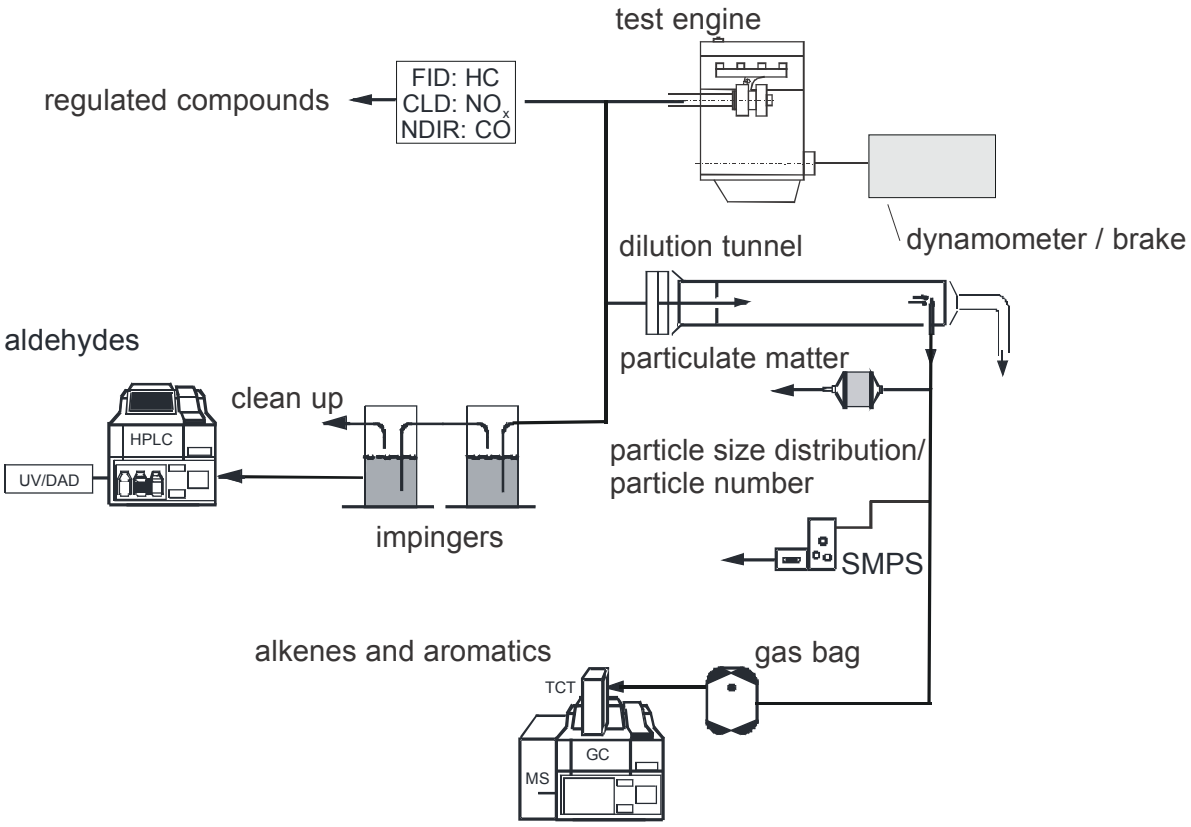

Figure 2. Schematic diagram of the used part of the emission test stand.

Furthermore, several other (non-regulated) exhaust gas components were analyzed:

- PM size distribution: Scanning mobility particle sizer (SMPS) type TSI (Bischof and Horn, 1999),
- Alkenes, alkynes and aromatics: GC/MS (Shimadzu Type GC 17A and QP 5000), equipped with a thermal desorption cold trap (TCT) type Chrompack CP 2040 (Krahl et al., 2001),
- Aldehydes and ketones: 2,4-dinitrophenylhydrazine (DNPH) method (Krahl et al., 1992) and HPLC type hp 1090 with UV-DAD.

MUTAGENICITY ASSAY

Particulate matter was collected on PTFE coated glass fiber filters (T60A20, Pallflex Products Corp., Putnam, CT, U.S.A.) from the dilution tunnel (Figure 2). The filters were conditioned (20°C, rel. humidity 50%) and weighed before and after the sampling procedure.

Three filters of each load mode and each fuel (in total 176 samples, including 44 reference filters) were cooled (<5°C) and transferred to the University of Göttingen, Germany. Every three analogous filters were extracted with 150 mL dichloromethane (Merck, Darmstadt, Germany) in a Soxhlet apparatus (Brand, Wertheim, Germany) for 12 h in the dark (cycle time 20 min). The extracts were reduced by rotary evaporation and dried under a stream of nitrogen. For the mutagenicity assay the extracts were redissolved in 4 mL dimethyl sulfoxide (DMSO).

The *Salmonella typhimurium* / mammalian microsome assay (Ames et al., 1975) 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 the most frequently used test system worldwide in order to investigate mutagenicity of complex mixtures like combustion products. This study employed the revised standard test protocol (Maron and Ames, 1983) with the tester strains TA98 and TA100.

Tests were performed with as well as without metabolic activation by microsomal mixed-function oxidase systems (S9 fraction). Preparation of the liver S9 fraction from male Wistar rats was carried out as described by Maron and Ames (1983). For induction of liver enzymes, phenobarbital and β-naphthoflavone (5,6-benzoflavone) were used instead of Arochlor-1254, which is a polychlorinated biphenyl mixture (PCB) and a carcinogen of great stability (Matsushima at al., 1976). The mutagens methyl methanesulfonate (MMS) and 2-aminofluorene (2-AF) were used as positive controls.

Immediately before use, the dried extracts were dissolved in 4mL DMSO, and the following dilutions were tested: 1.0, 0.5, 0.25, 0.125. The 2-AF was also dissolved in DMSO (100 µg/mL), and MMS was dissolved in distilled water (10 µg/mL). Every concentration was tested both, with and without 4 % S9 mix. Each extract was tested in duplicate. The tests were repeated during the following two weeks. The number of revertant colonies on the plates was recorded after 48 h of incubation in the dark at 37°C. The background bacterial lawn was regularly checked by microscopy, as high doses of the extracts proved toxic to the tester strains, resulting in a thinning out of the background. Counting was performed by the use of an electronically supported colony counting system (Cardinal, Perceptive Instruments, Haverhill, Great Britain). Results were considered positive, if the number of revertants on the plates containing the test concentrations was double the spontaneous reversion frequency and a reproducible dose-response relationship was observed.

RESULTS

The following figures summarize the weighted sums of measured specific emission rates for the modes of the 13-mode test. Detailed results for each of the modes can be found in the project report (Munack et al., 2003).

- CO; cf. Fig. 3: With all fuels, the emissions are clearly far below the legal limit of 4.0 g/kWh (Euro II) which is valid for the used engine. RME leads to a considerable decrease of CO emissions. This could partly be due to the oxygen in the ester bindings that allows more CO to be oxidized to CO_2.

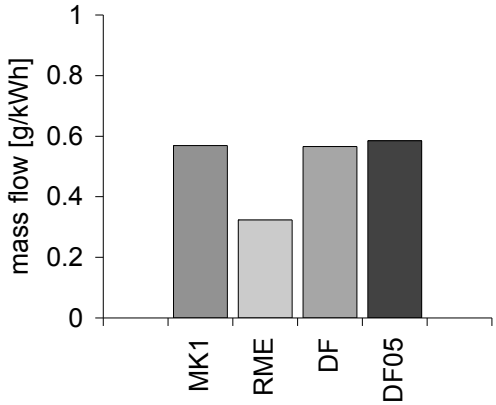

Figure 3. Specific CO emission rates.

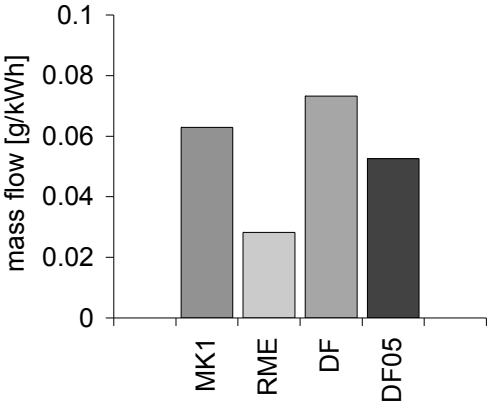

Figure 4. Specific HC emission rates.

- HC; cf. Fig. 4: Also for HC, the emission rates are far below the legal limit of 1.1 g/kWh. RME shows a significant decrease.
- NO_x; cf. Fig. 5: The emission rates lie below the legal limit of 7 g/kWh; however, they come quite close to it. This demonstrates that NO_x and, as shown below, PM are the critical components for diesel engines.
- As reported earlier in many publications, RME leads to an increase in NO_x emissions, if the engine management (timing and course of injection) isn't changed. However, it is possible to optimize diesel engines on RME by software means (Tschöke and Braungarten, 2002). A precondition for application of this strategy in practical use is a system for on-board fuel (blend) detection. Therefore, a biodiesel sensor was developed (Munack et al., 2002a/b).

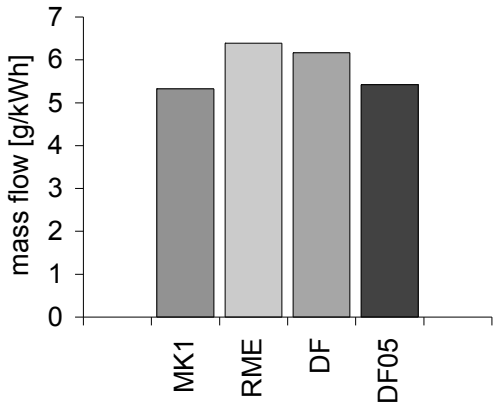

Figure 5. Specific NO_x emission rates.

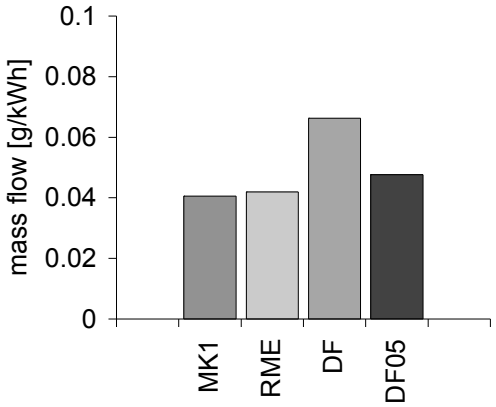

Figure 6. Specific PM emission rates.

- PM; cf. Fig. 6: The legal limit of 0.15 g/kWh is met by all four fuels. The non-conventional fuels lead to a reduction of 25 % to nearly 40 % compared to classical DF.
- Particle size distribution; cf. Fig. 7: Diesel engines are the source of a big part of the emissions of fine particles (diameter less than 2.5 μm) and are main sources of ultra-fine particles (diameter less than 0.1 μm). The ultra-fine particles are regarded as being toxicologically much more relevant, cf. Wichmann (2002). Main emissions from diesel engines, as far as the particle numbers are concerned, occur in the range of 10 nm to 300 nm. Therefore, this range was measured in our research. The four fuels cause quite different emissions. RME leads to more particles in the range of 10 to 40 nm compared to DF and less particles for the larger diameters. MK1 leads to a reduction over the whole measuring range. DF05 yields considerably higher numbers of particles over the whole measuring range. However, this must be different for higher diameters in the range which is not covered by the SMPS analyzer, since the overall emission is lower compared to diesel fuel.

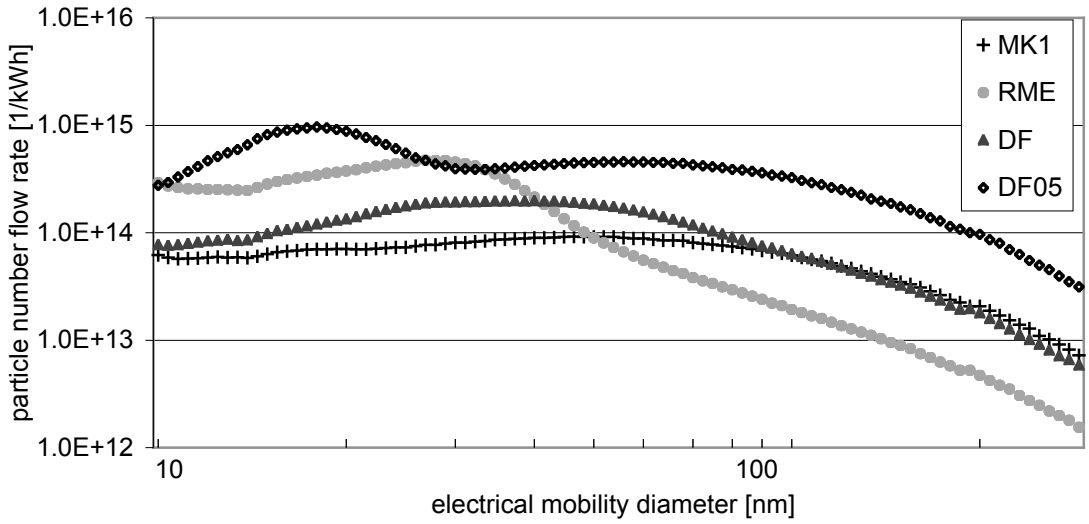

Figure 7. Size distribution of particles with respect to number of particles.

- Aromatic hydrocarbons; cf. Fig. 8: Aromatic compounds are mainly found in idle and the modes with light load. In the other modes, the concentration in the exhaust gas is less than 1ppb, such that they cannot be distinguished from the background concentration. The results show that, in contrast to the results published by the Olsson group, RME leads to a significant reduction of the emissions. As stated already in the introduction, the very different combustion conditions are regarded as being the reason for this discrepancy.

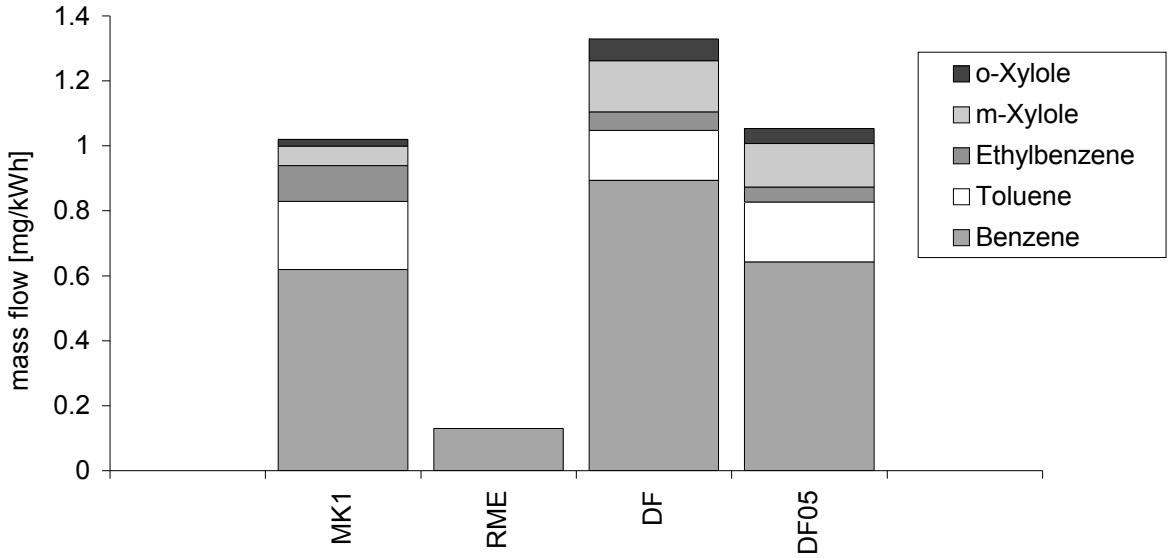

Figure 8. Specific aromatic hydrocarbons emission rates.

- Alkenes; cf. Ffig. 9: Concerning the unsaturated hydrocarbons, ethene, ethine, and propene are the main exhaust gas components. As found for the aromatics, they are hardly detectable with exceptions in idle and modes with light load. The "new" fuels MK1 and DF05 show in this case considerably higher emission rates, however, on a low level.

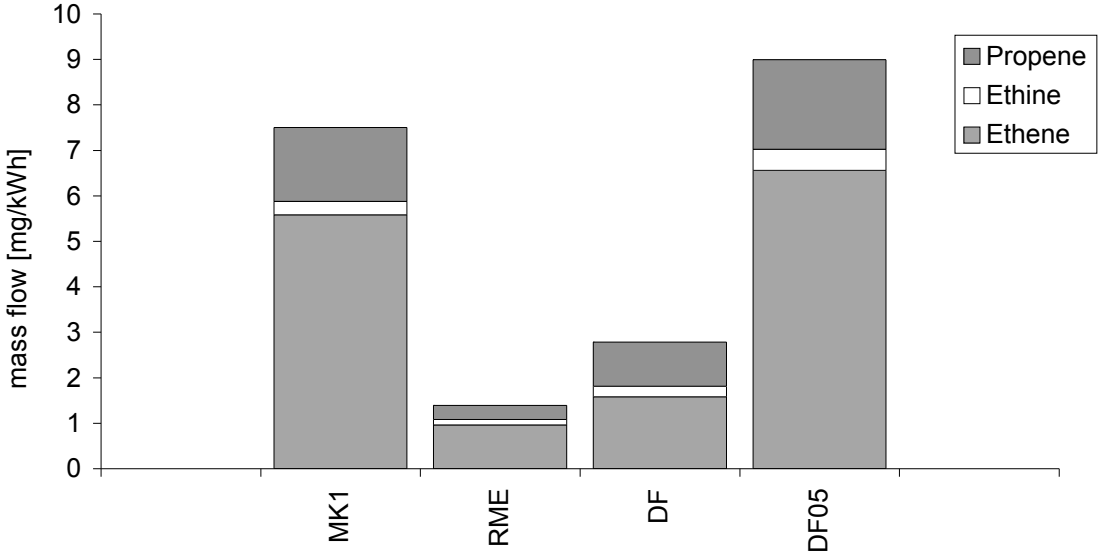

Figure 9. Specific alkenes emission rates.

- Aldehydes and ketones; cf. Fig. 10: Like the alkenes, the aldehydes and ketones contribute to summer smog formation. Aldehydes have a share of 30 % to 50 % in the overall HC emissions. The results show a reduction of 30 % for RME and DF05 compared to DF, and a slight increase for MK1.

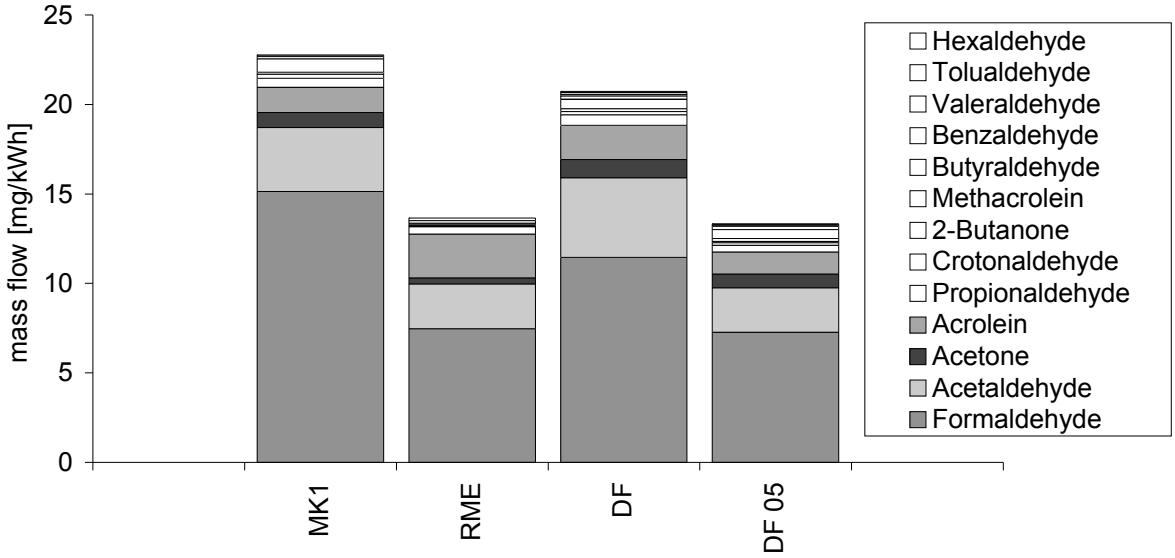

Figure 10. Specific emission rates for aldehydes and ketones.

- The results of the extraction of the particulate matter produced by the investigated fuels are compared in Figure 11. RME, MK1 and to a lower extent, DF05, produced a considerably decreased particle mass compared with DF. This is probably due to the lower sulfur content of these fuels compared to DF as described in previous studies (Sjögren et al., 1996; Bünger et al., 2000). The solid material (mainly soot/carbon) was lowest from RME, indicating a higher portion of unburned fuel in the

soluble organic fraction of these extracts. In some of the load modes (esp. 9, 10, 11), RME produced nearly no soot as already observed in a prior study (Schröder et al., 1999).

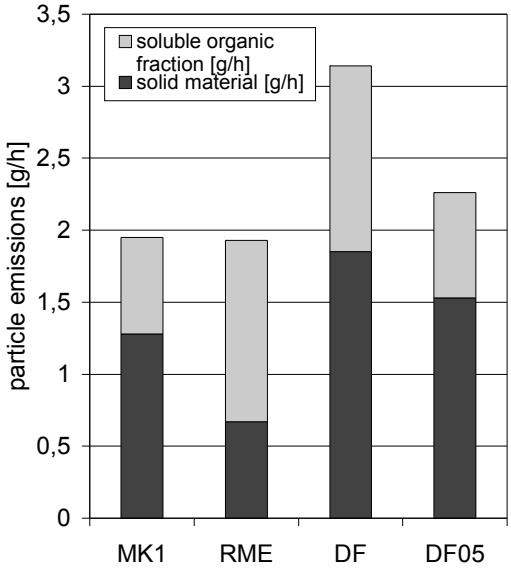

Figure 11. Particle emissions stratified for solid and soluble fraction.

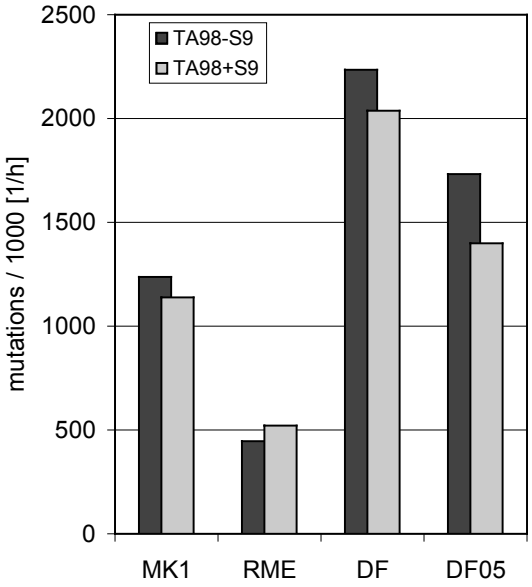

Figure 12. Mutagenic effects of the particle extracts with (+S9) and without (-S9) metabolic activation.

- The mutagenic effects of the particle extracts from the tested fuels showed a very strong variation. RME produced the lowest mutagenic effects. Mutagenicity of MK1-extracts was 2- to 3-fold higher. DF05 was 3- to 4- times more mutagenic and DF 4-5 times compared with RME. The results with (+S9) and without (-S9) metabolic activation by rat liver enzymes differed slightly but not significant.

The very small number of mutations for RME is ascribed to a lower content of polycyclic aromatic compounds (PAC) in particle emissions of biodiesel fuels (Bagley et al., 1998; Bünger et al., 2000). Mutagenicity induced by MK1- and DF05-particle extracts was also generally lower than mutagenicity by DF-extracts. This effect is probably due to the low sulfur content of these fuels. There is a correlation between sulfur content of DF and mutagenic effects of its exhaust (Sjögren et al., 1996; Bünger et al., 2000). Since RME, MK1, and DF05 contain nearly no sulfur, a similar range of mutagenic effects could be expected from the use of these fuels compared with DF containing 41 ppm of sulfur. However, mutagenicity of MK1- and DF05-particle extracts was stronger than the mutagenic effects of RME. This may be due to the content of aromatic compounds in MK1 and DF05, that is not found in RME. Aromatic compounds in DF have been proven to increase the mutagenic effects of particle emission extracts (Crebelli et al., 1995; Sjögren et al., 1996).

CONCLUSION

Exhaust gas emissions from a modern diesel engine were measured using (1) conventional diesel fuel according to DIN EN590, (2) Swedish low sulfur diesel fuel MK1, (3) biodiesel, consisting of rape seed oil methylester; and (4) a new diesel fuel with lowered boiling characteristics, low sulfur content, and a high level of aromatic compounds.

The results of non-regulated emissions must be interpreted with great care, since measurement errors are relatively high when analyzing gas components at very low concentrations. However, it can clearly be stated that the Swedish results, obtained by the group of Olsson at Chalmers University, Gothenburg, must be regarded as irrelevant concerning combustion of fuels in diesel engines. Biodiesel has positive and negative effects on the emissions; however, the reported high concentrations, in particular of benzene (10-fold higher than MK1) cannot be observed under the combustion conditions of a diesel engine. In addition, the mutagenicity of RME emissions is much lower compared to fossil fuels indicating a reduced health risk from cancer.

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