Influence of the phosphorus content in rapeseed oil methyl esters during a 1000 hours endurance test on the function of a SCR-system measured by exhaust gas emissions and health effects

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ABSTRACT

Two batches of rapeseed oil methyl esters containing approximately 10 ppm phosphorus (RME_{10}), one rapeseed oil methyl ester with a content of less than 1 ppm phosphorus (RME) and common diesel fuel (DF) were investigated regarding their effects on regulated and non-regulated emissions of a modern diesel engine (Euro IV) equipped with an SCR system (selective catalytical reduction of nitrogen oxides). The regulated emissions of carbon monoxide (CO), hydrocarbons (HC), nitrogen oxides (NO_x) and particulate matter (PM) were determined for RME_{10} and DF. Non-regulated emissions alkenes, alkynes, aromatics, aldehydes, ketones and the particle size distribution were measured for all fuels. Additionally the mutagenic potency of the PM emissions was determined using the Ames test.
RME_{10} led to lower regulated emissions than conventional diesel fuel. Regarding the non-regulated emissions RME showed the lowest values compared with RME_{10} and DF. The catalytic activity of the SCR system was reduced after an endurance test of 1000 hours using RME_{10} as fuel resulting in higher regulated and non-regulated emissions.

The mutagenicity of all PM extracts was very low compared to prior studies probably due to an effective PAH conversion by the SCR system. Nevertheless, mutagenic effects of PM extracts increased moderately after the endurance test.

INTRODUCTION

One characteristic of modern society is the striving for flexibility and mobility in all areas of the daily life. Worldwide a steady rising of traffic can be noticed. In the EU, since many years the traffic increases much stronger than the production capacity. This traffic growth is dominated by the road haulage [1].

Because of its efficiency and robustness the diesel engine became the dominating propulsion principle for trucks. The discussion about diesel exhaust related health effects led to a worldwide tightening up of the exhaust gas regulations, especially for heavy duty vehicles. Besides the emissions of particulate matter the limits for nitrogen oxides were substantially reduced. One possibility to keep these limits are engine measures. However, the problem is trade-off between particulate matter and nitrogen oxides. Therefore secondary measures have to be used to fulfill the regulations. The SCR technique (selective catalytic reduction) is one method that is well proven to reduce nitrogen oxides. In the result nitrogen oxides can be reduced to 95% and particulate matter up to 30%. Gaseous ammonia (NH_3), ammo-

nia in aqueous solution or urea in aqueous solution can be used as reducing agents [2,3,4]. Manufacturers of heavy duty engines already have introduced it to the market.

Due to the increasing price of crude oil diesel more and more vehicles run on biodiesel (In Europe: mainly rape seed oil methyl ester, RME). But the use of RME has specific demands to the engine and the exhaust after-treatment system.

To our knowledge no data are available about the influence of RME on SCR systems in heavy duty engines meeting the emission standard EURO IV, which were recently introduced to the market.

It was the goal of the investigations to figure out the influence of the maximum allowed phosphorus content of 10 ppm (European specification DIN EN 14214) on the long-term stability of the SCR system, because phosphorus acts poisonous to catalysts [5, 6]. However, it was not possible to buy RME with 10 ppm phosphorous on the German market. All qualities had significantly lower phosphorous concentrations. Therefore tributylphosphate was added to achieve a phosphorus content of 10 ppm.

MATERIALS AND METHODS

FUELS

Four different fuels were tested: one common fossil diesel fuel (**DF**), two rapeseed oil methyl esters with high contents of phosphorus (**RME$_{10}$**), and one rape seed oil methyl ester with a low (regular) content of phosphorus (**RME**), which was solely tested in the ESC-Test. The second badge of RME$_{10}$ (RME$_{10b}$) was tested after 800 operating hours of the catalyst in an endurance test. It was tested for further 200 operating hours. The high contents of phosphorus were obtained by adding tributylphosphate.

The first two badges of RME according to DIN EN 14214 were obtained from Mitteldeutsche Umesterungswerke GmbH & Co Kg, Greppin, Germany. The third charge was obtained from Hallertauer Hopfenveredlungsges. mbH Biodieselwerke, Mainburg, Germany.
The used diesel fuel met DIN EN 590. It was delivered by OMV, Germany. For this fuel no analysis was available. Characteristics of the three biodiesel fuels are given in Table 1.

Table 1. Characteristics of the biodiesel qualities..

	RME according to DIN EN14214	RME (RME$_{10a}$)	RME (RME$_{10b}$)	RME (RME)
density (15°C) [g/L]	860-900	882.8	886.6	883.8
kin. viscosity (40°C) [mm²/s]	3.5-5.0	4.5	n.d.	n.d.
flashpoint [°C]	min. 120	142	>140	151
C.F.P.P. [°C]	max. 0	-21	-16	-13
total sulfur [mg/kg]	max. 10	<1	n.d.	n.d.
total phosphorus [mg/kg]	max. 10	9.2*	14.7*	0.3
carbon residue [w/w %]	max. 0.3	<0.01	0.03	n.d.
cetane number [-]	min. 51	52.6	n.d.	n.d.
water content [mg/kg]	max. 500	149	463	322
copper corrosion [-]	1	1	n.d.	n.d.
acid number [mg KOH/g]	max. 0.5	0.168	0.28	0.08

n.d. : not detected   * with addition of tributylphosphate

ENGINE AND TEST CONDITIONS

A modern IVECO diesel test-engine, type Tector (F4A) with turbocharger and charge-air cooling was used as test engine. Technical data of this engine are given in Table 2.

Measurements have been carried out on a SCR test system, type SINO$_x$ (Argillon). The SCR test system consists of the catalyst, a controlling device and a dosing unit for the reducing agent. A 32.5% aqueous urea solution (DIN 70070), also known as AdBlue™, was used as reducing agent. The SCR-catalyst is a full-extruded, fine-cellular honeycomb catalyst consisting mainly of titanium oxide, doped with vanadium as activity enhancing substance.

Emissions were measured before and after the catalyst. Additionally measurements were carried out on a reference catalyst that was not used with RME$_{10}$.

The engine was run at two different test modes to determine the durability of the SCR in the E46-test (E46 Endurance Test) evolved by IVECO. The modes changed between high idling and rated power. Strong jumps of the exhaust gas temperature were reached and represented high stress for the SCR system.

Table 2. Technical data of the used engine IVECO Test-Engine (F4A).

Piston Stroke	120 mm
Bore of cylinder	102 mm
Number of cylinders	6
Engine displacement	5900 cm³
Rated speed	2500 min^{-1}
Rated power	220 kW
Maximum torque	1050 Nm at 1400 min^{-1}
Compression ratio	17:1

For the measurement of the regulated and non-regulated emissions the 13-mode ESC test was used (Figure 1).
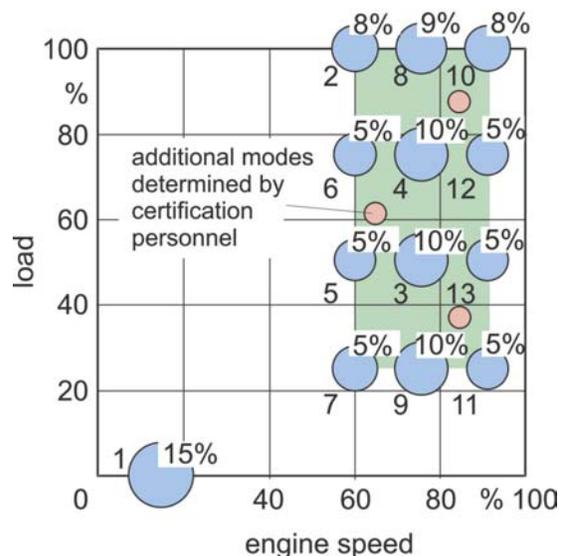

Figure 1. Modes of the ESC test.

ANALYTICAL EQUIPMENT

Figure 2 shows the part of the emission test stand that was used in the project. Regulated gaseous compounds were taken from the raw exhaust gas stream. CO was measured with gas analyzer IRD 4000 CO I (Pierburg Instruments), HC with FID 4000 hh (Pierburg Instruments) and NO$_x$ with CLD 4000 hh (Pierburg Instruments). The sampling of particulate matter (PM) was performed after passing a part stream dilution tunnel (Smart Sampler (AVL)). As filter material PTFE-coated filters T60A20 (Pall) were used. Before and after sampling filters were conditioned (20°C, rel. humidity 50%). The filters were weighted by µg-balance M5P (Sartorius).

Furthermore several non-regulated emissions were sampled and analyzed. For the PM size distribution a scanning mobility particle sizer (SMPS), type TSI and an electronic low pressure impactor (ELPI) from Dekati were used. The diluted exhaust gas was taken after passing the part stream dilution tunnel (Smart Sampler). Alkenes, alkynes and aromatics were taken directly from the pure exhaust gas and sampled in telco bags from Supelco and analyzed by GC/MS (Shimadzu, type GC 17A and QP5000). For the analysis of the aldehydes and ketones pure exhaust gas passed two 2,4-dinitrophenylhydrazine (DNPH) cartridges and were then eluted with acetonitrile. The hydrazones were analyzed by HPLC (hp 1090 with UV-DAD).
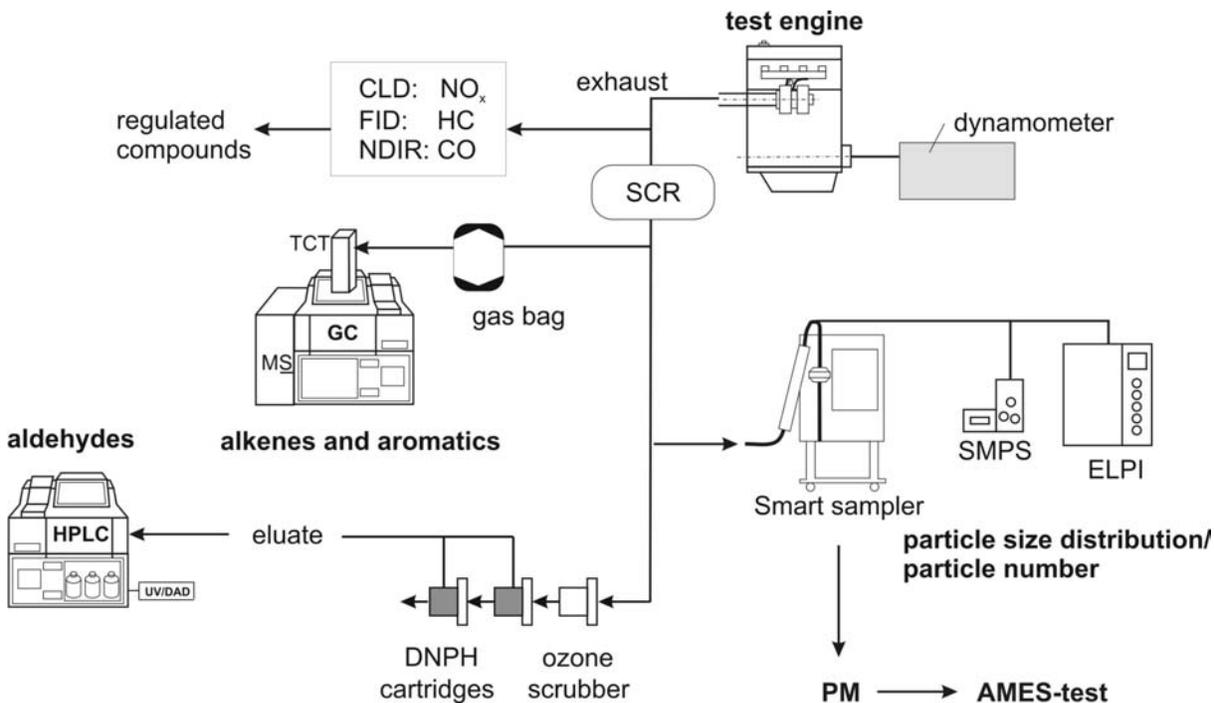
Figure 2. Scheme of the emission test stand.

COMPOSITION OF PARTICULATE MATTER

The soluble organic fraction (SOF) was determined after weighing the filters. The filters were extracted with dichloromethane. The loss of weight after extraction corresponds to the weight of the SOF.

In the same way the determination of the water soluble fraction (WSF) was carried out. For the extraction isopropanol/water in relation of 1 to 10 was used.

The remaining material on the filter after extraction of SOF and WSF was designated as non soluble fraction (NSF).

MUTAGENICITY ASSAY

PM was collected on PTFE coated glass fiber filters (T60A20, Pallflex Products Corp., Putnam, CT, U.S.A.) using the smart sampler. The filters were conditioned (20°C, rel. humidity 50%) and weighed before and after the sampling procedure.

Three filters of each fuel after the endurance test (1000 h) of the SCR system as well as for the reference catalyst (0 h) were cooled (<5°C) and transferred to the toxicological laboratory for mutagenicity testing. Every three analogous filters were extracted with dichloromethane (Merck, Darmstadt, Germany) in a Soxhlet apparatus (Brand, Wertheim, Germany) for 12 h in the dark (cycle time 20 min). The PM-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 [7] 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. The Ames test is the most frequently used test system worldwide in order to investigate mutagenicity of complex mixtures like combustion products. It was adopted as official OECD guideline 471 in 1997. This study employed the revised standard test protocol [8] with the tester strains TA98 and TA100.

Tests were performed with, as well as without, metabolic activation by an microsomal mixed-function oxidase system (S9 fraction). Preparation of the liver S9 fraction from male Wistar rats was carried out as described by Maron and Ames (1983) [8]. For induction of liver enzymes, phenobarbital and β-naphthoflavone (5,6-benzoflavone) were used instead of Arochlor-1254, which is a mixture of polychlorinated biphenyls (PCB) [9]. The mutagens methyl methanesulfonate (MMS), 3-nitrobenzanthrone (3-NBA) and 2-aminofluorene (2-AF) were used as positive controls.

Immediately before use, the dried PM-extracts were dissolved in 4mL DMSO, and the following dilutions were tested: 1.0, 0.5, 0.25, 0.125. The 2-AF was dissolved in 100 µg/mL and 3-NBA in 1 ng/mL DMSO, MMS was dissolved in distilled water (10 µg/mL). Every concentration was tested both, with and without 4% S9 mix. Each ex-

tract 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 at least the double of the spontaneous reversion frequency and a reproducible dose-response relationship was observed.

RESULTS

RME_{10} showed advantages for all regulated emissions in comparison to DF with the exception of NO_x. Even with the brand new SCR system (0 hours) the limit for NO_x is exceeded (Figure 4), since the dosing calibration was kept unchanged for the operation with RME_{10}.

All fuels were within the EURO IV limit for CO of 1.5 g/kWh. RME_{10} showed about 53% lower emissions compared with DF (Figure 3). Significant differences before (0 hours) and after the endurance test (1000 h) could not be determined for RME_{10}.
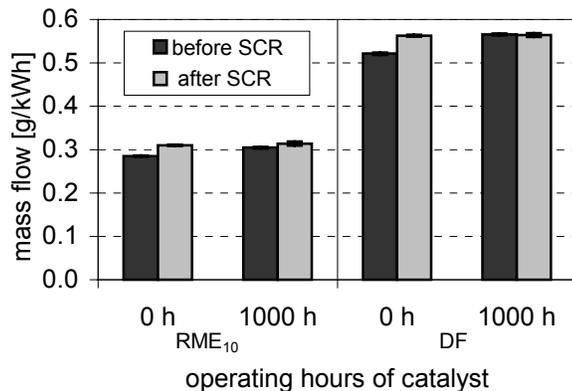

Figure 3. Specific CO emissions.

In contrast to the CO emissions the aging of the catalyst had a significant impact on NO_x (Figure 4). Moreover the high phosphorous content damaged the SCR system: After 1000 hours even with DF the limit of 3.5 g/kWh was exceeded. Simultaneously the slip of ammonia increased from 13 ppm to 79 ppm for RME_{10} and from 23 ppm to 94 ppm for DF, data not shown.

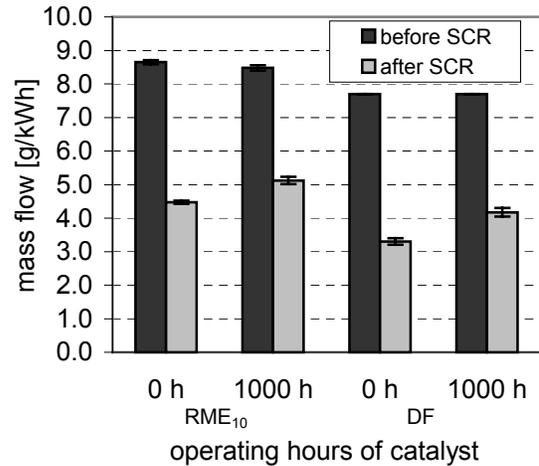The catalyst lost activity during the endurance test regarding NO_x and PM (Figure 6).

Figure 4. Specific NO_x emission .

RME_{10} emitted 55% less unburned hydrocarbons than DF (Figure 5). However, all results were within the EURO IV limit of 0.46 g/kW.
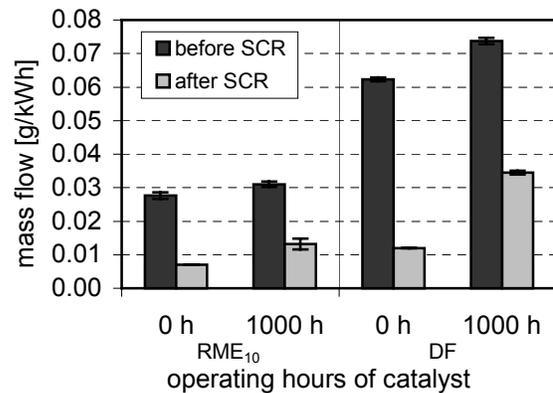

Figure 5. Specific HC emissions.

Diesel fuel led to an PM increase. The endurance test had a negative effect on the activity regarding PM. For both fuels the emissions increased after 1000 hours on RME_{10}.

Since engines are designed for DF more unburned fuel is emitted when running on RME_{10}. This leads to higher emissions of unburned fuel. This was verified by several studies [10, 11, 12,13].
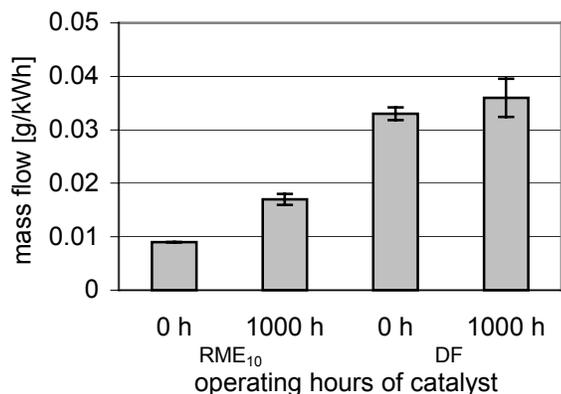
Figure 6. Specific PM emissions.

Figure 7. Composition of particulate matter.

For both fuels the quota of SOF, WSF and NSF increased after 1000 hours (Figure 7). The increase of the WSF could be referred to water soluble substances, which have been produced on the surface of the catalyst during the endurance test. With rising running hours the radius of the pores decreased and thereby the surface for the reduction of the NSF decreased. By that the particulate matter increased with running hours [14].
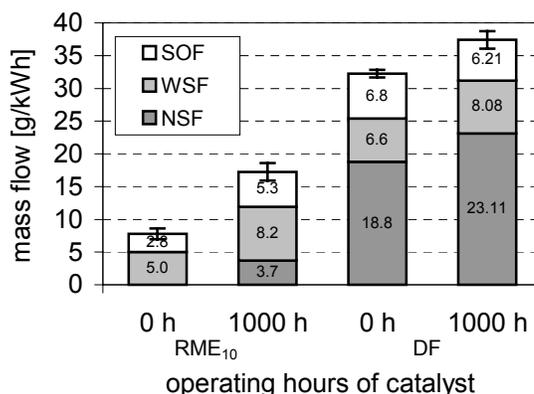
It was not possible to measure the particle size distribution at the beginning of the project. So after the 1000 hours endurance test a brand new SCR system was used as reference. Additionally RME without phosphorous additive was used for comparison. Particle size distribution was measured before and after the SCR system.

The results measured with ELPI showed the highest emissions for DF and the lowest emissions for RME (Figure 8). The emissions of RME_{10} were in-between. Higher emissions for RME_{10} in comparison to RME were attributed to the formation of phosphates, detected by ion chromatography, data not shown. The SCR system led to a reduction of the PM emissions for all fuels.
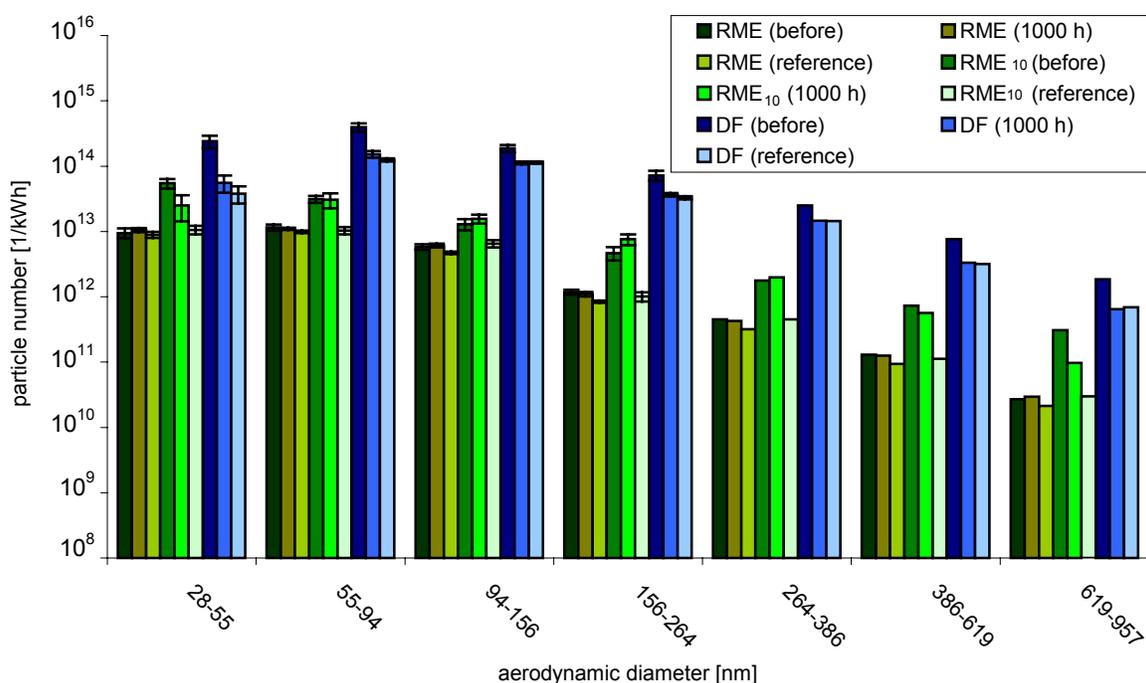

Figure 8. Size distribution of particles (ELPI).

An increase of PM emissions, especially for RME_{10}, was detected after 1000 hours.
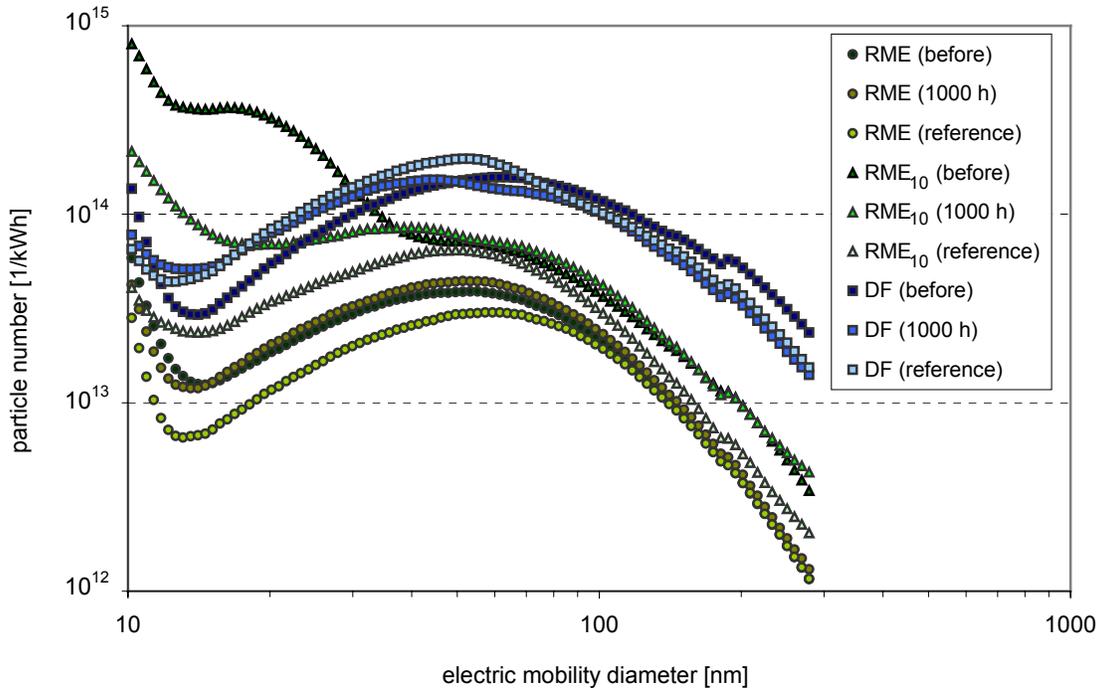

Figure 9. Size distribution of particles with respect to number of particles (SMPS).

The particle size distribution was additionally measured by SMPS (Figures 10, 11 and 12). RME shows lower emissions than diesel fuel. It is striking that RME_{10} leads to a severe increase of ultra-fine particles before the SCR system and especially after 1000 hours with high phosphorous fuel. So the fuel quality is main responsible for the ultra-fine particle emissions.
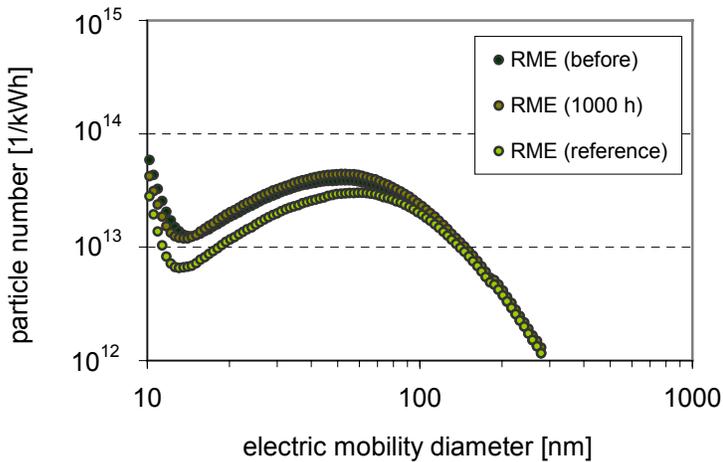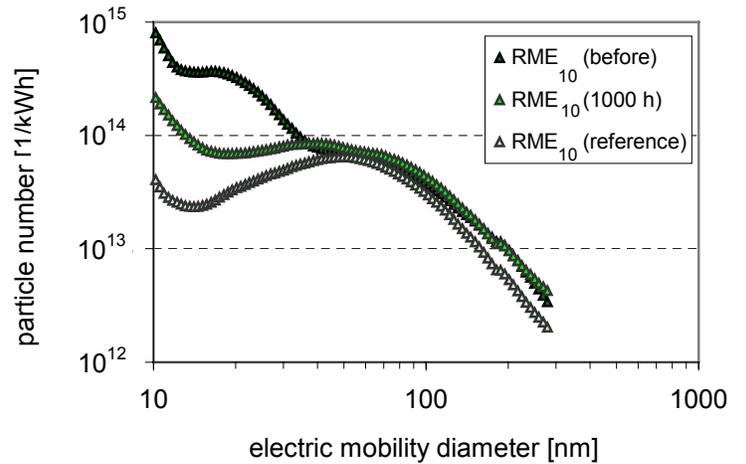

Figure 11. Size distribution of particles of RME_{10} (SMPS).

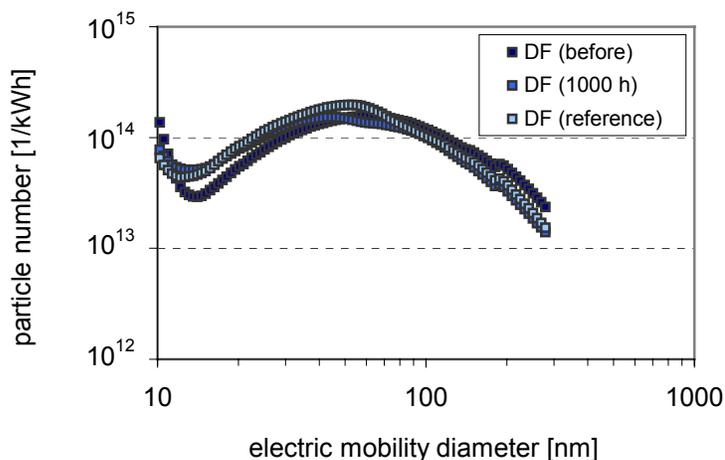Figure 10. Size distribution of particles of RME (SMPS).

Figure 12. Size distribution of particles of DF (SMPS).

Figure 14. Specific emission for aldehydes and ketones.

Generally, the emissions of alkenes, alkynes and aromatics was low (Figure 13). Significant differences between RME and RME_{10} could not be detected. In relation to the two RME qualities about 3- to 4-fold higher emissions were measured for DF. The reference catalyst led to a 25% increase of the emissions for RME and 40% for DF.

Generally, the mutagenic potency of all PM extracts was low and was further reduced in assays with metabolic activation (Figure 15). Significant differences of mutagenicity between extracts of the used fuels were not observed.
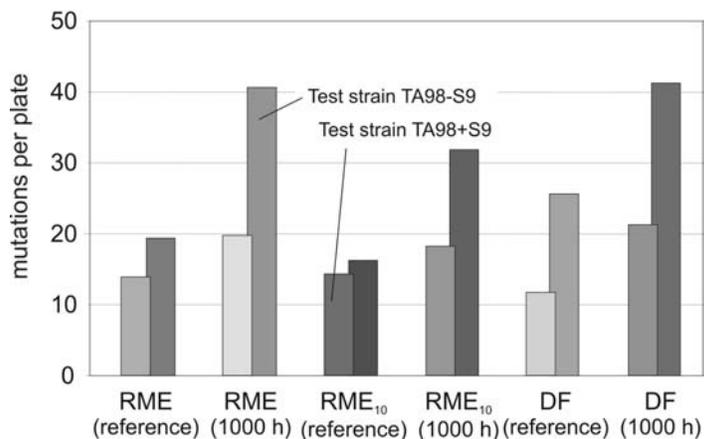
Figure 15. Mutagenic effects of PM extracts with (+S9) and without (-S9) metabolic activation.
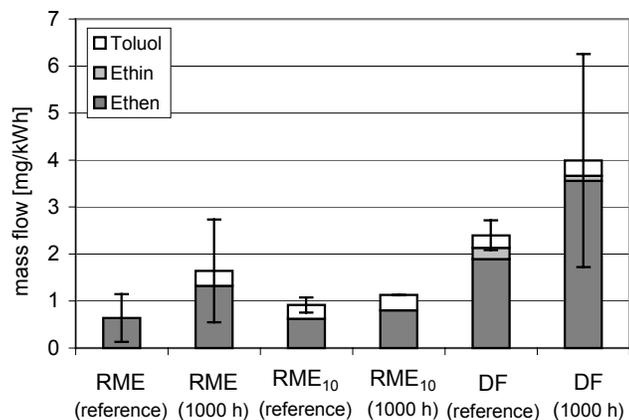

Figure 13. Specific emission for alkenes, alkynes and aromatics.

The emissions for aldehydes and ketones showed high emissions for DF and lower for RME (Figure 14). The 1000 hours endurance test led to a lowered conversion rate. Moreover using the reference SCR system RME_{10} had a 2-fold aldehyde emission versus RME. The reference catalyst led to a 25 % decrease of the emissions for RME_{10} and 40% for DF.
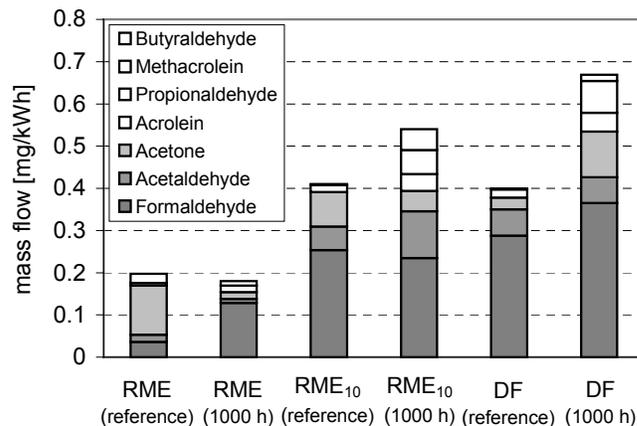
The numbers of mutations with and without metabolic activation were much lower in relation to earlier investigations without SCR catalyst indicating a very effective reduction of PAH and especially nitrated PAH of the system and a decreased health risk respectively [14, 15, 16, 17, 18, 19, 20]. Nevertheless, the endurance catalyst led to an increase of the number of mutations.

CONCLUSION

Exhaust gas emissions from a modern diesel engine (class EURO IV) with SCR system were measured with common diesel fuel, two rapeseed oil methyl esters with high contents of phosphorus and one rapeseed oil methyl ester with a regular low content of phosphorus. It was the goal to investigate the influence on the function of a SCR system.

The content of phosphorus in biodiesel has a significant influence on the emissions of the regulated and non-regulated emissions. Phosphorus acts poisonous to the catalyst and leads to a decrease of activity.

At the example of this test engine and the used SCR system the NO_x limit was exceeded with biodiesel.

The ultra-fine particle emissions increased by the influence of phosphorous.

The mutagenic potency was on a low level for both, diesel fuel and for biodiesel. However, the aging of the SCR system led to an increase of mutations.

In summary, the use of low phosphorous biodiesel is strongly recommended. The European maximum value of 10 ppm should be lowered. In the meantime the biodiesel producers should continue to produce fuel with phosphorus concentrations of a lower limit than required in the specification. OEMs should not allow 10 ppm phosphorous for their SCR systems.

ACKNOWLEDGEMENTS

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LIST OF ACRONYMS

2-AF	2-Aminofluorene
CLD	Chemoluminescence detector
CO	Carbon monoxide
DF	Diesel fuel
DMSO	Dimethyl sulfoxide
E46	Endurance test
ELPI	Electronic low pressure impactor
ESC	European stationary cycle
EU	European Union
FID	Flame ionization detector
GC/MS	Gas Chromatography coupled with mass spectrometry
HC	Hydrocarbons
HPLC	High performance liquid chromatography
IRD	Infrared detector
MMS	Methyl methane sulfonate
3-NBA	3-Nitrobenzanthrone
NO_x	Nitrogen oxides
NSF	Non soluble fraction
PAH	Polycyclic aromatic hydrocarbons
PCB	Polychlorinated biphenyls
PM	Particulate matter
PTFE	Polytetrafluoroethylene
RME	Rape seed oil methyl ester
RME_{10}	Rape seed oil methyl ester with tributylphosphate
SCR	Selective catalytic reduction
SMPS	Scanning mobility particle sizer
SOF	Soluble organic fraction
WSF	Water soluble fraction