Emissions and health effects from heavy-duty engines running on alternative fuels

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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 at 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 of alkenes, alkynes, aromatics, aldehydes, ketones and the particle size distribution were measured for all fuels. Additionally the mutagenic potency of the particulate matter was determined by Ames tests.

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. This is probably due to an effective conversion by the SCR system. Nevertheless, mutagenic effects of PM extracts increased moderately after the endurance test.

Key words: Diesel engine; exhaust gas emissions; SCR system; RME; phosphorus content; mutagenicity.

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 the 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 could be reduced in principle by up to 95 % and particulate matter by up to 30 %. Gaseous ammonia (NH_3), ammonia in aqueous solution or urea in aqueous solution can be used as reducing agents [2-4].

Due to the increasing price of fossil diesel fuel more and more vehicles run on biodiesel (In Europe: mainly rapeseed oil methyl ester, RME). But the use of RME has specific demands to the engine and the exhaust gas aftertreatment 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 phosphorus on the German market. All qualities had significantly lower phosphorus 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 rapeseed oil methyl ester with a low (regular) content of phosphorus (RME), which was solely tested in the ESC-Test. The second batch 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 content of phosphorus was obtained by adding tributylphosphate.

Engine and Test Conditions

A modern IVECO diesel test-engine, type Tector (F4A) with turbocharger and charge-air cooling was used. Technical data of this engine are given in Table 1.

Table 1. Technical data of the engine IVECO 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

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 fully 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 operated at two different test modes to determine the durability of the SCR in the so-called 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. For the measurement of the regulated and non-regulated emissions the 13-mode ESC test was used.

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 (EURO IV: 3.5 g/kWh) is exceeded (Fig. 2), 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 almost 50 % lower emissions compared with DF (Fig. 1). Significant differences before (0 hours) and after the endurance test (1000 h) could not be determined for RME_{10}.

In contrast to the CO emissions the aging of the catalyst had a significant impact on NO_x (Fig. 2). Moreover, the high phosphorus content damaged the SCR system: After running 1000 hours on RME_{10}, 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.

RME_{10} emitted 55% less unburned hydrocarbons than DF (Fig. 3). However, all results were very well within the EURO IV limit of 0.46 g/kWh.

The catalyst lost activity during the endurance test regarding NO_x, HC, and PM (Figs. 2-4).

Diesel fuel led to a PM increase. The endurance test had a further 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. This was verified by several studies [10-13].

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 behind the SCR system.

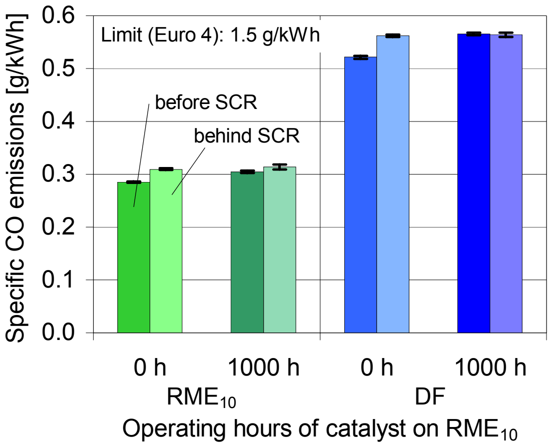

Figure 1. Specific CO emissions; ESC-Test.

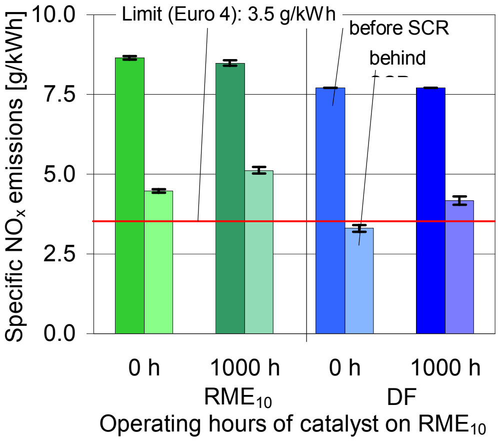

Figure 2. Specific NO_x emissions; ESC-Test.

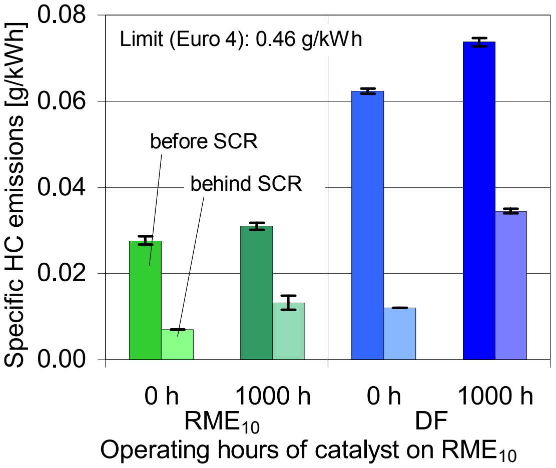

Figure 3. Specific HC emissions; ESC-Test.

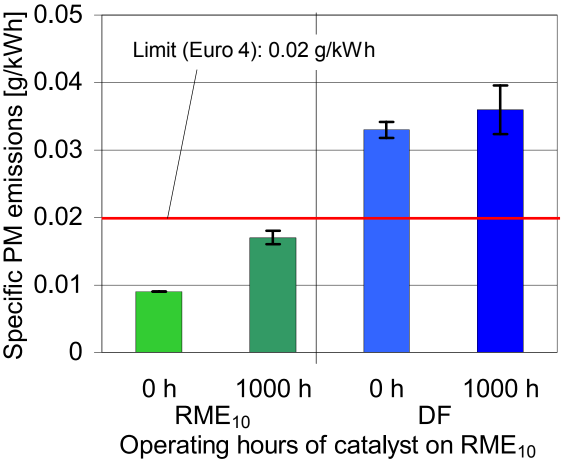

Figure 4. Specific PM emissions; ESC-Test.

The particle size distribution was measured by SMPS (Fig. 5). RME shows lower emissions than diesel fuel. It is striking that RME_{10} leads to severe increases of ultra fine particle emissions, as revealed by sampling before the SCR system (symbol "pre cat."). Furthermore, after 1000 hours of engine operation with high-phosphorous RME_{10}, performance of the SCR was substantially deteriorated. This is evident from comparing distribution curves "1000 h" and "reference". No such influence of the SCR on counts of finest particles was observed both for DF and regular RME. Thus, fuel quality seems to be mainly responsible for higher ultra fine particle emissions.

Generally, the mutagenic potency of all PM extracts was low and was further reduced in assays with metabolic activation (Fig. 6). Significant differences of mutagenicity between extracts of the used fuels were not observed. The numbers of mutations with and without metabolic activation were much lower in relation to earlier investigations without SCR catalyst indicating a probably very effective reduction of PAH and especially nitrated PAH of the system and a decreased health risk, respectively [14-20]. Nevertheless, the endurance test led to an increase of the number of mutations.

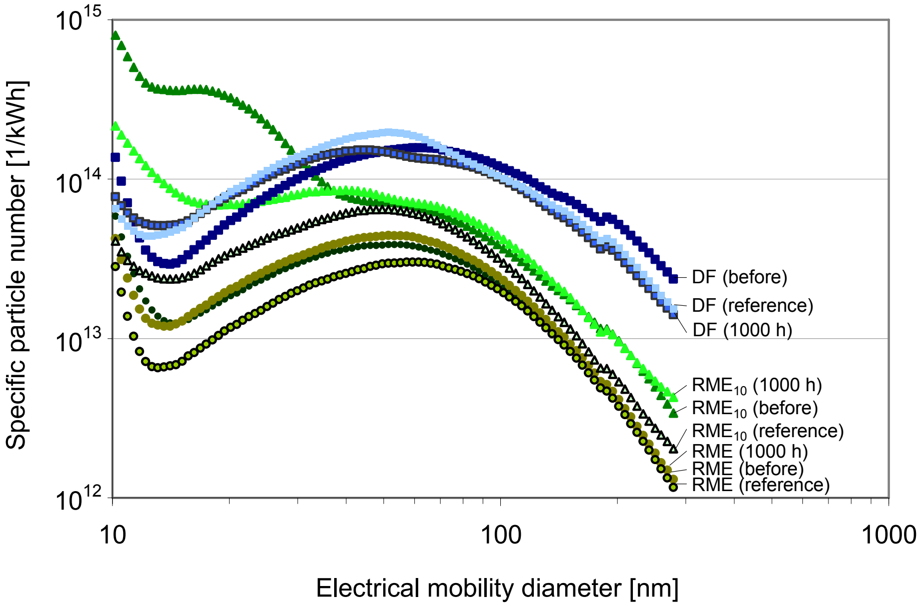

Figure 5. Size distribution of particles with respect to number of particles (SMPS).

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 low content of phosphorus (as found on the market). It was the goal to investigate the influence of phosphorus on the function of an SCR system.

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

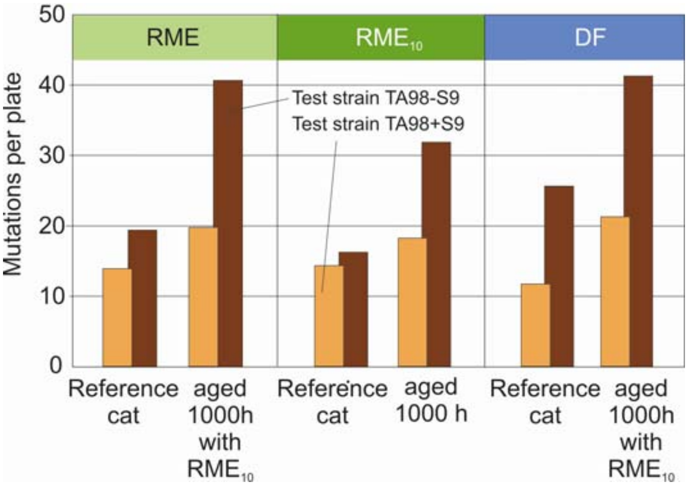

Figure 6. Mutagenic effects of PM extracts with (+S9) and without (-S9) metabolic activation. ESC tests on IVECO Tector F4A engine.

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. The ultra-fine particle emissions increased by the influence of phosphorus. The mutagenic potency was on a low level for both diesel fuel and biodiesel. However, the aging of the SCR system led to an increase of mutations.

In summary, the use of biodiesel with low phosphorus content 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 by the specification. OEMs should not allow 10 ppm phosphorus for their SCR systems.

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