ULTRAFINE PARTICLE EMISSIONS FROM BIODIESEL EXHAUST GAS

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INTRODUCTION

Particulate matter (PM) is recognized as one of the major harmful emissions generated by diesel engines and is subject to diesel engine emission regulations worldwide. PM consists of a variety of organic and inorganic substances and particles from diesel engines show a bimodal size distribution consisting of a nuclei mode in the size range from 9 nm to 30 nm and an accumulation mode. Nuclei mode particles, which can depose deeply in the lung, dominate the majority of particles but have only little effect on the total mass. Epidemiological and toxicological studies indicated that adverse health effects from exposure to PM may increase with decreasing particle size even if the particles consist of toxicologically inert materials [1]. Therefore the determination of the particle number distribution is of the same importance as the regulated PM mass. Consequently, a regulation for the particle number was announced for diesel passenger cars (Euro 5) beginning in 2011 as well as for heavy duty engines (Euro VI) coming into force in 2014. These stringent limits can be met by a combination of improvements in engine combustion, efficient exhaust gas aftertreatment and conversion to alternative fuels like biodiesel.
In previous investigations at the Johann Heinrich von Thünen-Institut (vTI) it was shown that biodiesel has great potential to reduce most regulated and unregulated emissions. Besides these positive results also higher emissions of particles in the nuclei mode were detected for RME versus fossil Diesel Fuel (DFref) [2]. Therefore more detailed information had to be obtained to what extent RME induces the formation of ultrafine particles, which are considered as harmful to human health.

ENGINE AND TEST CONDITIONS

Studies were carried out at the emission test laboratory of the Institute of Agricultural Technology and Biosystems Engineering at the Johann Heinrich von Thünen-Institut (vTI) in Braunschweig, Germany.
A six-cylinder (6370 cm^{-3}) Euro III Mercedes Benz OM 906 LA engine with turbocharger and intercooler was used. The Engine has a rated power of 205 kW at 2300 min^{-1} and a maximum torque of 1100 Nm at 1300 min^{-1}.
Exact engine load during test cycles is guaranteed by crankshaft coupling to a Froude Consine eddy-current brake. Engine test runs were in accordance with the 13-mode European Stationary Cycle (ESC). Studies were carried out with and without DOC (Oberland Mangold).

FUELS

RME (Rapeseed Oil Methyl Ester) was compared to two common diesel fuels (DFref: Fossil Reference Diesel Fuel and V-Power: Shell V-Power Diesel®) and one artificial blend (B5Ult: 5% RME + 95% Aral Ultimate Diesel®). Characteristics of the fuels are given in table 5
.
All four fuels were conforming to the current fuel standards. The parameters of the three fuels B5Ult, V-Power and DFref corresponded to the fuel standard DIN EN 590. The biogenous fuel RME was in accordance with the fuel standard DIN EN 14214.

Table 5: Characteristics of the tested fuels

	RME according to EN14214	RME	Diesel fuel according to EN590	B5Ult	V-Power	DFref
cetane number [-]	min. 51	54.5	min. 51	58.5	56.7	53.2
density (15°C) [g/L]	860 - 900	883.9	820 - 845	831.1	835.3	833.8
kin. viscosity (40°C) [mm²/s]	3.5 - 5.0	4.48	2.0 - 4.5	3.267	3.301	3.206
total sulfur [mg/kg]	max. 10	2.3	max. 50	1.1	7.6	< 1

ANALYTICAL EQUIPMENT

Measurements of the total mass of particulate matter as well as particle number and particle size distributions measured with SMPS were accomplished after dilution of raw exhaust gas in a dilution tunnel. Total mass of particulate matter was determined gravimetrically after sampling on glass fiber filters coated with PTFE (Teflon) (T60A20, Pallflex Products Corp.)
For the determination of particle mass a dilution factor of about 10 was applied. To perform correct measurements via SMPS an additional dilution factor of 9 was necessary. These are accepted dilution ratios at which particle losses due to coagulation and diffusive wall deposition are negligible.
A series of investigations were started especially concerning the emissions of the nuclei mode particles in the size range from 10 nm to 30 nm. To distinguish between solid soot and condensation particles a hot dilution device had been developed at the vTI. In this dilution device the exhaust gas is heated up to a temperature at which the volatile exhaust gas compounds evaporate. Afterwards the hot exhaust gas is diluted to such a degree that newly condensation of the volatile compounds is prevented. Volatile exhaust gas compounds remain in the gaseous phase and have no influence on particle number measurements [3].
The influence of the dilution temperature on the particle size distribution was investigated. Each measurement was four-fold repeated in mode 9 (1800 min^{-1}; 265 Nm) of the ESC test. This test mode was selected, since in this mode both the nuclei mode and the accumulation mode are present and therefore the influence of the temperature on both ranges was expected to be observable quite well. Studies were carried out in the temperature range from 20°C to 300°C.
For determination of the particle composition, particulate matter was taken from the raw exhaust gas and collected onto glass fibre filters coated with PTFE (Teflon) (T60A20, Pallflex Products Corp.). According to VDI Guideline 3872 part 1 the exhaust gas phase was cooled down below 50°C using an intensive cooler. In contrast to the ESC test procedure, this sampling was performed with a constant volume flow over the whole test including the transient phases.
The filters were extracted with cyclohexane. The loss of weight after extraction corresponds to the weight of the soluble organic fraction (SOF). The proportions of unburned fuel and lubricant in the SOF were determined with GC-FID.
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 insoluble fraction (ISF).

RESULTS

Emissions of total particulate matter remained below the Euro III limit of 0.1 g/kWh (Figure 7). Compared to the other fuels, which showed no difference amongst each other, the lowest emissions were obtained for RME. The DOC caused an additional slight decrease in the PM emissions for RME, which can be attributed to the reduction of SOF.

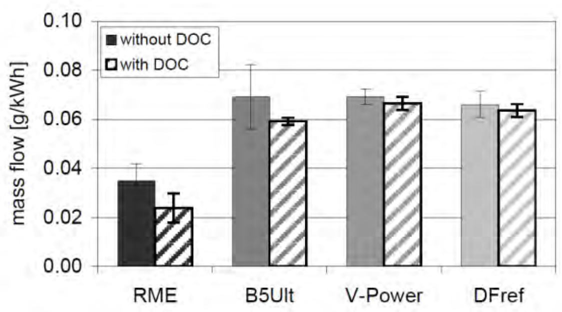

Figure 7: Specific PM emissions.

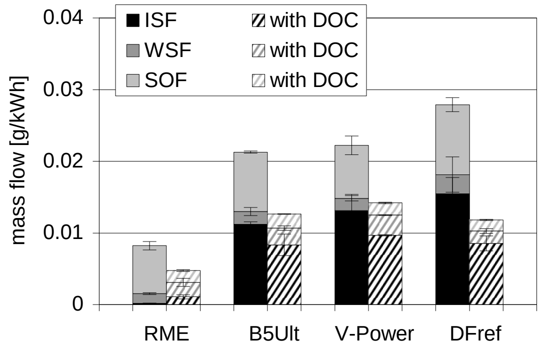

Figure 8: Composition of total particulate matter from raw exhaust gas.

Sampling out of the raw exhaust gas (Figure 2), less particle matter was found for all fuels. While RME has no insoluble fraction, the particle matter of other diesel fuels consists to over 50% of insoluble matter. For all four fuels a significant decrease in the SOF was achieved with exhaust gas aftertreatment by a DOC.
RME has the highest proportion of fuel in the SOF. For the three fossil diesel fuels a higher amount of lubricant was found (Figure 3).

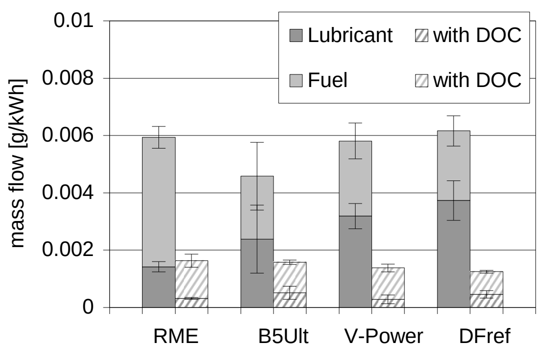

Figure 9: Composition of the SOF.

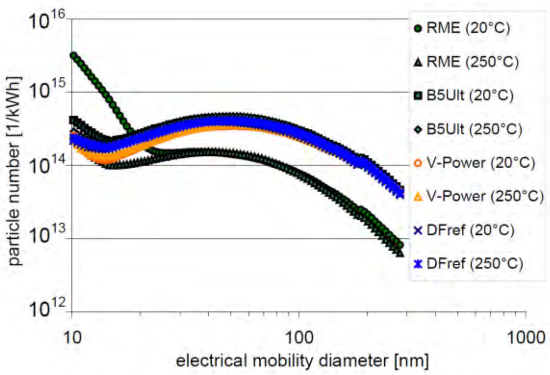

Figure 10: Size distribution of particles with respect to number of particles without DOC (SMPS).

The results obtained from SMPS measurements are summarized in figure 4**Error! Reference source not found.**, according to the tests without DOC carried out at 20°C and 250°C. Besides RME all diesel fuels showed comparable emissions. However, the particulate emissions of DFref were slightly increased in comparison with V-Power and B5Ult, especially at a dilution temperature of 20°C. RME demonstrated great potential to obtain a reduction in particle emission in the size range from 30 nm to 300 nm. However, in the size range from 10 nm to 20 nm RME showed the highest emissions of ultrafine particles versus the other fuels.
At a dilution temperature of 250°C, different distributions were detected. In detail, RME showed the lowest emissions over the entire size range. At 250°C a decrease in number of nuclei particles to one tenth was observed. A slight decrease in emissions of ultrafine particles was also observable for DFref, while no significant influence of dilution temperature was observable for V-Power and B5Ult. With regard to measurements via an SMPS after the DOC, less influence of the dilution temperature on the particle size distribution was observable.
The effect of reducing particles in the nuclei mode (10 nm to 30 nm) with a hot dilution started at a temperature of 80 °C. This suggests that particles in this size range may consist mainly of volatile substances. This result is supported by the results of the particle composition. As shown above a high amount of SOF and only a small amount of ISF was determined for RME. It can be assumed that particles within the size range from 10 nm to 30 nm, which were measured after hot dilution at temperatures greater than 80°C, are mainly soot, metallic ash or heavy hydrocarbons from lubricant [4].

CONCLUSION

Exhaust gas emissions with focus on particulate emissions from a diesel engine (class EURO III) equipped with and without DOC were investigated using common diesel fuel, rapeseed oil methyl ester, a premium diesel fuel as well as a blend of RME and another premium diesel fuel.
In course of the investigations it could be demonstrated that the nuclei mode particles did not mainly consist of soot, but most probably of unburned fuel. It was shown that the sampling conditions – especially the temperature in the dilution tunnel – had a significant effect on the detected particle size and number distributions. In particular, ultrafine particles in the nuclei mode from 10 nm to 40 nm decreased when the temperature increased to over 80°C.
RME led to reductions of particle number emissions versus all other fuels, whereas the fossil based diesel fuels DFref, B5Ult and V-Power did not vary significantly among each other. Regarding particulate matter emissions (PM) a reduction by factor two was detected for RME versus DFref.
In the result and at the example of the test engine it can be concluded that RME does not lead to higher ultrafine particle emissions than common diesel fuels. It can be stated that harmful effects due to higher numbers of carbon soot from biodiesel have not to be expected.

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