

# Ultrafine Particles from a Heavy Duty Diesel Engine Running on Rapeseed Oil Methyl Ester

**Jürgen Krah**

Coburg University of Applied Sciences

**Axel Munack and Olaf Schröder**

Johann Heinrich von Thünen Institute (vTI)

**Yvonne Ruschel**

APL - Automobil-Prüftechnik Landau GmbH

**Jürgen Bün**

BGFA – Research Institute of Occupational Medicine

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## ABSTRACT

Rapeseed oil methyl ester, two common fuels and one artificial blend were investigated their effects on particulate emissions. A heavy-duty diesel engine equipped with a diesel oxidation catalyst (DOC) was used for this test. Properties such as composition of particulate matter, as well as particle size and number distributions were measured using an electronic low pressure impactor (ELPI) and a scanning mobility particle sizer (SMPS) besides the regulated emissions: carbon monoxide (CO), hydrocarbons (HC), nitrogen oxides (NO<sub>x</sub>), and particulate matter (PM). Furthermore investigations were carried out regarding the influence of dilution temperature on particle number distribution measured via SMPS. Studies were carried out with and without a DOC. Additionally the mutagenic potency of the particulate and gaseous emissions was determined using the Ames test.

RME led to lower regulated emissions than common diesel fuel with exception of NO<sub>x</sub>. With DOC a further decrease in emissions was obtained. On the other hand also a light increase of NO<sub>x</sub> emissions was observed when the DOC was used. Regarding the non-regulated emissions RME showed the lowest values compared

with the other fuels. In measurements via SMPS higher emissions of particles in the nuclei mode were observed for RME compared to the other three fuels. In course of investigations regarding the composition of particulate matter from raw exhaust gas (PM<sub>reg</sub>) as well as investigations of the influence of dilution temperature it could be demonstrated that these nuclei particles mainly result from emission of unburned fuel.

The mutagenicity of all PM extracts was very low compared to prior studies. A further slight decrease of the mutagenic potential was obtained when using a DOC.

## INTRODUCTION

Particulate matter (PM) is recognized as one of the major harmful emissions generated by diesel engines. PM emissions are subject to diesel engine emission regulations worldwide. PM consists of a variety of organic and inorganic substances. The main constituents of the organic substances are unburned or partially burned fuel and lubricant. The inorganic substances include soot (carbon), sulphates, water and

metallic compounds. Metallic components originate from the engine or the exhaust gas system as well as derivatives of organometallic fuel and lubricant additives. The percentage of these substances in the total particle mass depends on a multitude of parameters. In addition to constructive parameters such as design of the combustion chamber and the injection system, the mode of operation, or rather the overall load configuration, the fuel and lubricant quality as well as the wear of the engine affect the PM composition [1].

Recently, emissions of fine and ultrafine particles from diesel engines caused a broad discussion in Europe. Since January 2005 the limit for the emission of fine particles has been tightened in the context of a council directive of the European Union (99/30/EG) [2]. According to this directive the limit of 50  $\mu\text{g}/\text{m}^3$  particles in ambient air should not be exceeded on more than 35 days per year. The compliance of the limit cannot be guaranteed yet all over in Europe. In 2007, the limit was exceeded in more than 11 European countries. For instance in Germany a transgression of the threshold value was recorded on more than 35 days at 34 of the 415 measuring stations [3].

In detail, 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 deposit deep 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 [4, 5]. Ultrafine particles can penetrate into the alveolar region, resting there for months. Here the particles can cause inflammatory reactions leading to bronchitis and asthma [6]. 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 Thuenen Institute (vTI) it was shown that biodiesel, attributable to its high oxygen content, 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 ( $\text{DF}_{\text{ref}}$ ) [7, 8, 9].

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.

## MATERIALS AND METHODS

### FUELS

RME was compared to two common diesel fuels and one artificial blend. The following four fuels were used for engine operation:

$\text{DF}_{\text{ref}}$ : Fossil Reference Diesel Fuel

RME: Rapeseed Oil Methyl Ester

B5Ult: 5% RME + 95% Aral Ultimate Diesel<sup>®</sup>

V-Power: Shell V-Power Diesel<sup>®</sup>

RME was provided by Carl Böttner Mineralöl-GmbH in Leer;  $\text{DF}_{\text{ref}}$  from Haltermann Products BSL Olefinverbund GmbH in Hamburg; Aral Ultimate Diesel<sup>®</sup> and Shell V-Power Diesel<sup>®</sup> were obtained from public filling stations in Braunschweig. Characteristics of the four fuels are given in table 1.

Table 1. Characteristics of the biodiesel and the diesel qualities.

|                                            | RME according to DIN EN14214 | RME   | Diesel fuel according to DIN EN590 | B5Ult | V-Power | $\text{DF}_{\text{ref}}$ |
|--------------------------------------------|------------------------------|-------|------------------------------------|-------|---------|--------------------------|
| 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) [mm <sup>2</sup> /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                      |

All four fuels were conforming to the current fuel standards. The parameters of the three fuels B5Ult, V-Power and DF<sub>ref</sub> correspond to the fuel standard DIN EN 590. The biogenous fuel RME is in accordance with the fuel standard DIN EN 14214.

As a consequence of the different cetane numbers, differences in the emission behavior are to be expected for the four diesel fuels. Generally the ignition delay time decreases with increasing cetane number. In consequence a better mixture of air and fuel will result and consequently a more complete combustion. This is reflected in lower HC-, CO and particulate emissions [10, 11].

In addition to the cetane number, the emissions are also directly affected by the kinematic viscosity as well as the density of the fuel. These parameters affect the processes during injection and combustion [12]. Increasing density and kinematic viscosity will lead to an insufficient atomization of the fuel during injection and therefore an unfavorable air to fuel mixture which will involve increasing emissions of HC, CO and particles [13].

Several studies had provided evidence that the formation of ultrafine particles during dilution is inter alia influenced by the sulfur content of the fuel. However, little is known to what extent fuels with sulfur contents lower 10 ppm will lead to the formation of particles during dilution. According to the surveys of Engeljehringer and Schimpl (2008) higher emissions of particulate matter result even for ultra low sulfur fuels ( $S < 10$  ppm) when the engine is equipped with a DOC [14]. With regard to these studies higher emissions of particles are to be expected for V-Power (8 ppm) compared to the other three fuels ( $\leq 2$  ppm).

## ENGINE AND TEST CONDITIONS

Studies were carried out at the emission test facility of the Institute of Agricultural Technology and Biosystems Engineering at the Johann Heinrich von Thünen Institute (vTI) in Braunschweig, Germany.

A six-cylinder Euro III Mercedes Benz OM 906 LA test engine with turbocharger and intercooler was used. Technical data of this engine are given in table 2.

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), for which the present torque and revolution rates (related to maximum load at the actual speed or related to rated speed, respectively) as well as the time courses of engine torque and speed are displayed in figure 1.

Table 2. Technical data of the test engine Mercedes-Benz OM 906 LA.

|                     |                                   |
|---------------------|-----------------------------------|
| Piston stroke       | 120 mm                            |
| Bore of cylinder    | 102 mm                            |
| Number of cylinders | 6                                 |
| Engine displacement | 5900 cm <sup>3</sup>              |
| Rated speed         | 2500 min <sup>-1</sup>            |
| Rated power         | 220 kW                            |
| Maximum torque      | 1050 Nm at 1400 min <sup>-1</sup> |
| Compression ratio   | 17:1                              |

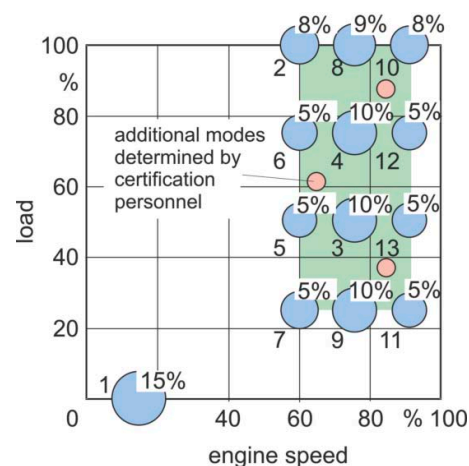


Figure 1. Modes of the ESC test.

Studies were carried out with and without DOC (Oberland Mangold). In table 3 the catalyst characteristics are presented.

Table 3. Technical data of the used DOC.

|                         |                         |
|-------------------------|-------------------------|
| Catalyst matrix         | Ø 225 mm, 90 mm         |
| Catalyst covering       | 229 mm, 110 mm          |
| Cells/inch <sup>2</sup> | 400 cpsi                |
| Noble metal             | 50 g/ft <sup>3</sup> Pt |

## ANALYTICAL EQUIPMENT

Regulated gaseous compounds carbon monoxide (CO), hydrocarbons (HC) and nitrogen oxides (NO<sub>x</sub>) were sampled each second from the raw exhaust gas stream and determined with commercial gas analyzers.

CO was measured with gas analyzer Multor 710 (Maihak Company) that uses the non dispersed infrared light (NDIR) process. HC were measured with an FID detector from Ratfish Company (RS 55-T). Nitrogen oxides were analyzed with a CLD 700 EL ht chemical luminescence detector from the EcoPhysics Co.

The emissions of particles were determined by five different ways. Measurements of the total mass of particulate matter as well as particle number and particle size distributions measured with ELPI and 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 and ELPI measurements a dilution factor of about 10 is 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 [15].

Dilution factors were calculated from separate recordings of carbon dioxide (CO<sub>2</sub>) contents in exhaust gas, fresh air, and diluted exhaust gas.

For determining mutagenicity and 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 under 50°C using an intensive cooler (Schott, Germany). All sampled filters were conditioned (20°C, relative humidity 50%), weighed before and after sampling and stored at -18°C. Further investigations were carried out regarding the composition of particles in different size ranges. Therefore a Berner impactor was used to separate the particles according to their aerodynamic diameter in the size range from 15 nm up to 16 µm.

Each impactor stage was extracted separately with cyclohexane and the amounts of unburned fuel and lubrication oil in the soluble organic fraction (SOF) were determined by gas chromatography with flame ionization detector (GC-FID).

## INFLUENCE OF THE TEMPERATURE DURING DILUTION

In previous investigations higher emissions of particles in the size range from 10 nm to 30 nm were detected for RME compared to other fuels.

Therefore a series of investigations were started especially concerning the emissions of these nuclei mode particles. 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 [16].

The influence of the dilution temperature on the particle size distribution was investigated at the example of RME and DF<sub>ref</sub>. Each measurement was fourfold repeated in mode 9 (1800 min<sup>-1</sup>; 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.

Figure 2 displays the general scheme of the used hot dilution device developed at the vTI.

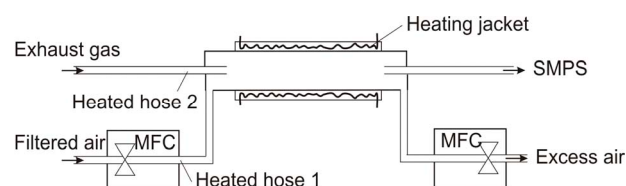


Figure 2. General scheme of the hot dilution device.

Studies were carried out in the temperature range from 20°C to 300°C.

## COMPOSITION OF PARTICULATE MATTER

The soluble organic fraction (SOF) was determined after weighing the filters. The filters were extracted with cyclohexane. The loss of weight after extraction corresponds to the weight of the 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. Ion chromatography was used to examine the WSF for chlorides, sulfates, nitrates and phosphates.

The remaining material on the filter after extraction of SOF and WSF was designated as insoluble fraction (ISF).

## MUTAGENICITY ASSAY

Mutagenicity assays were conducted at the BGFA in Bochum. Every three analogous filters were extracted with dichloromethane (Merck, Darmstadt, Germany) in a Soxhlet apparatus (Brand, Wertheim, Germany) for 6 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 [17] 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 [18] with the tester strains TA98 and TA100.

Tests were performed with and without metabolic activation by a 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) [18]. For induction of liver enzymes, phenobarbital and beta-naphthoflavone (5,6-benzoflavone) were used instead of Arochlor-1254, which is a mixture of polychlorinated biphenyls (PCB) [19]. 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, and 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 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 exhibited a reproducible dose-response relationship.

## RESULTS

RME showed advantages for all regulated emissions in comparison to the other fuels with exception of NO<sub>x</sub>. With the used DOC further significant reductions in the regulated emissions except NO<sub>x</sub> were achieved.

All fuels were within the EURO III limit for CO of 2.1 g/kWh. RME showed about 56% lower emissions compared with the other three fuels (figure 3).

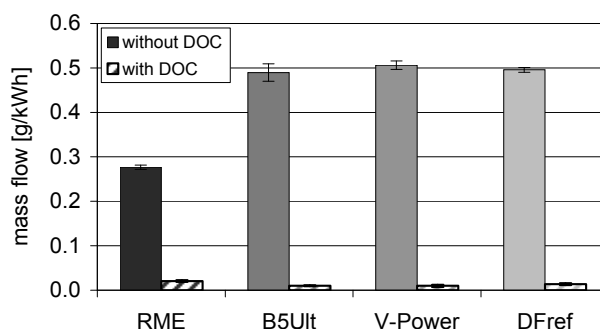


Figure 3. Specific CO emissions.

No differences were observed between B5Ult, V-Power and DF<sub>ref</sub>. Further significant reduction e.g. up to 98% for V-Power could be determined with DOC.

Contrary results were determined for NO<sub>x</sub> emissions. With RME the Euro III limit of 5.0 g/kWh was exceeded, whereas the other fuels remained below it, even when the DOC was used (figure 4).

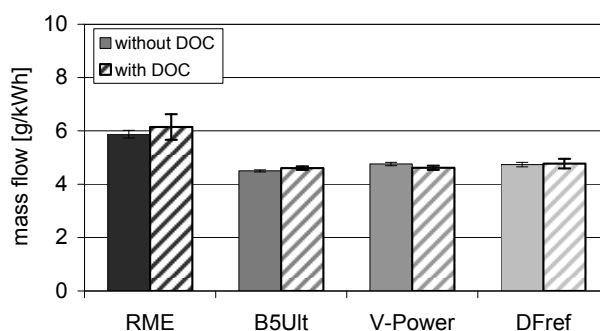


Figure 4. Specific NO<sub>x</sub> emissions.

The DOC caused a slight increase in the NO<sub>x</sub> emissions for the three fuels RME, B5UI and DF<sub>ref</sub>.

Emissions of total hydrocarbons during ESC tests were within the Euro III limit of 0.66 g/kWh (figure 5).