Federal Agricultural
Research Centre

Institute of Technology
and Biosystems Engineering

Research Project Final Report

Comparison of Shell Middle Distillate, Premium Diesel Fuel and Fossil Diesel Fuel with Rapeseed Oil Methyl Ester

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Abbreviations

B5GTL	Blend of RME and GTL (See Table 3-1)
BTL	Biomass to Liquid Fuel
CO	Carbon Monoxide
CO_2	Carbon Dioxide
DF	Diesel Fuel
DEE	Diesel Engine Emissions
DMSO	Dimethyl Sulfoxide
ELPI	Electronic Low Pressure Impactor
EPA	Environmental Protection Agency
ESC	European Stationary Cycle
GTL	Gas to Liquid Fuel
HC	Hydrocarbons
IARC	International Agency for Research on Cancer
MAK	German Guideline for Maximal Workplace Concentration
NO	Nitric Oxide, Nitrogen Monoxide
NO_2	Nitrogen Dioxide
NO_x	Nitrogen Oxides ($NO + NO_2$)
PAH	Polycyclic Aromatic Hydrocarbons
PDF	Premium Diesel Fuel (See Table 3-1)
PM	Particulate Matter
PTFE	Polytetrafluoroethylene
RME	Rapeseed Oil Methyl Ester
SMDS	Shell Middle Distillate
SMPS	Scanning Mobility Particle Sizer
TRGS	German Technical Rules for Dangerous Substances
TRK	German Technical Concentration Guidelines
UFP	Ultra-fine Particles (average diameter $< 0.1\ \mu m$)
WHO	World Health Organization

Index

Summary and Outlook

In its report on sustainable development (Presse- und Informationsamt der Bundesregierung, 2004) the previous German government reached the conclusion for fuels that by 2020 the increase in efficiency in diesel and Otto engines as well as innovative power generation concepts will play a central role. Biofuels such as biodiesel will in the future particularly be incorporated as components of blends. The same conclusion was reached by the previous German government for the future use of both Gas to Liquid fuels (GTL) as well as Biomass to Liquid fuels (BTL). Even if in the report it is assumed that mentionable production capacities for BTL will first be available beginning in the year 2010, for comprehensive use, both bio-diesel and BTL blended diesel fuels must be tested in terms of environmental effects from the exhaust gas emissions. The project can be seen as a partial project for research to be conducted in the future to test fuel quality with biogenic fuel components.

This final report informs about a network project of the Institute for Technology and Biosystems Engineering of the German Federal Agricultural Research Centre (FAL) in cooperation with the Steinbeis Transfer Center for Bio Fuels and Environmental Measurement Technology in Coburg and the Center for Occupational and Social Medicine at the University of Göttingen.

The goal of the project was to make comparative exhaust gas studies using Shell Middle Distillate (GTL) with lubrication additives, fossil diesel fuel (DF), rapeseed oil methyl ester (RME) premium diesel fuel (PDF – comprised of 60 % DF, 20 % RME and 20 % GTL) as well as a blend of 95 % GTL and 5 % RME (B5GTL). In the latter, RME is used as an additive to improve the lubricity. For the studies, a truck engine OM 906 LA from Mercedes-Benz (Euro 3) was used in the ESC test with the mentioned fuel types. The limited exhaust gas components, the particle size distribution as well as the mutagenicity of organically soluble particle fractions are determined.

Overall the GTL fuel consistently produced lower emissions as regular DF, while the particularly low nitrogen oxide emission and the significantly lower mutagenicity are to be emphasized. RME showed advantages in the hydrocarbon, carbon monoxide and particle mass emissions. The premium diesel fuel joins these advantages but causes – like rapeseed oil methyl ester – high emissions of ultra fine particles. While in almost all values, B5GTL showed the expected combination of GTL with little shifting to RME; in the case of premium diesel fuel non-linear effects are seen. These include a lower particle mass emission but also unexpectedly high mutagenicity, the causes of which must be further studied.

In summary, the project served to study the use of fuels with perceptible biogenic content as well as the effects of GTL (pure and in mixtures) on the emissions. In this sense, it can be called a fuel system technical research approach. In addition, GTL is a prototype for future BTL.

The preliminary test series were conducted on a Euro 3 truck engine without exhaust gas after-treatment. Particularly the non-linear emissions and impact changes show that the studies must be extended to Euro 4 vehicles with exhaust gas after-treatment in order to identify the advantages and dangers of random mixtures of fuels, to recognize the interactions, and to pass them on the engine developers. The project is also the start of the future formulation of an engine and environmentally tolerable biofuel that lies in between neat BTL and neat RME. It shows the potential of fuel research and encourages continuing along the path already started.

1. Introduction – The Environmental Relevance of Diesel Engine Emissions

Since the Second World War, diesel engines have been used in many branches of industry and in the fields of transportation and traffic. In addition to their good energy efficiency, the particular environmental tolerability of diesel engines was mentioned in this context, since the carbon monoxide and hydrocarbon emissions are comparably low. This led to a German tax advantage for vehicles running on diesel fuel in the mid 1980s.

Advanced knowledge led to a new evaluation of diesel engines in the past years. At the forefront of these discussions are the significantly higher nitrogen oxide and particle emissions of diesel engines in comparison with the Otto engine. Naturally this is also of significance for the use of biogenic fuels and shall receive particular attention in the framework of this project.

According to the Technical Rules for Dangerous Substances (TRGS), diesel engine emissions (DEE) are only elementary carbons of the particle percentage – obtained after a special filtering procedure (Bundesarbeitsblatt, 1996). The elementary carbon and the organically soluble carbon compounds can be differentiated with coulometric analysis (Mayer et al., 1998). The TRK Value (Technical Guideline concentration) for DEE was previously about 0.1 mg/m_ (TRGS 900). Since the taking effect of the new Dangerous Substance Regulations on Jan. 1, 2005, this threshold is no longer valid. The use of the term “Diesel Engine Emissions” is, however, generally used in a broader sense, because it describes the emissions of gas and particle phases in general.

The genetic and cancerous effects (mutagenicity and carcinogenicity) of DEE have been known for a fairly long time. Although clear proof of the cancerous effect on humans was not yet made, in 1987 DEE were placed in the Group 2 of the Cancerous Work Substances in Germany (MAK List, 2004) due to clear in vitro and animal studies (Heinrich et al., 1986; Ishinishi et al., 1986; Mauderly et al., 1987). The International Agency for Research on Cancer (IARC, 1989), the World Health Organization (WHO, 1996) and U.S. agencies also classified DEE as carcinogenic for humans based on additional evaluation of epidemiological studies (NIOSH, 1988; EPA, 1998). The carcinogenic effect comes from the particle phase with mutagenic substances attached to it. Here, polycyclic aromatic hydrocarbons are of significance (Scheepers and Bos, 1992; Health Effects Institute, 1995). But other health dangers, primarily affecting the upper respiratory tract and the heart and circulatory system, were also observed (Health Effects Institute, 1995).

This project includes a comparison of emissions from the combustion of the fuels Shell Middle Distillate, premium diesel fuel, normal fossil diesel fuel and rapeseed oil methyl ester. Here the legally regulated exhaust gas components, the particle number and particle size distribution in the exhaust gas as well as the mutagenicity of organically soluble particle fractions are considered. These individual exhaust gas components are briefly described in terms of their formation and effect on humans and the environment.

1.1. Regulated Exhaust Gas Components

1.1.1. Hydrocarbons (HC)

The combustion of organic materials ideally follows the described gross reaction equation under the creation of carbon dioxide and water

$$C_n\,H_m + \left(n + \frac{m}{4}\right) O_2 \rightarrow n\,CO_2 + \frac{m}{2} H_2O\,.$$

In real combustion processes, this ideal conversion of fuel to water and carbon dioxide is not achieved. Depending on the engine and its operating conditions (load level, engine temperature, etc.) partially oxidized compounds can develop or unburned fuels can be emitted. The sum of these components are called hydrocarbons, and are measured as a lumped parameter.

Through the multiplicity of substances belonging to this class of substances, no simple statement on the direct impact on humans is possible. Hydrocarbon emissions can sometimes be of low toxicological relevance (i.e., alkanes or alkenes), but they can also be carcinogenic (i.e., benzene). Furthermore, the hydrocarbons are of significance in atmospheric chemistry since some of these substances contribute to the development of summer smog. A correlation between a total hydrocarbon emission value and the resulting health and environmental damage cannot be undertaken due to the complex composition of this group of substances.

1.1.2. Carbon Monoxide (CO)

Carbon monoxide is also the result of the incomplete combustion of fuels. In addition to these engine processes, household and industrial combustion processes, the oxidation of methane in the troposphere as well as the decomposition of chlorophyll can be named as sources of emissions. CO is constantly oxidized to CO_2 in the atmosphere or eliminated by soil bacteria. The average residence time in the troposphere is less than half a year. Through the high conversion of CO in the atmosphere, the main danger is less at the global level than at the local level, and particularly in closed rooms. Carbon monoxide is a colorless and odorless gas and links 250 times more strongly to hemoglobin than oxygen. With increased carbon monoxide concentrations in inhaled air, this suppression of oxygen leads to suffocation symptoms through to death. Acute poisoning occurs beyond 2,000 ppm, sub acute at just 500 ppm CO (Marquardt and Schäfer, 1994). The MAK Value is 35 mg/m_ (MAK List, 2004). Overall the carbon monoxide emissions occurring through engine combustion, in consideration of the other environmental pollution caused by vehicle traffic, is insignificant (Henschler, 1994).

1.1.3. Nitrogen Oxides (NO_x)

The nitrogen oxides nitrogen monoxide (NO) and nitrogen dioxide (NO_2) are, in contrast to CO and HC, by-products of complete combustion. Nitrogen monoxide results as so-called “thermic NO” in the oxygen rich parts of the flame, or in the subsequent reaction zone (Baumbach, 1993) in accordance with

$$O + N_2 \rightleftharpoons NO + N$$

$$N + O_2 \rightleftharpoons NO + O.$$

The reaction begins at about 1300° C as a consequence of the start of oxygen dissociation. In the engine a noteworthy NO level can first be seen beyond about 1900° C (Mattes et al., 1999). In addition the nitrogen oxide known as “prompt NO” results from the reaction of HC radicals with air nitrogen and intermediary developed hydrocyanic acid. (Warnatz et al., 2001). The latter plays only a minor quantitative role. Overall more than 90 percent of the total nitrogen oxide emissions are nitrogen monoxide. Characteristic of NO is its efforts to react with oxygen – and particularly quickly with ozone – to form NO_2. Thus NO wastes ozone. Pure nitrogen monoxide does not irritate the lungs, but if no conversion to NO_2 occurs, it develops methemoglobin after resorption via the respiratory tract. NO is an endogenous modulator of the blood vessel tone and thus a well studied substance in terms of physiology and metabolism (Lenz et al., 1993).

Nitrogen dioxide is a gas with a piercing odor and red-brown color. It irritates the lungs and mucosa at a very low concentration. As a free radical, NO_2 is basically in a position to abstract hydrogen from fatty acids and thus to cause lipid peroxidation. This peroxidation ultimately leads to a loss of function in biological membranes. The destruction of membranes is the higher-ranking toxicity principle, while the lipid peroxidation presents the initial reaction. Living cells counteract this process with protective and reparative mechanisms so that it first occurs by extremely high concentrations of NO_2 which are hardly attainable in the free atmosphere. In the presence of water, NO_2 disproportions to nitrous acid and nitric acid. The nitrous acid (HNO_2) or its salts can react with secondary amines to mutagenic nitrous amines. Nitrite in the blood system can oxidize hemoglobin to methemoglobin through which the capacity to transport oxygen can be lost. NO_2 works in the same way, probably through the nitric acid (HNO_3) which develops as a cellular poison in the respiratory tract. Exposure to 9 mg/m_ NO_2 causes reduced fluidity of plasma membranes. Changes in the fluidity of membranes affect a range of fundamental cellular functions such as transmembrane transport, certain enzyme activities and receptor-ligand interactions. An activation of anti-oxidative enzymes and lipid peroxidation were observed after exposure to about 0.7 mg/m_ NO_2 (Marquardt and Schaefer, 1994). Although the MAK Commission raised the MAK value, the limit of 9.5 mg/m_ (TRGS 900, 2004) is still valid. According to the MAK List (2004), nitrogen dioxide is a substance for which evidence of a carcinogenic effect can be found in in vitro and animal studies. It fits in Category 3B of carcinogenic substances.

Of additional significance is the ability of NO_2 to serve as a preliminary substance for photo oxidant development, particularly for ozone. The leaching of nitrous oxide from the atmosphere takes place through developed nitrous acid or nitric acid and their subsequent wet deposition as so-called acid rain.

1.1.4. Particulate Matter (PM)

In contrast to the concept “diesel engine emissions,” no general definition for diesel particles exists. According to the definition of the Environmental Protection Agency (EPA) in the U.S.A., particles shall be understood in the following as all substances present in diluted exhaust in solid or liquid form at a temperature of under 51.7° C (meaning 125° F) and which can be deposited on a filter (Code of Federal Regulations). The exhaust gas sample temperature is limited to ensure that all organic compounds with higher boiling points that could be of concern for health reasons and which could be adsorbed on carbon particulate matter are documented by the analysis. The temperature reduction of the exhaust gas samples is achieved by mixing the exhaust gas with air in a dilution system. In this manner the exit of the exhaust gas into the environment is simulated.

The emitted particle mass consists of a multiplicity of organic and inorganic substances. The main constituents of the organic substances are unburned or only partially burned fuel and lubrication oil. The inorganic substances include soot (carbon), sulfates, water and metallic compounds. Shavings and rust particles originating directly from the engine or the exhaust gas system, as well as derivates of organo-metallic fuel and lubricant additives, are included in the metallic compounds. The percentage of these substances in the total particle mass is due to many parameters. In addition to constructive parameters such as form of the combustion chamber and design of the injection system, the point of operation, or rather the overall load configuration, the fuel and lubricant quality as well as the wear of the engine are also included here (Wachter and Cartellieri, 1987).

The development of particles is initiated by the soot development in the combustion chamber. Soot develops if the fuel enters an area with high temperature and low oxygen supply. The reactions leading to soot or particle formation are only incompletely clarified in a quantitative manner. The most probable hypothesis is the Acetylene Theory (Klingenberg et al., 1992). According to this theory, crack and dehydration reactions occur at the beginning of the soot development, which lead to the decomposition of long-chain fuel molecules into short-chain unsaturated hydrocarbons like acetylene. Through accumulation, with further hydrogen split off, acetylene develops cyclic and polycyclic aromatic hydrocarbons (PAH). Further addition and dehydration reactions lead to an increase in the carbon portion of the molecules, until ultimately the first particles develop with a diameter of more than 0.001 µm, from which the so-called primary particles coagulate with a diameter of 0.01 to 0.08 µm. The form in which the particles leave the combustion chamber is very diverse. Both small primary particles as well as larger agglomerates that are composed of primary particles and partly form some spatially-branched chains and spherical clusters have been observed (Lipkea and Johnson, 1978; Amann and Siegla, 1982; Jing et al., 1996).

In the consideration of particle development it is always differentiated between the processes in the combustion chamber, those in the exhaust tract, and those in the mixing of exhaust gas with ambient air, i.e. at the exit into the atmosphere.

For the particle development in the combustion chamber, the soot oxidation that starts practically simultaneously to the soot formation is of great significance. The speed of the soot formation, initiated by crack reactions as well as oxidation reactions are strongly dependent on pressure, temperature and air ratio. At high temperatures and low levels of oxygen (small air ratio) the speed of the crack reactions is higher than that of the oxidation reactions, which leads to an increased development of soot. At high temperatures and large air ratios, in contrast, the oxidation speed is higher so that a subsequent soot combustion is possible (Meurer, 1966; Hühn, 1970; Houben and Lepperhoff, 1990).

A non-homogenous mixed preparation of fuel and air in the combustion chamber always causes particle development in diesel engines. These can thus be considered products of incomplete combustion, which can be reduced through higher temperatures, but that at the cost of higher NO_x emissions. These inescapable conflicts are at the moment considered the greatest problem of direct injection diesel engines and are called the “diesel dilemma” or “NO_x / PM trade-off.” Publications show that even modern, direct injection Otto engines tend to show analogue behavior (Lake et al., 1999). To solve this problem, three different methods are used simultaneously: fine tuning of the engine and its injection system, the exhaust gas treatment, and the optimization of fuels. The three methods mentioned should be adjusted to each other in order to reduce the particle and nitrogen oxide emissions at the same time.

In environmental studies it was observed that short increases in particle concentration in the air led to an increase in the number of patients with respiratory and circulatory illnesses brought to hospitals or who die (Dockery and Pope, 1994; Samet et al., 1995; Katsouyanni et al., 1997). Long term studies showed that in urban areas with high particle air pollution featured more chronic respiratory and circulatory diseases than in non rural areas (Dockery et al., 1993; Pope et al., 1995). A study published in 1999 found a link between a risk of lung cancer with particles but also with ozone and sulfur dioxide (Abbey et al., 1999). Overall the available data show that particle emissions could be linked to negative health impacts, above all for sensitive persons (children, older people and the sick). An estimate of the global health risks with consistently increasing particle air pollution resulted worldwide in 8 million additional deaths for the years 2000 to 2020 (Working Group on Public Health and Fossil Fuel Combustion, 1997).

In new studies, the particle size distribution of the emissions is being increasingly considered since fine (< 2.5 µm) and ultra-fine (< 0.1 µm) particles are more strongly linked to health risks than the particle sizes already used for evaluation (< 10 µm) (Seaton et al., 1995; Peters et al., 1997; Frampton et al., 2004). Please see Chapter 1.2.1.

1.2. Non-Regulated Exhaust Gas Components

1.2.1. Number of Particles and Particle Size Distribution

As an enhancement for the measurement of particle mass, the number of particles and the distribution of particle sizes were measured. As described above, very different types of particles exit the combustion chamber. In addition to ultra fine primary particles, agglomerates of these can also be found. Typically, most particles from today's diesel engine run on conventional diesel fuel have a diameter of between 10 and 300 nm.

The health impacts of particles are strongly dependent on their diameter, which makes the measurement of particle size distribution especially important. Epidemiological studies of different research institutes show that the impact of ultra fine particles (UFP) can possibly be stronger than the impact of larger particles. The reason for this is the possible penetration of these particles into the bronchioles and alveoles of the human lung and the subsequent entrance into the bloodstream.

How the UFP function in the body has only been partially clarified. The following characteristics have been observed and different impact mechanisms discussed (Marhold, 2003; Frampton et al., 2004):

- compared to larger particles, the deposition rate of the UFP is increased;
- UFP have a larger surface area in relation to their mass;
- the triggering of infection reactions is more clearly defined;
- UFP have a higher oxidative capacity;
- UFP are reabsorbed from the alveoles and transported through the circulatory system to other parts of the body.

This should lead to different negative health effects:

- increased susceptibility to infection
- infections of bronchial mucosa and the alveoles
- risk for heart and circulatory diseases (heart attack, stroke).

Particularly children and persons with respiratory and vascular diseases should be at higher risk for these effects. However in a study published in December 2004 on health volunteers and persons with mild asthma, only very weak acute symptoms were seen after exposure to carbon UFP (Frampton et al, 2004).

In the meantime, many epidemiologists, toxicologists and other related scientists are calling for a limit on the number of emitted fine and ultra fine particles in addition to the existing exhaust gas laws limiting particle emissions.

An example should show how low the contribution of this particle fraction to the total mass is: If the density 1 g/cm_ and spherical geometry are assumed for the particle, then it holds that one particle of 1µm has the same mass as 64,000 particles with a diameter of 25 nm.

1.2.2. Mutagenicity of the Organically Soluble Particle Fraction

For a health related assessment of different diesel fuels it is necessary not only to determine the exhaust gas emissions from diesel engines but also perform toxicological studies.

Combustion exhaust gases contain a multiplicity of different toxic elements that have not yet be conclusively studied. In the group of PAH-related compounds, far more than 150 individual substances have been identified, of which the larger portion shows a mutagenic or carcinogenic effect. Since chemical analytical proof of all substances in exhaust gas is not technically or financially feasible, and provides no statement on their toxic potency, a laboratory test method was searched for in order to document the genetic impacts of individual substances or mixtures of substances, such as, for example, combustion residues.

In 1973, Ames and his colleagues published the experimental instructions for an in vitro test system which showed the mutagenic characteristics of a broad spectrum of substances through a re-mutation of genetically manipulated *Salmonella typhimurium* strains. The study of bacterial mutations has in the meantime gained a permanent place as a scientific method for estimating the gene-toxicological and carcinogenic effects of working substances and chemical pollution of the environment (OECD Guideline 471). Between 80 and 90 percent of the carcinogenic substances have also been shown to be mutagenic (Maron and Ames, 1983).

In 1978, the ability of DEE to cause genetic damage was first shown in an Ames Test (Salmonella Microsome Test) by Huisingh et al., and was then confirmed in further extensive studies (Clark and Vigil, 1980; Claxton and Barnes, 1981; Siak et al., 1981; Belisario et al., 1984).

2. Materials and Methods

2.1. Engine and Engine Testing Conditions

The studies were carried out on an emissions test facility of the Institute for Technology and Biosystems Engineering at the German Agricultural Research Centre in Braunschweig. A modern Mercedes-Benz engine OM 906 LA with a turbocharger and intercooler is available (Table 2-1).

Tab. 2-1: Technical data of the test engine OM 906 LA

Stroke of cylinder	130 mm
Bore of cylinder	102 mm
Number of cylinders	6
Stroke volume	6370 cm^3
Normal rate of revolutions	2300 min^{-1}
Rated power	205 kW
Maximum torque	1100 Nm at 1300 min^{-1}
Exhaust gas standard	Euro III

This six cylinder engine works with a pump line injector system. The version mounted at the emissions test stand is the same as a motor in compliance with EURO III emission limits. Mercedes Benz builds this engine for their truck line ATEGO, for city busses and for UNIMOG among others.

The crankshaft of the test engine is coupled with a controllable eddy-current brake which determines the engine load and thus enables an automatic drive to different load points. In the framework of this project all test processes were carried out in accordance with the regulation of the ESC Test Cycle (European Stationary Cycle). In Fig. 2-1 the preset torque and revolution rates, related to the maximal load or to the normal rate of revolutions, are presented graphically.

The time course is given through the numbering of the individual operating points, the weighting is, in each case, denoted above the individual point. Fig. 2-2 shows the implementation of these requirements, meaning the actual course on the emission test stand of the institute. In order to document that this course was recorded at a single run, the number of the experiment and the fuel used are denoted in the figure caption.

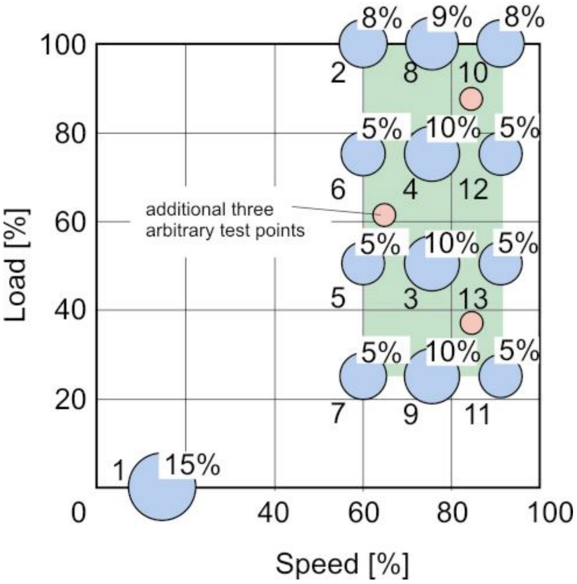

Abb. 2-1: ESC test cycle

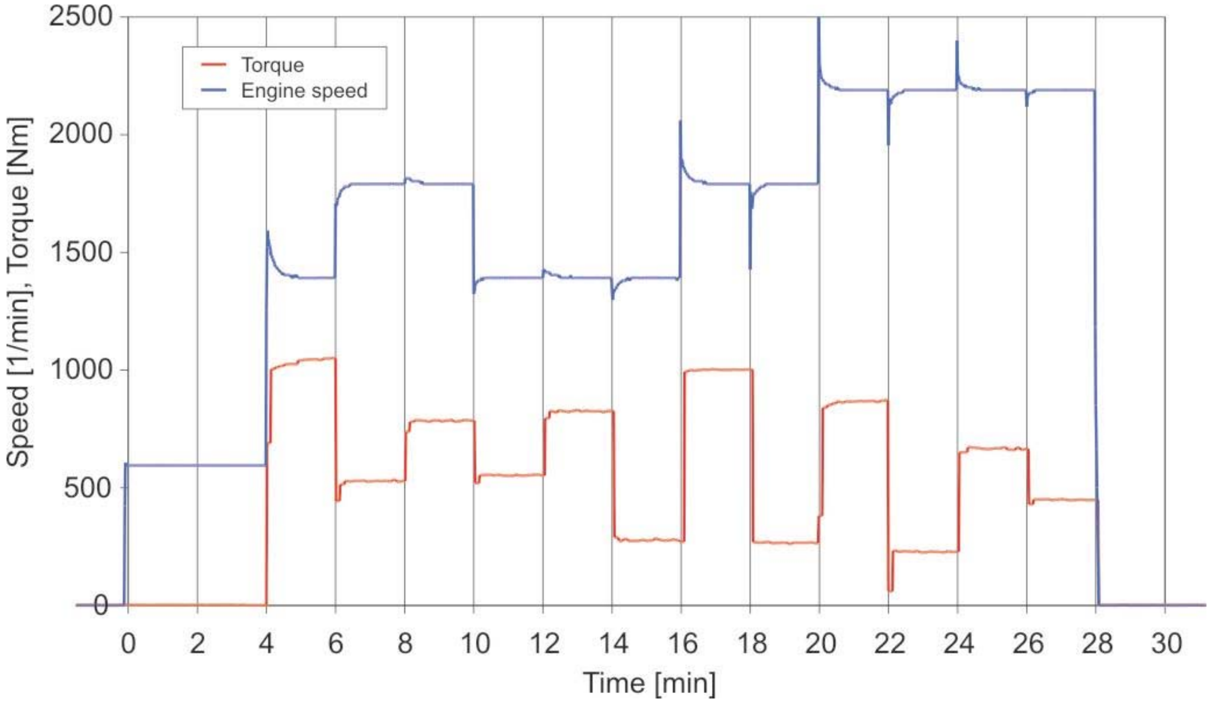

Abb. 2-2: Actual course of speed and torque (Run SMDS06, PDF)

Further variables noted during the ESC test are presented in the Appendix in Figures A-1 to A-8.

To determine the individual emissions, at least three repetitions of the ESC cycle were carried out. Since individual samples could not be taken simultaneously (i.e., samples for PM emissions and mutagenic tests), between six and nine measurements were carried out to completely determine all emissions.

2.2. Fuels

A total of five fuels were studied. They can be found in the following table with the appropriate abbreviations.

Tab. 3-1: Studied fuels

Fuel appellation	Fuel
PDF	Premium Diesel Fuel 60 % (v/v) DF 20 % (v/v) RME 20 % (v/v) GTL with additive
GTL	Shell Middle Distillate (SMDS) with additive (Gas to Liquid Fuel)
B5GTL	Blend 5 % RME with GTL 95 % (v/v) GTL without additive 5 % (v/v) RME
RME	Rapeseed Oil Methyl Ester
DF	Fossil Diesel Fuel

GTL fuel (with and without additives – related to an additive to improve its lubrication ability) was delivered by Shell Research Ltd., the biodiesel RME was provided by the Oil Mill Leer Connemann GmbH & Co. KG, the DF from Haltermann Products BSL Olefinverbund GmbH in Hamburg. The so-called premium diesel fuel PDF and the blend B5GTL are mixtures of these fuel qualities.

The background behind the formulation of the premium fuel is the consideration that biodiesel in its pure form can only be used in commercial vehicles or approved cars without a particle filter (DPF). A maximum portion of 5 % RME in DF is today the probable upper limit for compatibility with diesel particle filters. Maybe a B20 fuel (20% RME and 80% DF) will be appropriate in the future. The inclusion of 20 % GTL to DF and RME was carried out because GTL can at the moment be seen as a possible prototype for future Biomass to liquid fuels (BTL). Thus PDF would, in the form tested here, be a forerunner for a diesel fuel with 40 percent biogenic portion, the range of use of which should also be DPF-compatible.

The B5GTL fuel was formulated in order to improve the inadequate lubricity of the GTL fuel without additives through a biogenic additive.

2.3. Analytical Methods for Regulated Exhaust Gas Emissions

The regulated exhaust gas components carbon monoxide, hydrocarbons and nitrogen oxides were determined with a commercial gas analyzer and sampled each second. A mean was determined from the values sampled in the last minute of an operating point.

2.3.1. Hydrocarbons

A gas analyzer from the Ratfisch Company (RS 55-T) was used to determine the hydrocarbons. This measurement instrument works with a flame ionization detector (FID). The test gas is led into a helium hydrogen flame which burns in an electrical field. The hydrocarbons contained in the test gas are ionized through the flame and thus lead to a change in the electrical field, through which the HC content is calculated. The hot and previously filtered exhaust gas is led to the HC analyzer through a pipe, heated to 190° C and controlled by a thermostat. The purpose of the heated gas path is to prevent a premature condensation of the hydrocarbons with a high boiling point.

2.3.2. Carbon Monoxide

The CO gas analyzer Multor 710 (Maihak Company) works with non dispersed infrared light (NDIR process). Here the test gas flow (filtered and cooled below its dew-point) is divided into two equal flows each flowing through a cuvette. One of the cuvettes is irradiated with an infrared light, the wavelength of which is tuned to the characteristic absorption of carbon monoxide. Thus this partial flow is heated and it leads in a joint canal of both cuvettes to a compensatory flow which is measured through a micro flow sensor and a can be calibrated as a measure for the content of the component CO.

2.3.3. Nitrogen Oxides

The nitrogen oxides are analyzed with a chemical luminescence detector (CLD) from the EcoPhysics Co. (CLD 700 EL ht). In the oxidation from NO to NO_2, about 10 percent of the NO_2-molecules reach an electronically stimulated condition, from which they immediately, and under the emanation of protons, return to a non stimulated condition (luminescence). These photons are identified and are a measure of the NO content. To determine the total content of NO_x ($NO + NO_2 = NO_x$), a branch current of the hot and filtered sample is first led through a converter in which NO_2 is reduced to NO. The nitrogen dioxide content is calculated as the difference in the measured values of NO_x and NO.

2.3.4. Particle Mass

The taking of samples to determine particle mass takes place in an exhaust gas branch flow dilution tunnel (Fig. 2-3), which dilutes the exhaust gas and cools it to under 51.7° C. The particles are collected in a two stage filter, from which the branch flow stream is taken from the diluted exhaust gas and channeled through the filter. With the help of a mass flow controller, a defined volume flow is achieved. The total volume V_{SAM} that is drawn through the filter, results from the requirement that the filter time for each testing phase must be at least 4 seconds per 0.01 weighting factor. This must also take place as late as possible and may not be concluded earlier than five seconds before the end of the phase. For the sample taking, a dilution factor is calculated for each operating point and the mass flow controller is set in such a manner that it is in accordance with the weighting in the ESC test. Each sample-taking then takes 60 seconds and ends three seconds before the end of the mode point. Here the dilution level is constantly monitored so that the exhaust gas sample volume can be corrected through a lengthening or shortening of the sample time as needed. The weighting factor which results from the following equation must be kept at ±7 %.

$$\frac{\mathrm{V}_{\mathrm{SAM,i}} \cdot \sum_i \left(\mathrm{V}''_{\mathrm{EDF,i}} \cdot WF_i\right)}{\mathrm{V}_{\mathrm{SAM}} \cdot \mathrm{q}_{\mathrm{i}} \cdot \mathrm{V}''_{\mathrm{EDF,i}}} \overset{!}{=} \mathrm{WF}_{\mathrm{i}}$$

with

$\mathrm{V}_{\mathrm{SAM}}$: Total volume of samples
$\mathrm{V}_{\mathrm{SAM,i}}$: Volume of sample in mode point i
$\mathrm{V}''_{\mathrm{EDF,i}}$: Volume flow of exhaust gas in mode point i
WF_{i}: Weighting factor of mode point i
q_{i}: Exhaust gas dilution factor i.

The filters are PTFE coated fiberglass filters (T60A20, Pallflex Products Corp.) for which the gravimetric analysis is conducted with a microgram scale (Sartorius M5P)

The particulate emission can then be calculated as

$$PT = \frac{M_{PF} \cdot \sum_i \left(\mathrm{V}''_{\mathrm{EDF,i}} \cdot WF_i\right)}{V_{SAM} \cdot \sum_i \left(P_i \cdot WF_i\right)}$$

with

PT: Specific particulate emission
M_{PF}: Total mass on the particle filters
$\mathrm{V}_{\mathrm{SAM}}$: Total volume of samples
$\mathrm{V}''_{\mathrm{EDF,i}}$: Volume flow of exhaust gas in mode point i
WF_{i}: Weighting factor of mode point i
P_{i}: Power in mode point i.

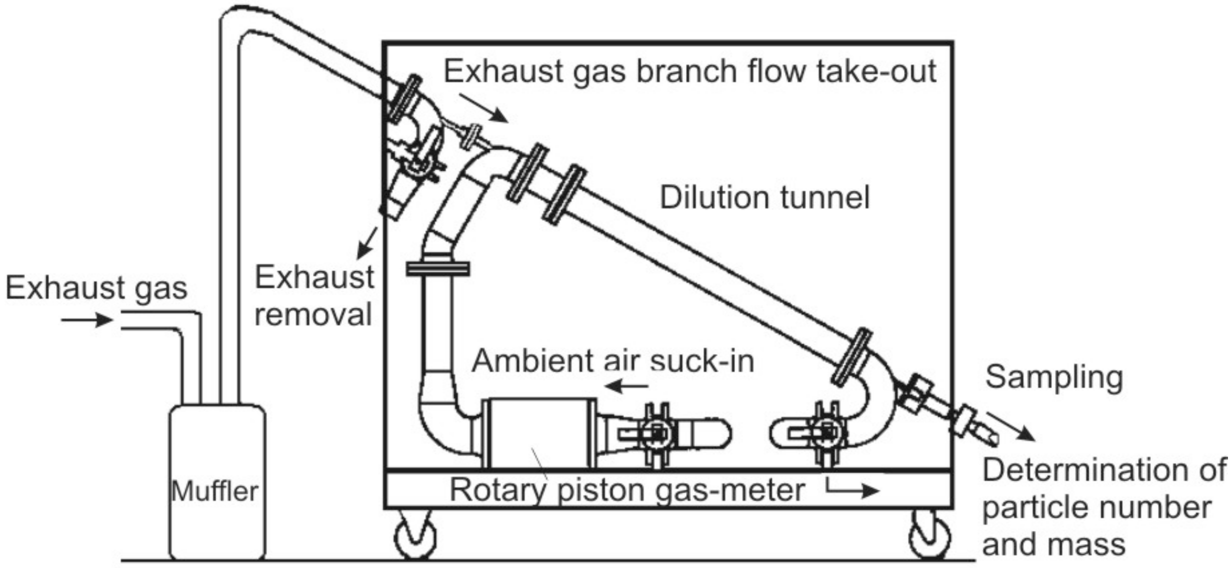

Fig. 2-3: Schematic presentation of the exhaust gas dilution tunnel

2.4. Analysis Methods for Non-regulated Exhaust Gas Emissions

2.4.1. Number of Particles and Particle Size Distribution

Determination with the SMPS (Scanning Mobility Particle Sizer)

The determination of the particle distribution takes place after the taking of samples with a multi-hole probe at the end of the exhaust gas dilution tunnel through a Scanning Mobility Particle Sizer (SMPS) System from the TSI Company. But a secondary dilution by factor 7 with an additional mixing pipe is required to avoid overloading the measurement instrument.

Principally the SMPS system consists of a size classifier (Differential Mobility Analyzer, DMA) and a condensation particle counter (CPC). Figures 2-4 and 2-5 show the schematic design of the system.

Particles above the SMPS limit are intercepted by a pre-impactor. The exhaust gas with the remaining particles is then passed into a neutralizer through which a load balance of the particles in the form of a bi-polar load division is achieved. The classifier itself consists of two concentrically mounted metal cylinders, the outer of which is grounded. The inner cylinder is constantly surrounded with laminar circulating filtered air (encasing gas) and functions as central electrode to which a time varying negative voltage (20 to 10,000 Volts) is applied. The aerosol also flows laminarly into the classifier. In the electrical field of the two metal electrodes, the positively loaded particles are then accelerated to the central electrode according to their electrical mobility. On the bottom end of the inner electrode, a small slit is made through which only a specific particle size class from the poly-disperse aerosol can leave the classifier. The particle size classes created in this manner have an electrical mobility diameter of 10 to 300 nm. This electrical mobility diameter is determined by density, form and electrical characteristics and must not be identical to the geometrical diameter. The mono-disperse aerosol from the classifier is led into the CPC. There the particles are first enlarged according to the principle of a wet dust collector and then counted with a scattered light measurement technique. A differentiation between solid and liquid exhaust particles or, respectively, exhaust particles and droplets, is not possible with the SMPS equipment.

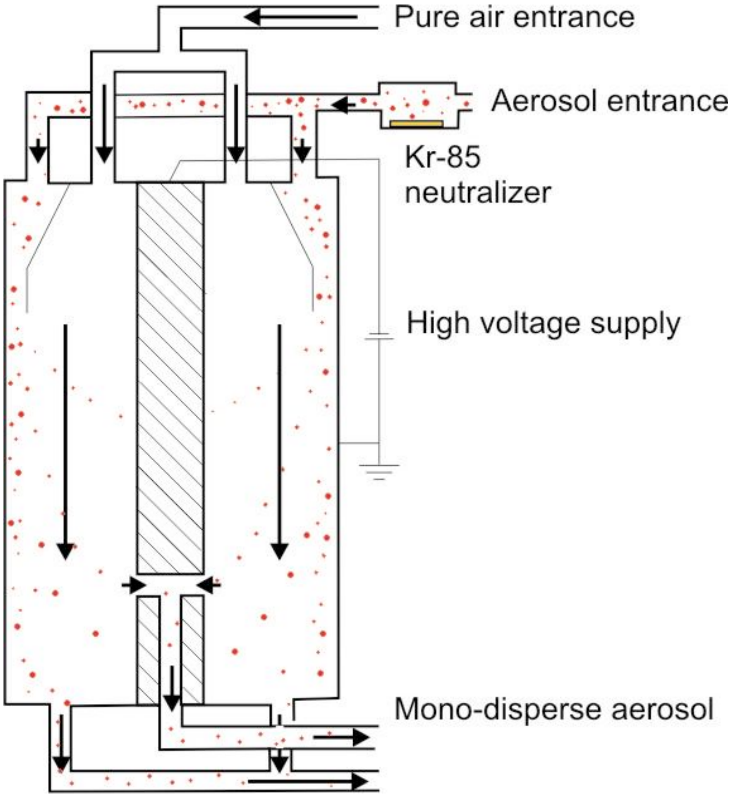

Fig. 2-4: Simplified presentation of a DMA

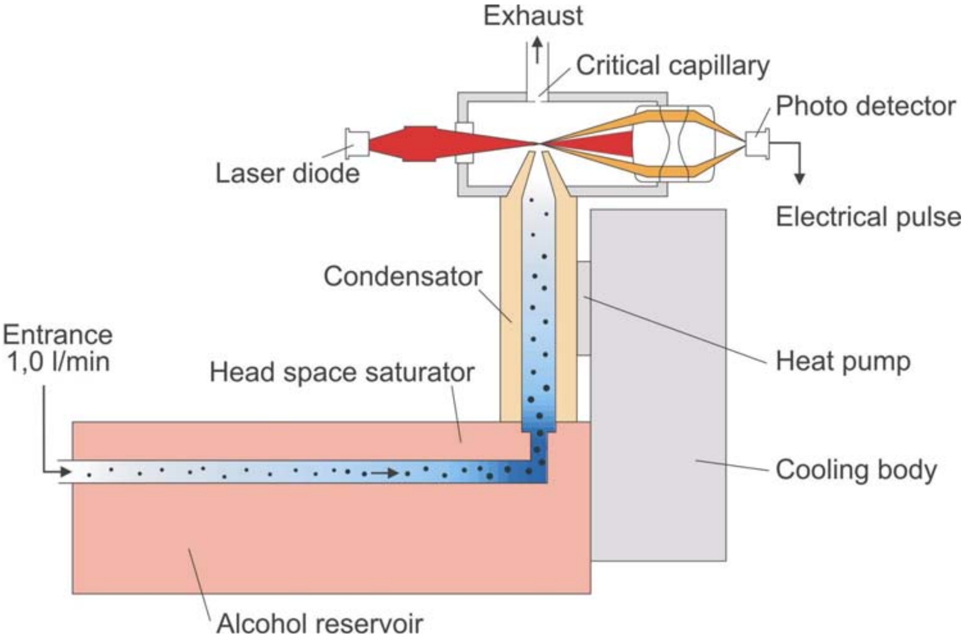

Fig. 2-5: Simplified presentation of a CPC

Determination with ELPI (Electrical Low Pressure Impactor)

As an alternative to the described SMPS, DEKATI Ltd. in Finland offers an “Electrical Low Pressure Impactor” (ELPI). This is a real time particle measurement instrument which covers a size range from 30 nm to 10µm. To filter the particles, the ELPI uses a cascade impactor. This is built in 13 stages, of which the first stage works as a pre-filter and the twelve further stages are monitored electronically.

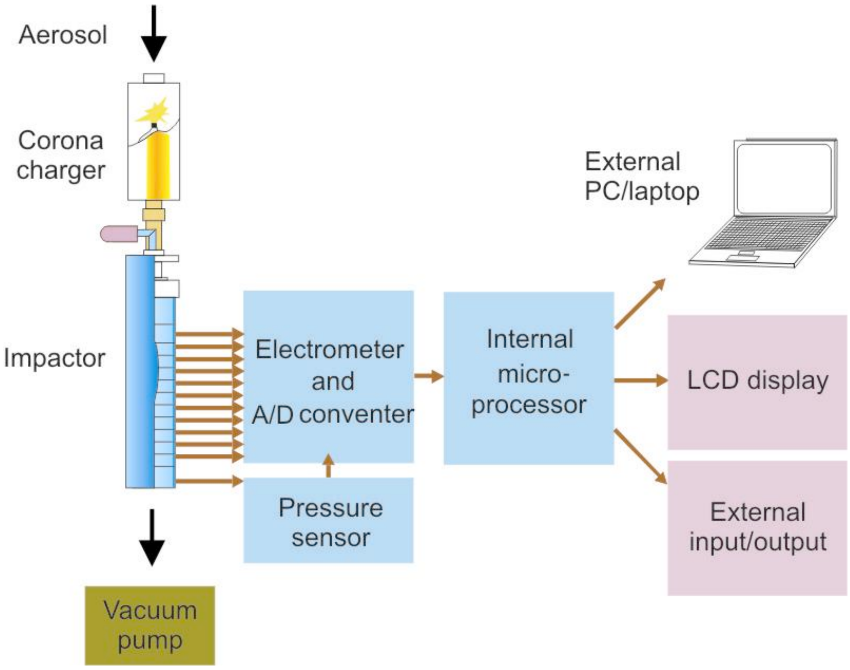

Fig. 2-6: Functioning principle of ELPI (Dekati, 2002)

Fig. 2-6 illustrates the measurement principle of the ELPI. The aerosol probe to be tested is taken via a multi-hole probe located at the end of the exhaust gas dilution tunnel, and first led through an antechamber. There the particles are unipolarly loaded by ions that are produced from a corona discharge. In the subsequent classification in the impactor the particles are then discharged at the appropriate impact stage. The resulting current flow is proportional to the number of particles and is measured by an electrometer. With knowledge of the loading efficiency, which is a function of particle size, and the separation characteristics of the cascade impactor, the current intensities of all single stages can be recalculated in a particle size distribution. This size distribution is always related to the aerodynamic diameter of the particles (Dekati, 2001). With the help of a computer and an evaluation software, which primarily serves to store the data, the results can virtually be followed in real time during a measurement.

Since, depending on the measurement area, ELPI reacts very quickly (2 to 20 seconds) to changes in the aerosol composition, it is particularly well-suited for measuring transient processes. An additional advantage of the ELPI is the simultaneous measurement and presentation of results for all impactor stages. Thus for each particular time point in the measurements, the particle concentration for all size fractions is available.

2.4.2. Mutagenicity of the Organically Soluble Particle Fraction

For the fuel comparison, PTFE coated fiberglass filters (T60A20, Pallflex Products Corp.) are each placed under the same motor conditions. Storage of the imposed filters is at -20° C. The samples are also cooled during the transport to the Center for Occupational and Social Medicine of the University of Göttingen.

The extraction takes place in a Soxhlet apparatus with 150 mL dichloromethane, since the greatest mutagenic activity can be gained with this solution (Siak et al., 1981). The length of extraction is 12 hours and amounts to 50 to 60 extraction cycles. The extracts are then forced into a rotary evaporator, dried in a stream of nitrogen and placed into a dimethyl sulfoxide solution (DMSO), which is non-toxic for the bacteria. Then different concentrations of this total extract are produced and their mutagenic effect tested in the subsequently described Ames Test.

The Salmonella Microsome Test, which is also called the Ames Test after the developer of the assay, exposes the mutagenic characteristics of a broad spectrum of chemical substances and mixtures by re-mutating a series of different test strains (Ames et al., 1973 and 1975). These carry mutations in the histidin operon. The mutations cause a histidin auxotrophy of the test strains in contrast to the wild varieties of *Salmonella typhimurium*, which are histidin prototrophic. The Ames Test is the most widely used and best validated method to test mutagenesis of substances in toxicology and environmental research in the world (OECD Guideline 471). The test was carried out for the strains TA98 and TA100 after a redrafting of the standard protocol by Maron and Ames (1983). TA98 exposes frameshift mutations and TA100 base pair substitutions. The test strains were kindly made available by Prof. B.N. Ames.

In order to consider enzyme-caused changes in mutagenicity in foreign substances in higher organisms, an additional test is used after the exposure of enzymes from warm blooded animals that metabolize foreign substances. The acquisition of these so-called S-9 fractions from rat livers follows the description by Maron and Ames (1983). Nembutal and ß-Naphthoflavon were used instead of Arocholor for enzyme system induction (Matsushima et al., 1976).

As a positive control the mutagens methylmethane sulfone, 3-nitrobenzanthrone and 2-aminofluorene are used. All samples were tested in parallel both without a metabolizing system as well as with four percent S-9 additives in four different concentrations of the extracts. The double tests series were repeated at least three times. According to criteria by Ames, a doubling of the mutations vs. the controls (spontaneous mutation rates for TA98 = 20 to 35 per plate, for TA100 = 120 to 140) with simultaneous dose-dependent increase of mutations is evaluated as a positive result.

3. Results

For all evaluations at least three measurements were included (unless otherwise stated), whereby the average was created from all individual results. Overall more than 50 engine test runs were needed, since not all measurements or sample takings could be carried out in parallel. The measurements were carried out in two measurement campaigns: In the first the fuels PDF, GTL, DF and RME were compared to each other. In a second measurement series, B5GTL was compared to GTL, DF and RME. At the two instants the room temperatures differed significantly. In the first measurement campaign, the temperature was about 15° C, in contrast in the second series the temperature was up to more than 30° C. These climatic differences had an effect on the measurement results for CO, NO_x and the particle size distribution.

For the common presentation of results from the measurements of both measurement series, the approach was as follows: concerning CO and NO_x, the results for B5GTL were both corrected by adding the deviation that also occurred with other fuels between the two measurements. The results for the particle size distribution are discussed separately.

3.1. Results for the Regulated Exhaust Gas Components

3.1.1. Hydrocarbon Emissions

The limit according to the Exhaust Gas Regulation EURO III for the test carried out is 0.66 g/kWh. The measured values were significantly lower for all types of fuel (Fig. 3-1). In addition the clear advantage of rapeseed oil methyl ester can be seen. The hydrocarbon emissions of PDF and B5GTL are about the same as these emission levels, which theoretically result from addition of the partial emission values for the neat components.

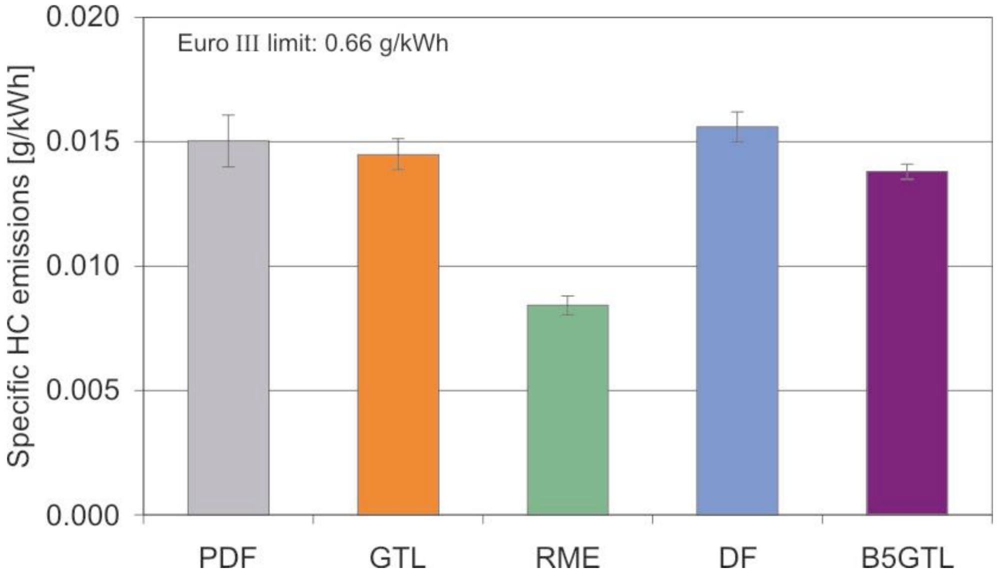

Fig. 3-1: Specific HC emissions

Fig. 3-2 shows the exemplary course of the hydrocarbon concentration in exhaust gas in the course of time of the ESC test. A comparably high emission level can be seen in the idling time and in the weak load points. Emission peaks caused by load changes remain unconsidered since for the evaluation only measurement values from the last minute of each operating point were used.

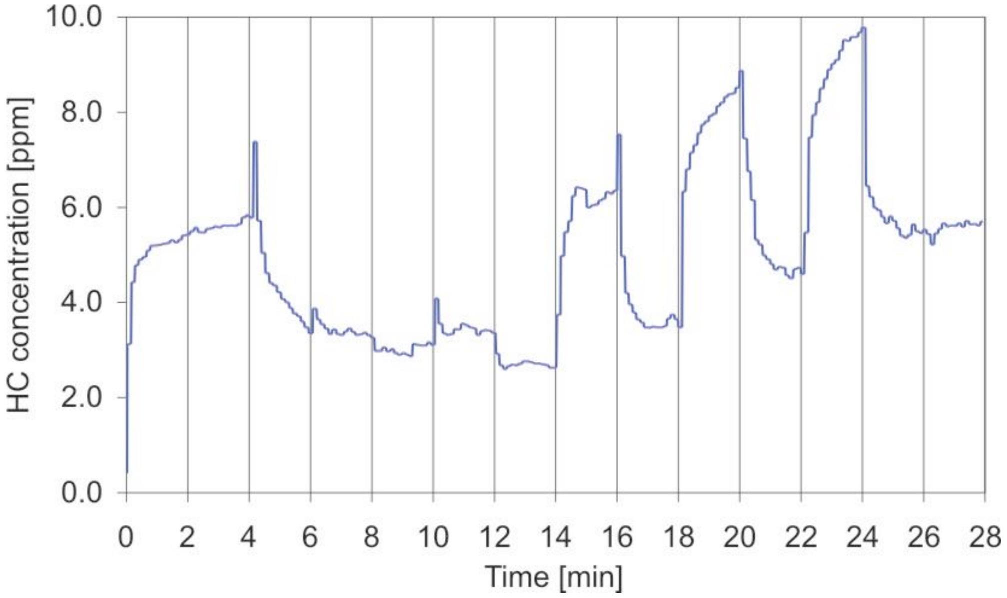

Fig. 3-2: Exemplary course of the HC concentrations (Run SMDS23, GTL)

3.1.2. *Carbon Monoxide Emissions*

The CO emissions for all fuels are far under the limit of 2.1 g/kWh for Euro III engines. Rapeseed oil methyl ester shows again clear advantages, but the premium diesel fuel also causes lower CO emissions than the usual diesel fuel and GTL (Fig. 3-3). The CO emissions of PDF are also somewhat lower than they could theoretically be expected to be (0.42 g/kWh). The CO emissions of B5GTL are in contrast as expected, just slightly under those of GTL.

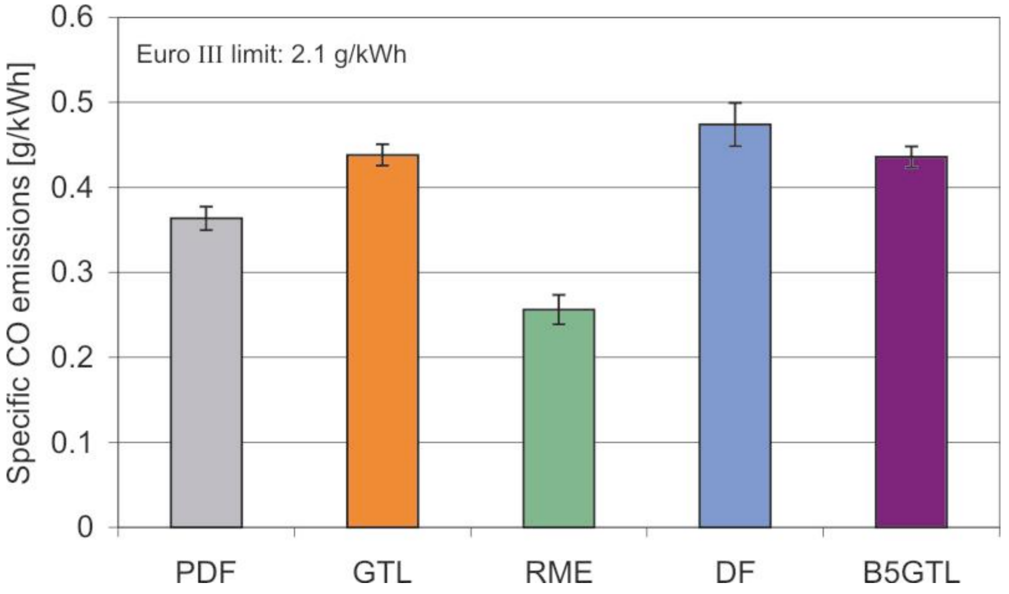

Fig. 3-3: Specific CO emissions

The carbon monoxide concentrations in exhaust gas in the time course of the ESC test cycle are presented in Fig. 3-4. Here too, the peak emissions occurring at the first load point after idling (after 4 minutes of the test cycle) do not enter into the above results.

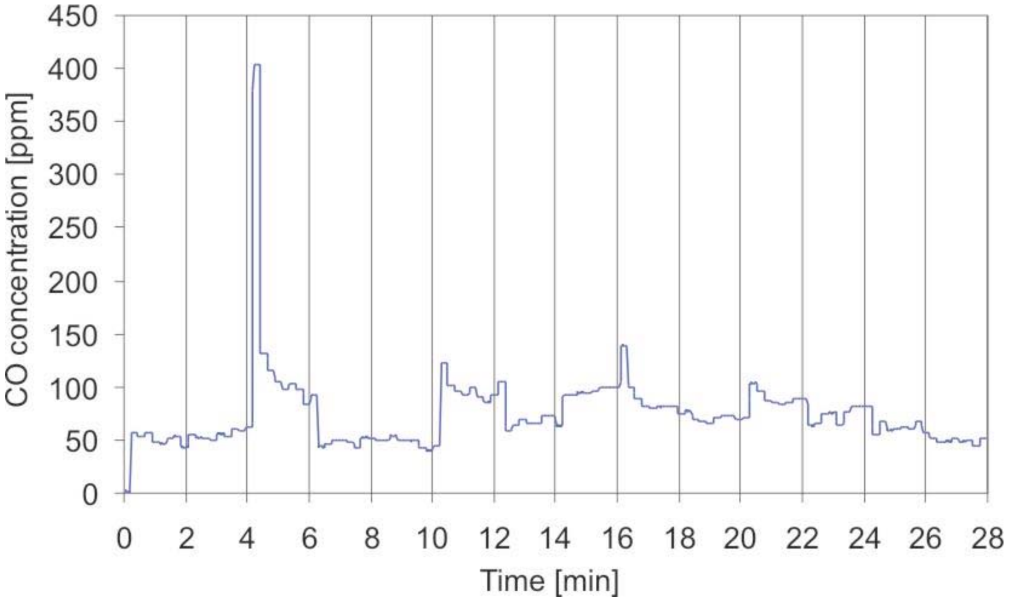

Fig. 3-4: Exemplary course of the CO concentrations (Run SMDS23, GTL)

3.1.3. Nitrogen Oxides Emissions

The Euro III limit of 0.5 g/kWh was exceeded by rapeseed oil methyl ester whereas the other fuels are just below this limit (Fig. 3-5). This result underscores the significance of this toxic substance for the diesel engine and emphasizes the good results of the GTL fuel. The premium diesel fuel also profited here above average and lies both under the limit as well as just under the theoretical value of 4.8 g/kWh; calculated from the emission values on the basis of percentage of the neat fuels. As expected, the percentage of RME in B5GTL increases the emissions slightly over GTL.

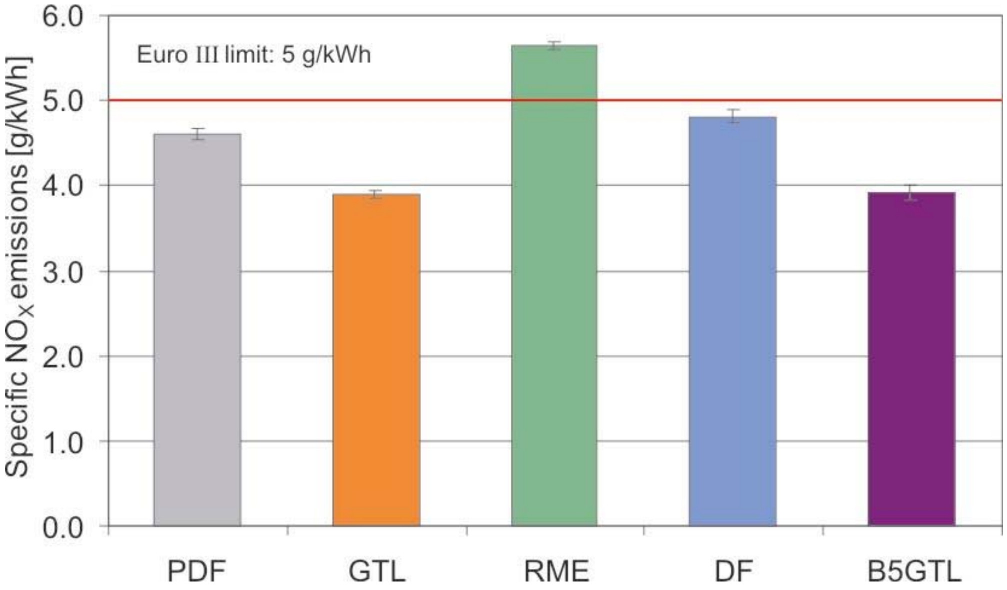

Fig. 3-5: Specific NO_x emissions

Figure 3-6 shows the exemplary course of nitrogen oxides concentrations in exhaust gas in the time course of the ESC test. The nitrogen oxides are primarily emitted as nitrogen monoxide; nitrogen dioxide, in comparison, only plays a minor role. In contrast to the HC and CO emissions, the heavy load points with accordingly high combustion temperatures are the cause of high emissions.

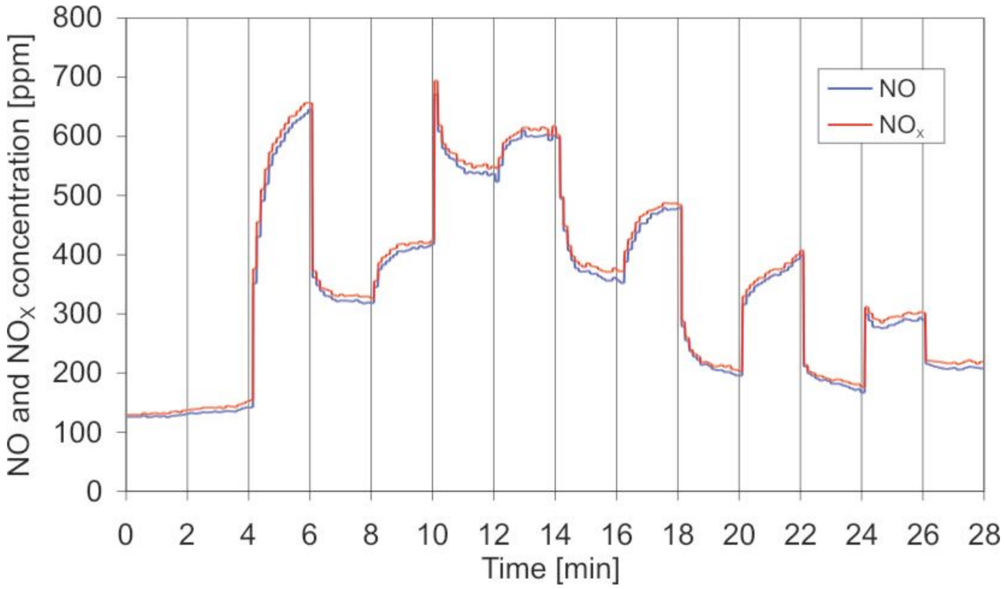

Fig. 3-6: Exemplary course of the NO and NO_x concentrations (Run SMDS23, GTL)

3.1.4. Particulate Matter Emissions

The particles are collected on a filter during the course of the ESC test, which is the reason why no differentiation can be made between individual operating points. The use of RME causes a reduction of 55 % vs. DF. PDF and GTL also cause a significant improvement in comparison to DF. The emission limits of maximally 0.1 g/kWh are maintained by all fuels (Fig. 3-7). While the emissions of B5GTL are slightly below the emissions of GTL, PDF features a mixing effect which can be positively evaluated. The emissions are lower than the expected 58 mg/kWh.

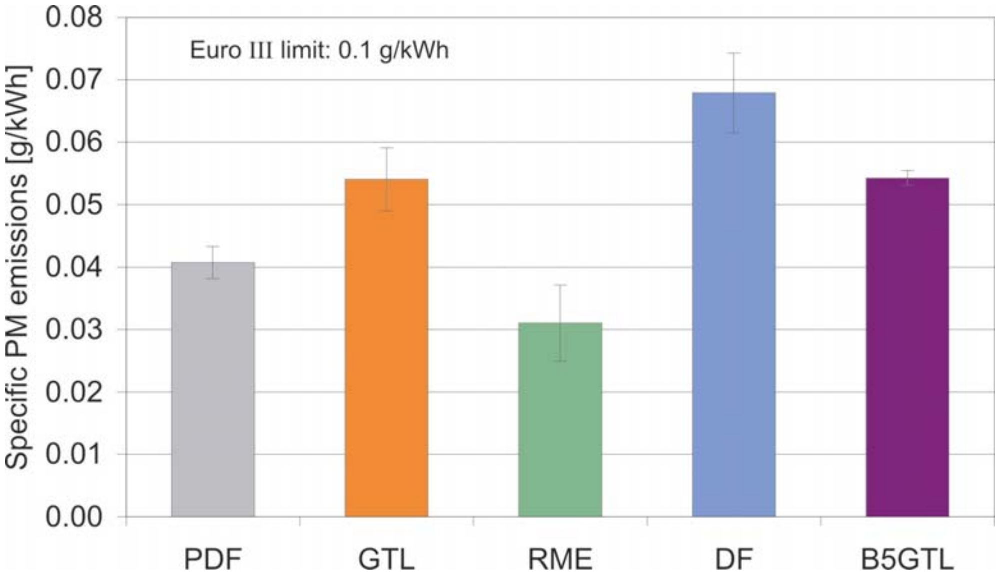

Fig. 3-7: Specific PM emissions

3.2. Results of the Non-regulated Exhaust Gas Components

3.2.1. Number of Particles and Particle Size Distribution

Figure 3-8 shows the particle number distribution measured with the help of the SMPS. Shown here are the averages of at least five individual measurements. The SMPS measurements make clear that the fuels GTL and DF differ only slightly. In contrast, rapeseed oil methyl ester causes an emission of a much higher particle number in the range of ultra fine particles with an electrical mobility diameter of about 20 nm. On the other side, RME shows clear advantages in the further course of the size distribution. The premium diesel fuel also follows this course initially, but is much higher than the RME emissions in the segment of large particles.

In the second test series the results in the area of ultra-fine particles could not be reproduced. The measured emissions of fossil fuels are nearly 10 times less in the range around 10 nm. (Fig. 3-9). This could be an indication concerning the composition of the ultra-fine particles. Since the temperature of the diluted exhaust gas in the second measurement campaign was between 30 and 50° C, and thus up to 20° C higher than in the first measurement campaign, fluid particles could have evaporated and thus reduced the number of particles in the ultra fine category. On the other hand, all particles larger than 30 nm appear to be strongly increased in comparison to the first test series. The cause for these measurement results must be clarified in further experiments; time constraints made it impossible to address this question in the framework of this study.

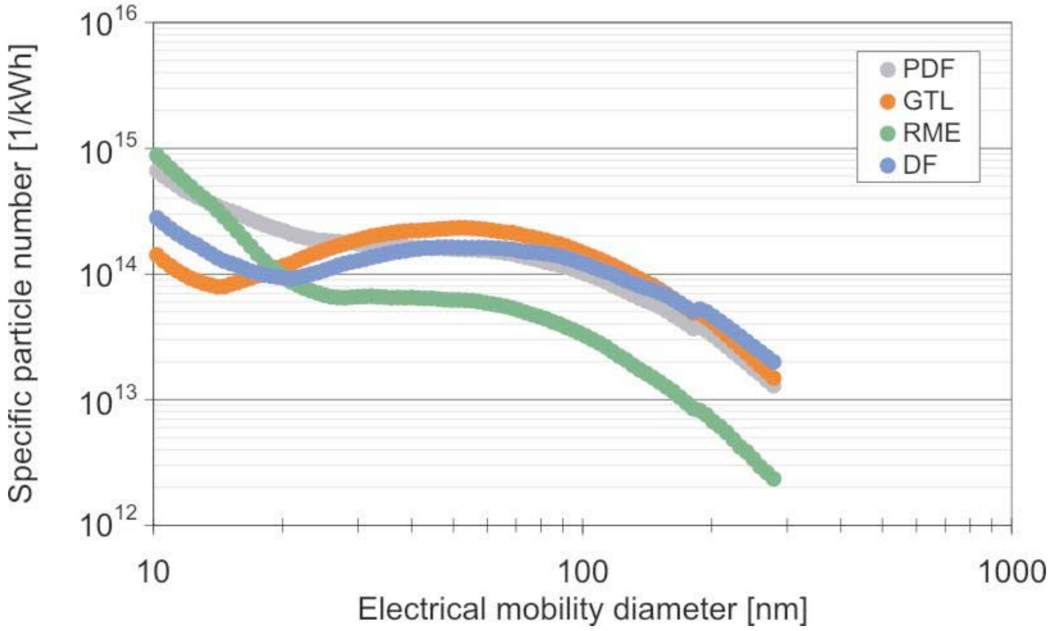

Fig. 3-8: Specific particle number distribution in crude exhaust gas (SMPS – 1st test series)

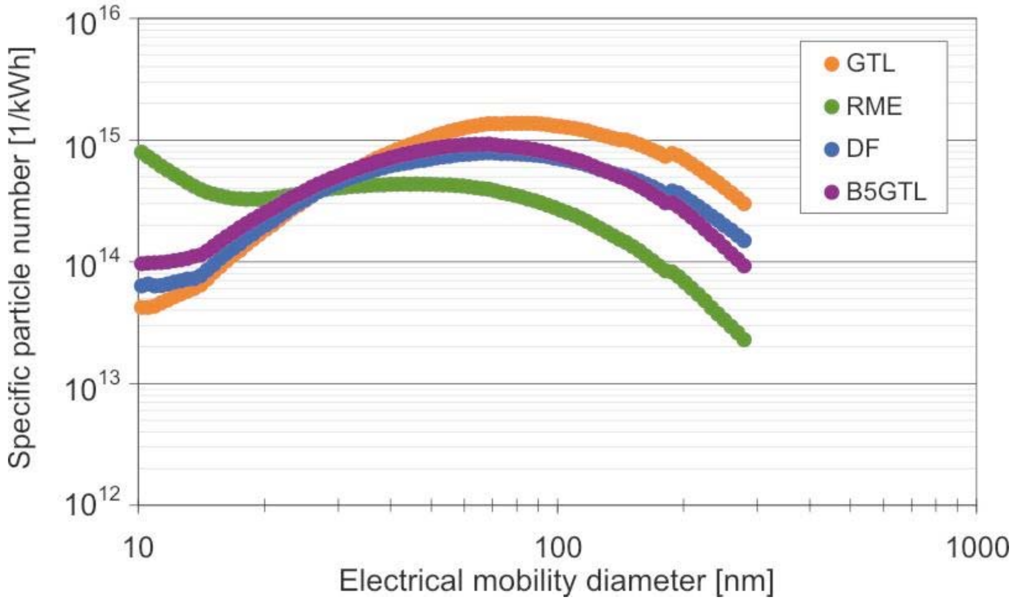

Fig. 3-9 Specific particle count distribution in crude exhaust gas (SMPS – 2nd test series)

Since the individual SMPS measurements for the studied fuels used to develop the mean values vary strongly in part, these are shown in the following figures in detail.

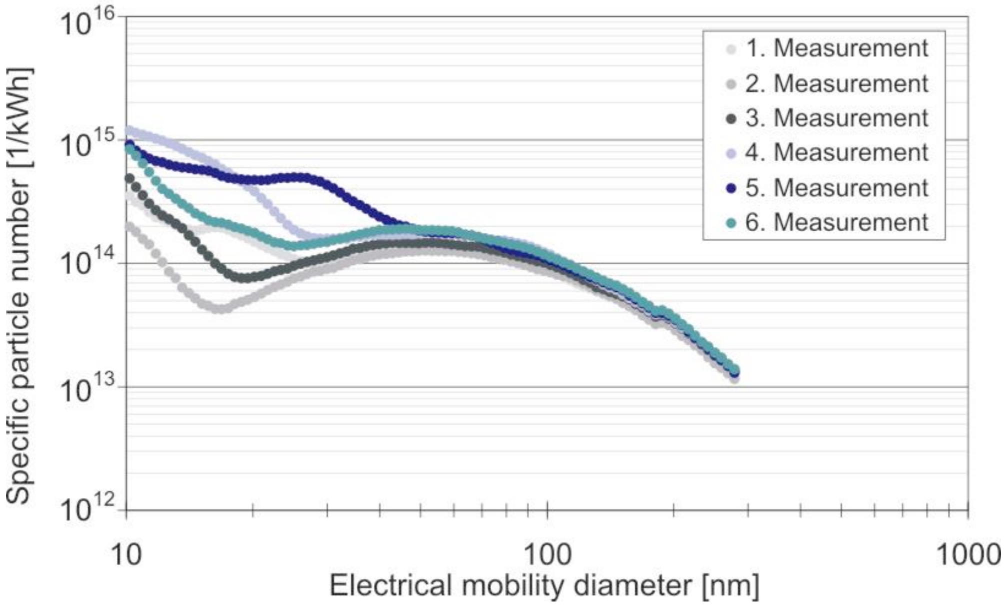

Fig. 3-10: Single measurements for PDF (SMPS – 1st test series)

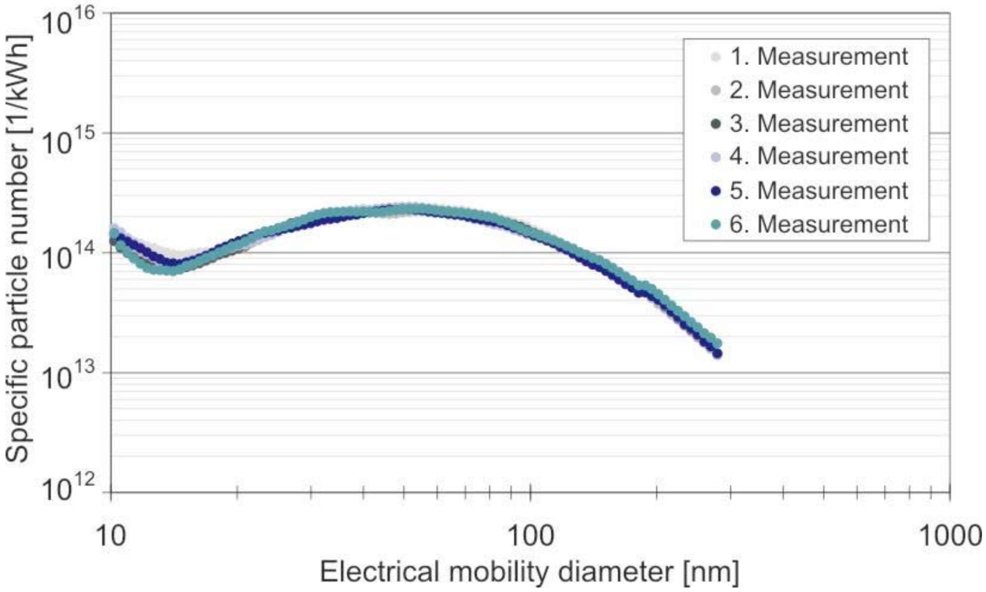

Fig. 3-11: Single measurements for GTL (SMPS – 1st test series)

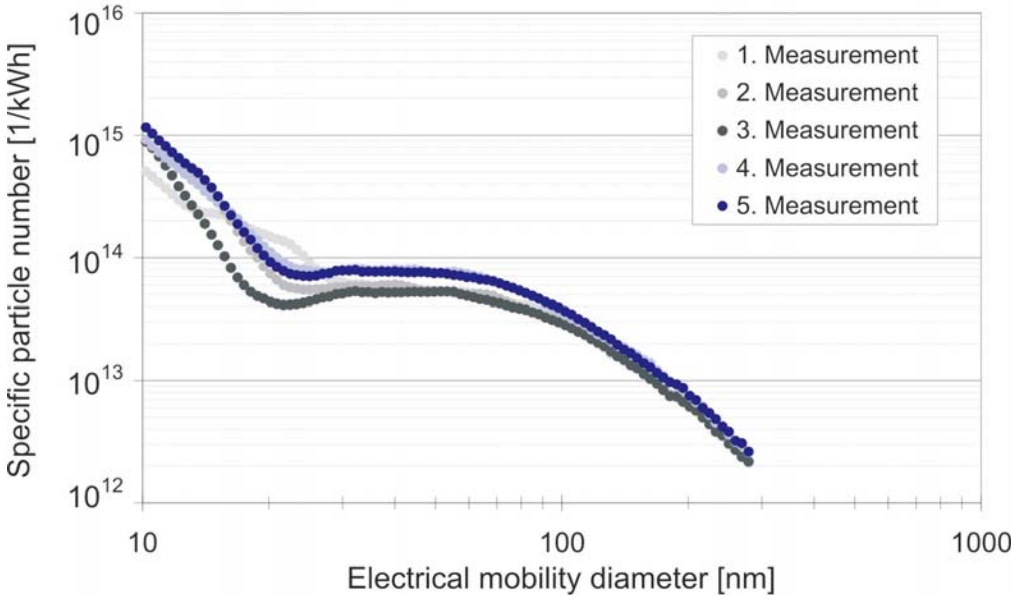

Fig. 3-12: Single measurements for RME (SMPS – 1st test series)

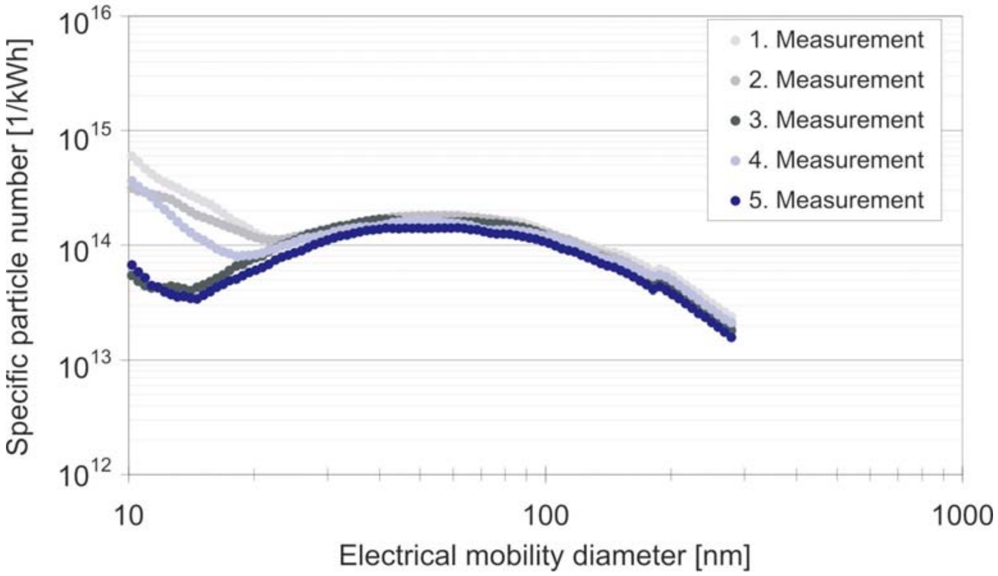

Fig. 3-13: Single measurements for DF (SMPS – 1st test series)

It can be seen from Figures 3-10 to 3-13 that large swings were made between the single measurements, particularly for PDF fuel and DF. The uncertainty here is particularly in the category of ultra fine particles. The causes for this are currently fully open. They are a subject of ongoing studies.

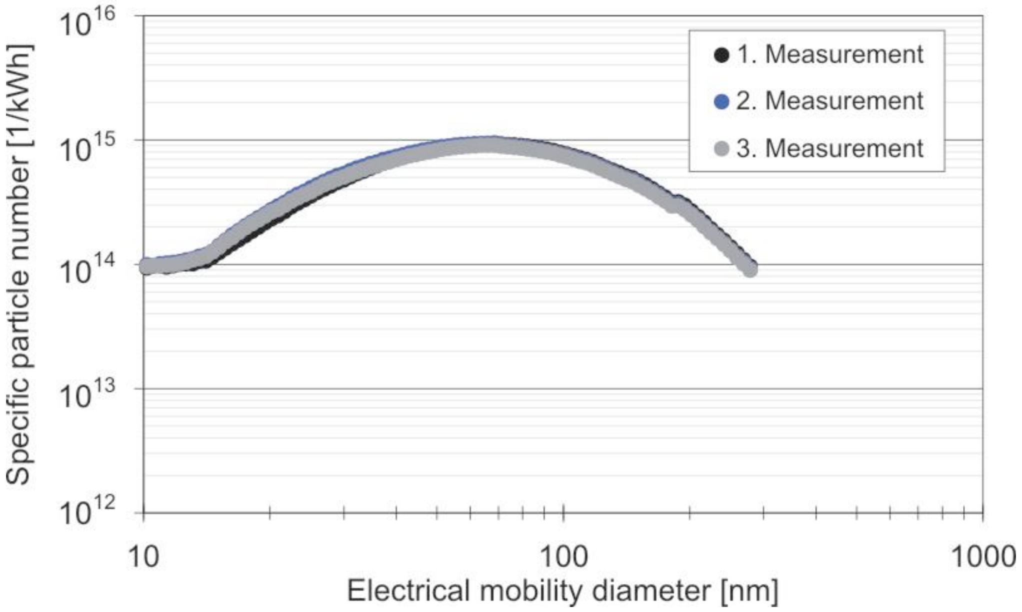

Fig. 3-14: Single measurements for B5GTL (SMPS – 2nd test series)

The ELPI results (Fig. 3-15) confirm the comparable emission behavior for GTL and DF that was already observed in the studies on particle size distribution via SMPS. Caused by the equipment-related measurement range difference in comparison to SMPS, these fuels show here disadvantages vs. RME in all sizes. The Premium Diesel fuel follows the course of GTL in the areas up to 386 nm, but emits considerably fewer large particles. The particle number distribution confirms overall the trend of the PM results from Chapter 3.1.4, although it must be observed that, for the PM determinations, the large particles are of primary significance.

In the second measurement campaign, in contrast to the SMPS measurements, no clear difference could be observed to the measurements of the first campaign. Fig. 3-15 summarizes both measurement series for a better comparison. Although RME shows low emissions throughout the whole measurement range, for GTL and DF no significant difference can be seen. Here it must be stated however, that in the second campaign, only two measurements were taken for RME and GTL and for DF only one measurement. The emissions of B5GTL (here again three repetitions) are generally in accordance with the emissions of pure GTL.

3.2.2. Mutagenicity of the Organically Soluble Particle Fraction

The extraction of the particle filters, which was performed at the University of Göttingen, resulted in similar relations for the total particle mass as for the gravimetric determination in the Institute of Technology and Biosystems Engineering of the FAL in Braunschweig (Fig. 3-16). The lowest PM emissions were measured for RME. The percentage of soluble particle mass varied strongly between the fuels. As earlier studies have shown, RME has a lower percentage of insoluble particle mass in comparison to fuels of fossil origin.

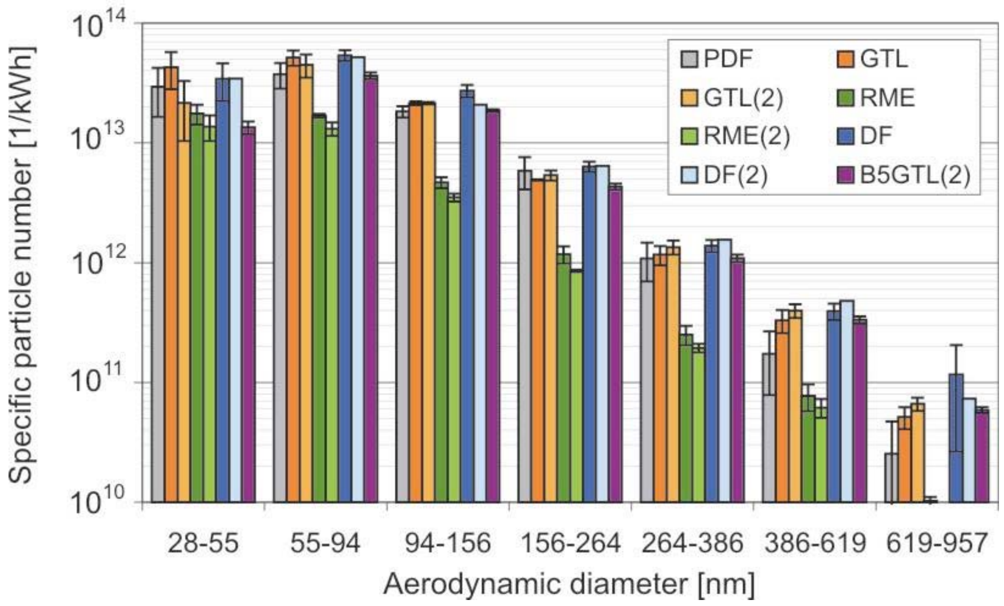

Fig. 3-15: Specific particle number distribution in raw exhaust gas (ELPI)

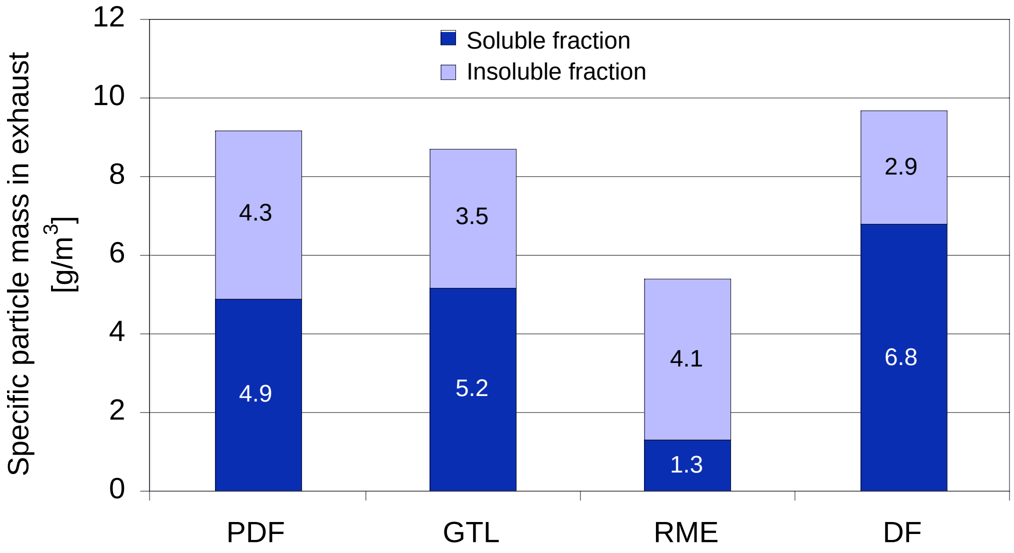

Fig. 3-16: Soluble and insoluble particulate matter fractions in raw exhaust gas

In test strain TA98, the mutagenicity of GTL was significantly lower – compared to the other fuels (Fig. 3-17). An unexpectedly high mutagenicity was found for PDF. The cause of this phenomenon is not yet clear.

In all fuels the direct (-S9) mutagenicity is higher than the indirect (+S9) after metabolic activation of extracts by rat liver enzymes. This speaks for the theory that the largest part of the mutagenicity was caused by substituted PAH (for example, Nitro-PAH). These are mostly direct mutagens while the native PAH require a metabolic activation through the formation of epoxides.

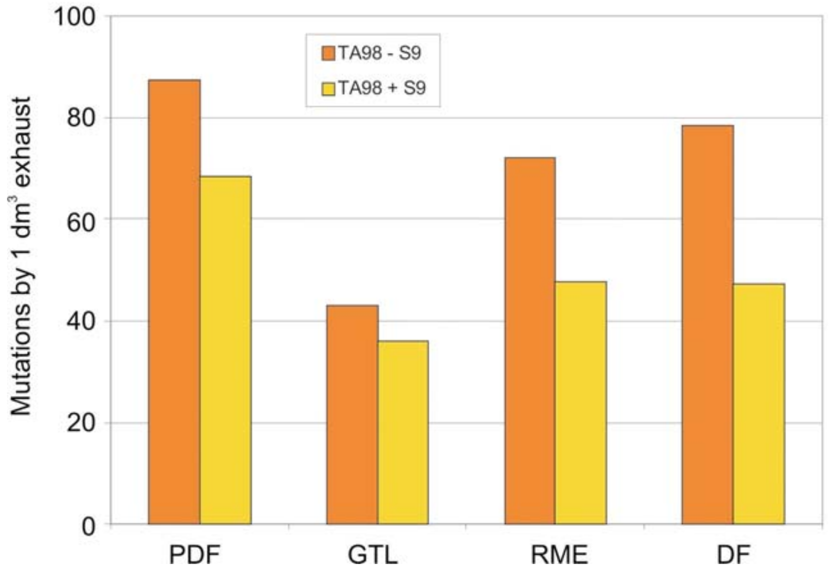

Fig. 3-17: Mutagenicity of particulate matter extracts in strain TA98

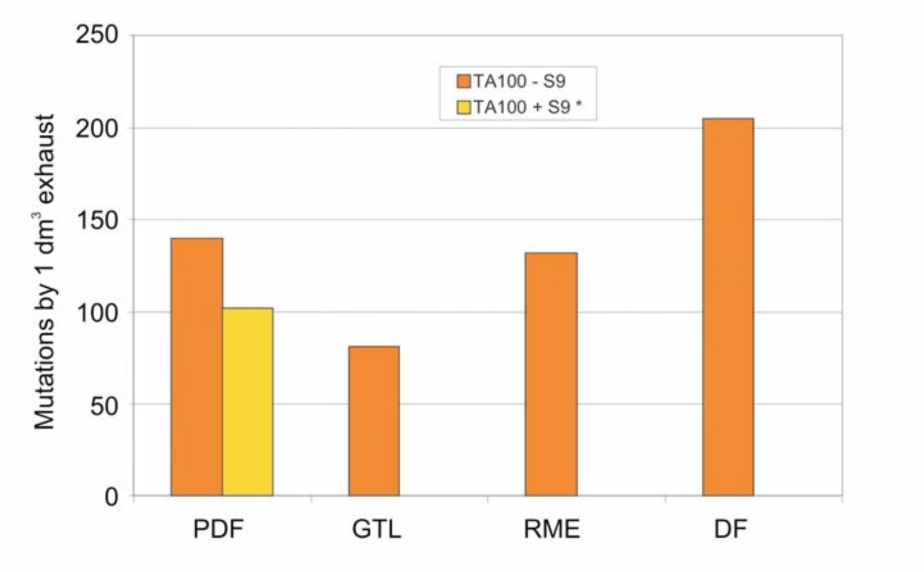

Fig. 3-18: Mutagenicity of particulate matter extracts in strain TA100 (* the number of mutations increased significantly only for PDF)

The fewest mutations in the case of GTL were also found in the somewhat less sensitive test strain TA100 (Fig. 3-18). The PDF with TA100 proves less strongly mutagenic than with TA98, but is the only fuel to show a significant increase in spontaneous mutations in the test with metabolic activation. None of the other three fuels led to a doubling of spontaneous mutations.

References

Abbey D.E., Nishino N., McDonnel W.F., Burchette R.J., Knutsen S.F., Beeson L.W., Yang J.X. (1999). Long-term inhalable particles and other air pollutants related to mortality in nonsmokers. American Journal of Respiratory Diseases and Critical Care Medicine 159, 373 - 382

Amann C., Siegla D. (1982). Diesel particulates - what they are and why. Journal of Aerosol Science and Technology 1, 73 - 101

Ames B.N., Lee F.D., Durston W.E. (1973). An improved bacterial test system for the detection and classification of mutagens and carcinogens. Proc Natl Acad Sci USA 70, 782 - 786

Ames B.N., McCann J., Yamasaki E. (1975). Methods for detecting carcinogens and mutagens with the Salmonella/mammalian-microsome mutagenicity test. Mutat Res 31, 347 - 363

Baumbach G. (1993). Luftreinhaltung: Entstehung, Ausbreitung und Wirkung von Luftverunreinigungen - Messtechnik, Emissionsminderung und Vorschriften. Springer Verlag Berlin, Heidelberg, New York

Belisario M.A., Buonocore V., De Marinis E., De Lorenzo F. (1984). Biological availability of mutagenic compounds adsorbed onto diesel exhaust particulate. Mutation Reseaarch 135, 1 - 9

Bundesarbeitsblatt (1996). Technische Regeln für Gefahrstoffe (TRGS 554): Dieselmotoremissionen (DME), Nr. 3, 69 - 77; geändert durch BArbBl. (1997) Nr. 4, 44 - 45 und BArbBl. (1998) Nr. 5, 58 - 63

Clark C.R., Vigil C.L. (1980). Influence of rat lung and liver homogenates on the mutagenicity of diesel exhaust particulate extracts. Toxicology and Applied Pharmacology 56, 100 - 115

Claxton L.D., Barnes H.M. (1981). The mutagenicity of diesel-exhaust particle extracts collected under smoke-chamber conditions using the Salmonella typhimurium test system. Mutatuin Research 88, 255 – 272

Code of Federal Regulations. Title 40: Protection of Environment; Chapter I: Environmental Protection Agency, Part 86: “Control of Air Pollution from New Motor Vehicles and New Motor Vehicle Engines: Certification and Test Procedures.” Federal Register, US Government Printing Office.

Dekati (2001). ELPI - User Manual. Version 3.13, Tampere.

Dekati (2002). Technical Brochures ELPI - Electronical Low Pressure Impactor, Tampere.

Dockery D.W., Pope C.A. III, Xu X., Spengler J.D., Ware J.H., Fay M.E., Ferris B.G., Speizer F.E. (1993). An association between air pollution and mortality in six US cities. New England Journal of Medicine 329 (24), 1753 - 1759

Dockery D.W., Pope C.A. III (1994). Acute respiratory effects of particulate air pollution. Annual Review of Public Health 15, 107 - 132

EPA (1998). Health assessment document for diesel emissions: SAB Review draft. EPA/8-90/057C. Office of Research and Development, Washington, DC, USA

Frampton M.W., Utell M.J., Zareba W., Oberdörster G., Cox C., Huang L.S., Morrow P.E., Lee F.E., Chalupa D., Frasier L.M., Speers D.M., Stewart J. (2004). Effects of exposure to ultrafine carbon particles in healthy subjects and subjects with asthma. Research Report Health Effects Institute 126, 1 - 47

Health Effects Institute (1995). Diesel exhaust: A critical analysis of emissions, exposure and health effects. Health Effects Institute, Cambridge, MA, USA

Heinrich U., Muhle H., Takenaka S., Ernst H., Fuhst R., Mohr U., Pott F., Stöber W. (1986). Chronic effects on the respiratory tract of hamsters, mice and rats after long-term inhalation of high concentrations of filtered and unfiltered diesel engine emissions. Journal of Applied Toxicology 6, 383 - 395

Henschler D. (1994). Persönliche Mitteilung. Universität Würzburg

Houben L., Lepperhoff G. (1990). Untersuchungen zur Rußbildung während der dieselmotorischen Verbrennung. Supplement Motortechnische Zeitschrift 51, Anhang im Jahresband, XI – XVI

Huisingh J., Bradow R., Jungers R., Claxton L., Zweidinger R., Tejada S., Bumgarner J., Duffield F., Waters M. (1978). Application of bioassay to the characterization of diesel particle emissions. In: Waters M.D., Nesnow S., Huisingh J.L., Sandhu S.S., Claxton L. (eds.): Application of short-term bioassay in the fractionation and analysis of complex environmental mixtures. Plenum Press, New York, 383 - 418

Hühn W. (1970). Rußbildung bei der dieselmotorischen Verbrennung und Möglichkeiten ihrer Verminderung. Motortechnische Zeitschrift 31(3), 109

IARC (1989). Evaluation of carcinogenic risks to humans: Diesel and gasoline exhausts and some nitroarenes. IARC Monographs, Vol. 46

Ishinishi N., Kuwahara N., Nagase S., Suzuki T., Ishiwata S., Kohno T. (1986). Longterm inhalation studies on effect of exhaust from heavy and light duty diesel engines on F344 rats. In: Ishinishi N., Koizumi A., McClellan R.O., Stöber W. (eds.): Carcinogenic and mutagenic effects of diesel engine exhaust. Developments in toxicology and environmental science, Vol. 13, 329 - 348, Elsevier, Amsterdam,

Jing C., Forss A.M., Bach C., Graf R., Eggenberger U. (1996). Umfassende, wirkungsorientierte Charakterisierung von Partikeln aus Dieselabgasen. Gefahrstoffe Reinhaltung der Luft 56, 139 - 145

Katsouyanni K., Touloumi G., Spix C., Schwartz J., Balducci F., Medina S., Rossi G., Wojtyniak, Sunyer J., Bacharova L., Schouten J.P., Ponka A., Anderson H.R. (1997). Short-term effects of ambient sulphur dioxide and particulate matter on mortality in 12 European cities: results from time series data from the APHEA project. Air pollution and health: a European approach. British Medical Journal 314 (7095), 1658 - 1663

Klingenberg H., Lies K.-H., Winneke H. (1992). Dieselabgas - Entstehung, Messung und Gesundheitsgefahren. VDI-Fortschrittberichte Reihe 12, Nr. 172, 1 - 21, VDI-Verlag, Düsseldorf

Lake T., Bending R.G., Williams G.P., Beanmont A.J., Waburton A., Andersson J. (1999). Entwicklung eines Regel- und Abgasnachbehandlungssystems für einen GDI-Motor. MTZ Motortechnische Zeitschrift 60(12), 800 - 807

Lenz H.P., Pucher E., Kohoutex P., Rennenberg H., Hahn J., Elstner E.F., Hippels S. (1993). Emissionen, Immissionen und Wirkungen von Abgaskomponenten. VDI-Fortschrittbericht, Reihe 12, Nr. 183

Lipkea W., Johnson J. (1978). The physical and chemical character of diesel particulate emissions – measurement techniques and fundamental considerations. SAE-Paper 780108

Lofti C.F.P., Brentani M.M., Böhm G.M. (1990). Assessment of the mutagenic potential of ethanol auto engine exhaust gases by the Salmonella typhimurium microsomal mutagenesis assay, using a direct exposure method. Environ. Research 52, 225 - 230

MAK-Liste (2004) Deutsche Forschungsgemeinschaft: Senatskommission zur Prüfung gesundheitsschädlicher Arbeitsstoffe. Mitteilung 40: MAK- und BAT-Werte-Liste. Wiley-VCH Verlag, Weinheim

Marhold H. (2003). Feinstaubproblematik in Linz. Grüne Reihe, Bericht Nr. 1/2003, Amt für Umwelt und Naturschutz, Linz

Maron D.M., Ames B.N. (1983). Revised methods for the Salmonella mutagenicity test. Mutation Research 113, 173 - 215

Marquardt H., Schäfer S.G. (1994). Lehrbuch der Toxikologie. Wissenschaftsverlag Mannheim, Leipzig, Wien, Zürich

Matsushima T., Sawamura M., Hara K., Sugimura T. (1976). A safe substitute for polychlorinated biphenyls as an inducer of metabolic activation system. In: Serres FJ, Fouts JR, Bend JR, Philpot RM (eds) In vitro metabolic activation in mutagenesis testing. Elsevier/North-Holland, Amsterdam, 85 - 88

Mattes P., Remmels W., Sudmanns H. (1999). Untersuchungen zur Abgasrückführung am Hochleistungsdieselmotor. MTZ Motortechnische Zeitschrift 60(4), 234 - 243

Mauderly J.L., Jones R.K., Griffith W.C., Henderson R.F., McClellan R.O. (1987). Diesel exhaust is a pulmonary carcinogen in rats exposed chronically by inhalation. Fundamental and Applied Toxicology 9, 208 - 221

Mayer A., Czerwinski, Scheidegger W., Wyser-Heusi M., Kieser D., Weidhofer J. (1998). VERT - Verminderung der Dieselemission im Tunnelbau. Gefahrstoffe Reinhaltung der Luft 58 (1/2), 26 - 32

Meurer S. (1966). Der Wandel in der Vorstellung vom Ablauf der Gemischbildung und Verbrennung im Dieselmotor. Motortechnische Zeitschrift 27(4), 131 - 139

NIOSH (1988) Carcinogenic effects of exposure to diesel exhaust. NIOSH Current Intelligence Bulletin 50. DHHS (NIOSH) Publication No. 88 - 116. Centers for Disease Control, Atlanta, GA, USA

Peters A., Wichmann H.E., Tuch T., Heinrich J., Heyder J. (1997). Respiratory effects are associated with the number of ultrafine particles. American Journal of Respiratory Diseases and Critical Care Medicine 155, 1376 - 1383

Pope C.A. III, Thun M.J., Namboodiri M.M., Dockery D.W., Evans J.S., Speizer F.E., Heath C.W. (1995). Particulate air pollution as a predictor of mortality in a prospective study of US adults. American Journal of Respiratory Diseases and Critical Care Medicine 151, 669 – 674

Presse- und Informationsamt der Bundesregierung (2004). Fortschrittsbericht 2004 – Perspektiven für Deutschland – Unsere Strategie für eine nachhaltige Entwicklung. Presse- und Informationsamt der Bundesregierung, Postfach 301163, 53191 Bonn

Samet J.M., Zeger S.L., Birhane K. (1995). The association of mortality and particulate air pollution. In: Particulate Air Pollution and Daily Mortality: Replication and Validation of Selected Studies. The Phase I. A Report of the Particle Epidemiology Evaluation Project. Health Effects Institute, Cambridge, MA, USA

Scheepers P.T.J., Bos R.P. (1992). Combustion of diesel fuel from a toxicological perspective. International Archives of Occupational and Environmental Health 64, 163 - 177

Seaton A., MacNee W., Donaldson K., Godden D. (1995). Particulate air pollution and acute health effects. Lancet 345, 176 - 178

Siak J.S., Chan T.L., Lee P.S. (1981). Diesel particulate extracts in bacterial test systems. Environment International 5, 243 - 248

TRGS 900 (2004). Grenzwerte in der Luft am Arbeitsplatz - Luftgrenzwerte -. Ausgabe Oktober 2000, BArbBl. 10/2000, 34 - 63; zuletzt geändert BArbBl. 7/8-2004

Wachter F., Cartellieri W.P. (1987). Wege zukünftiger Emissionsgrenzwerte bei LKW-Dieselmotoren. 8. Int. Wiener Motorensymposium 1987, VDI-Bericht Nr. 86, 206 - 239, VDI-Verlag Düsseldorf

Warnatz J., Maas U., Dibble R.W. (2001). Verbrennung - Physikalisch-Chemische Grundlagen, Modellierung und Simulation, Experimente, Schadstofferkennung. 3. Auflage, Springer-Verlag, Berlin

WHO (1996). Diesel fuel and exhaust emissions: International program on chemical safety. World Health Organisation, Genf, CH

Working Group on Public Health and Fossil-Fuel Combustion (1997). Short-term improvements in public health from global-climate policies on fossil-fuel combustion: an interim report. Lancet 350 (9088), 1341 - 1349

4. Appendix

A.1 Fuel Analyses

Table A-1: Fuel analyses for GTL and DF and limits according to DIN EN 590

Property	Results		Unit	Limits	
	GTL	DF		Min.	Max.
Density (15° C)	0.7846	0.8338	g/mL	0.8330	0.8370
Kin. Viscosity (40° C)	3.497	2.712	mm_/s	2.300	3.300
Cetane Number	79	54.0	-	51.0	
Flash Point	101	84	°C	55	
CFPP	-1	-18	°C		-5
HFRR		374	µm		400
Water Content		40	mg/kg		200
Oxidation Stability		3	g/m_		25
Acid Number		0.00	mg KOH/g		0.02
Sulfur Content	< 5	3	mg/kg		10
Carbon Residue		< 0.01	Weight %		0.20
Sulfated Ash		< 0.005	Weight %		0.010
Hydrogen Content	15.0	13.54	Weight %		
Carbon Content	85.0	86.46	Weight %		
Monoaromatics	0.1	20.3	Weight %		
Diaromatics	< 0.1	4.5	Weight %		
Triaromatics	< 0.1	< 0.1	Weight %		
Polyaromatics		4.5	Weight %	3.0	6.0
Total Aromatics	0.1	24.8	Weight %		
Calorific Value		43.152	MJ/kg		

Table A-2: Fuel analysis for RME and limits according to EN 14214

Property	Result	Unit	Limits	
	RME		Min.	Max.
Ester Content	98.0	Weight %	96.5	
Density (15° C)	0.88	g/mL	0.875	0.900
Kin. Viscosity (40° C)	4.476	mm_/s	3.5	5.0
Flash Point	>171	°C	120	
Sulfur Content	n.d.	mg/kg		10.0
Carbon Residue	n.d.	Weight %		0.3
Sulfated Ash	n.d.	Weight %		0.02
Water Content	393	mg/kg		500
Total Contamination	n.d.	mg/kg		24
Acid Number	0.17	mg KOH/g		0.5
Iodine Number	113	-		115
Monoglycerides	0.66	Weight %		0.8
Diglycerides	0.17	Weight %		0.2
Triglycerides	0.02	Weight %		0.2
Free Glycerol	< 0.005	Weight %		0.02
Total Glycerol	0.194	Weight %		0.25
CFPP	-14	°C		0/-10/-20
Soap Content	0	mg/kg		

n.d.: not determined

Table A-3: Fatty Acid Spectrum for RME

Acids	**Result**	**Unit**
	RME	
Lauric Acid	-	Weight %
Myristic Acid	0.06	Weight %
Myristoleic Acid	-	Weight %
Palmitic Acid	4.62	Weight %
Palmitoleic Acid	0.25	Weight %
Stearic Acid	1.68	Weight %
Oleic Acid	60.59	Weight %
Linoleic Acid	20.41	Weight %
Linolenic Acid	9.17	Weight %
Arachidic Acid	0.56	Weight %
Eicosenic Acid	1.34	Weight %
Eicosadienoic Acid	0.08	Weight %
Behenic Acid	0.34	Weight %
Erucic Acid	0.29	Weight %

A.2 Exemplary Courses of Other Variables

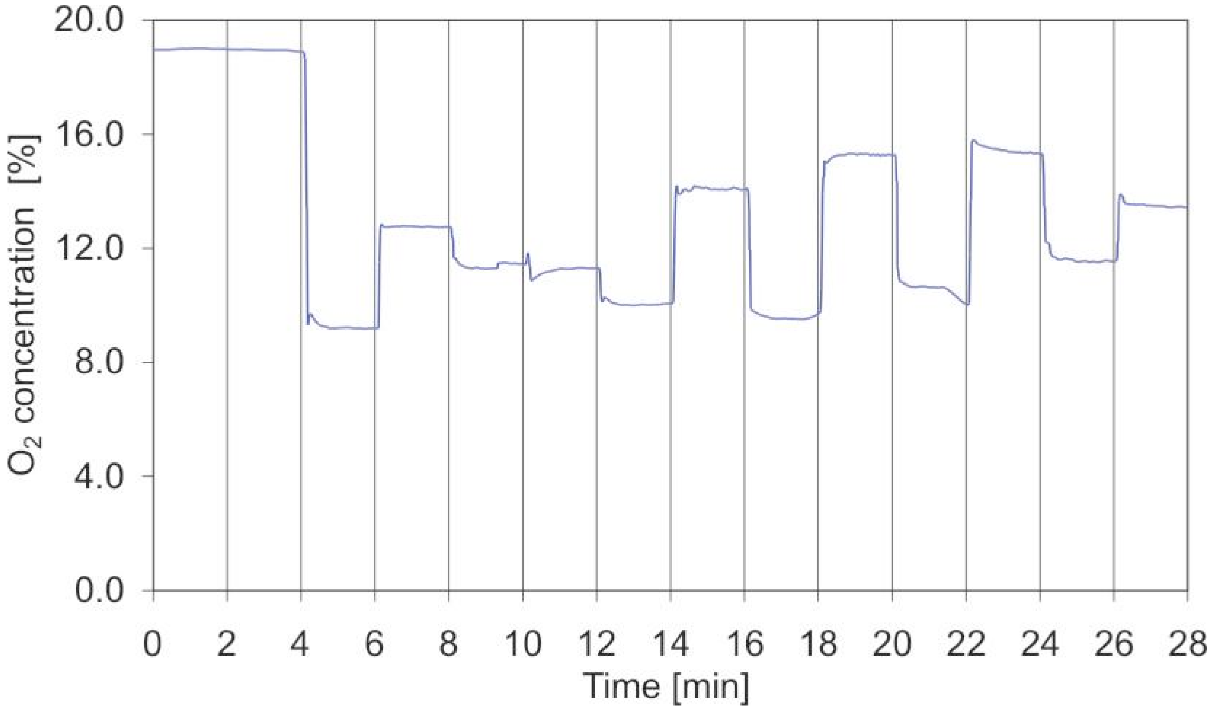

Fig. A-1: Exemplary course of oxygen concentration (Run SMDS23, GTL)

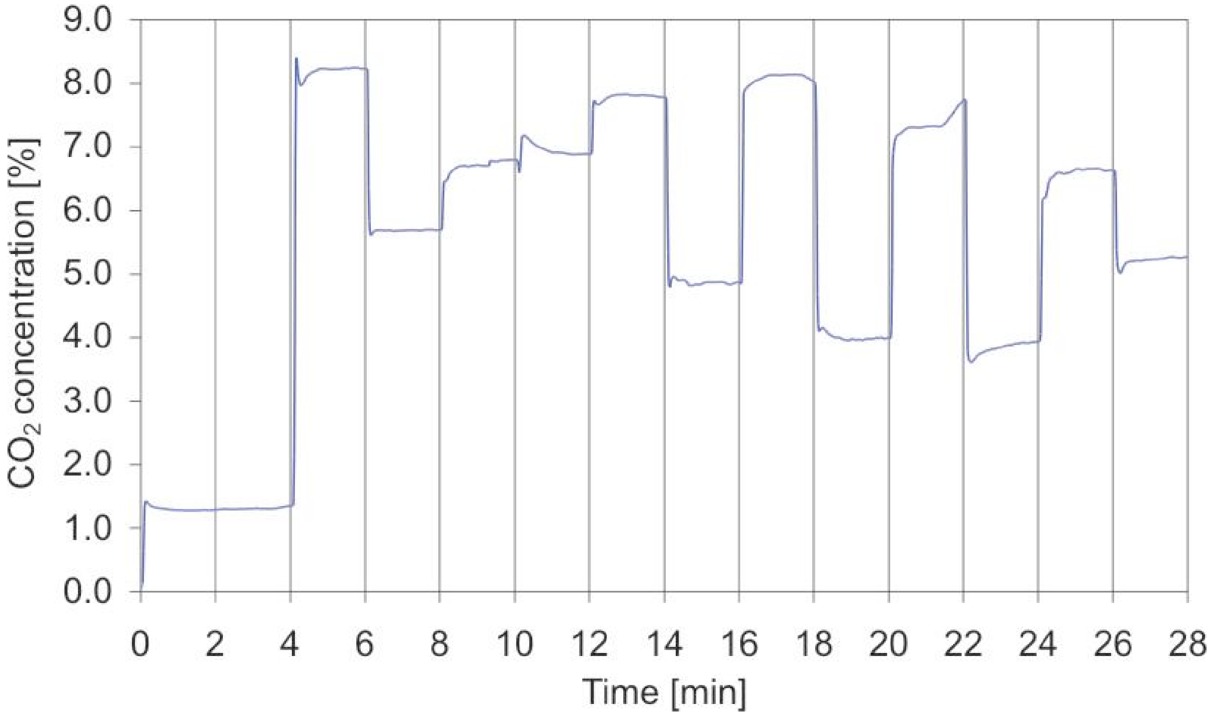

Fig. A-2: Exemplary course of carbon dioxide concentration (Run SMDS23, GTL)

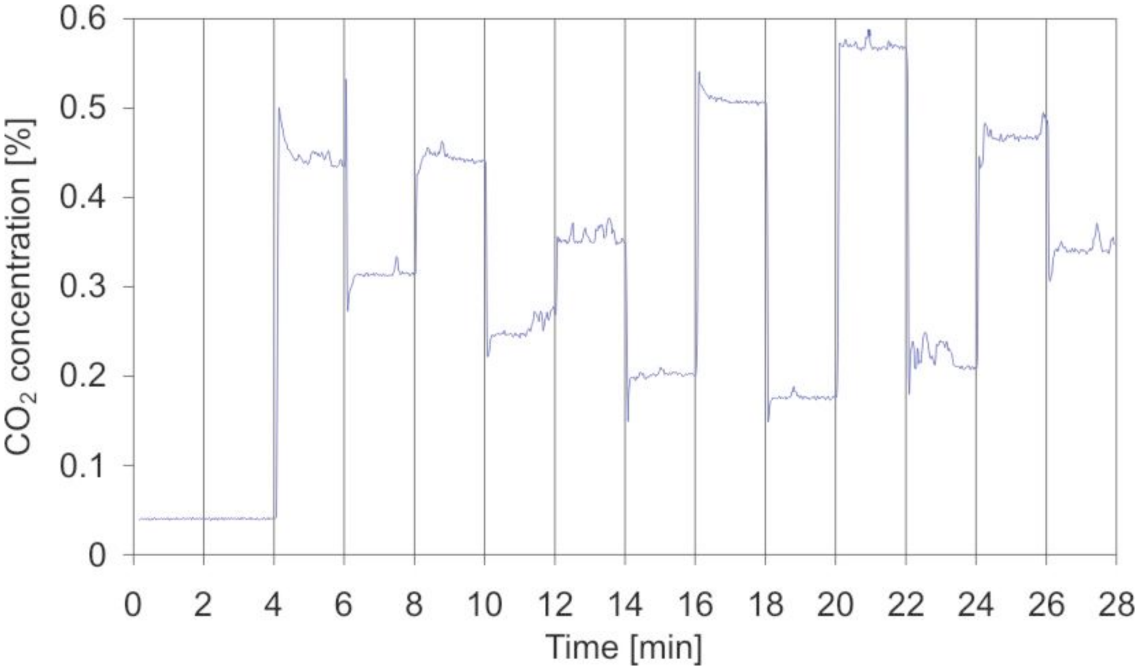

Fig. A-3: Exemplary course of carbon dioxide concentration in the dilution tunnel (Run SMDS23, GTL)

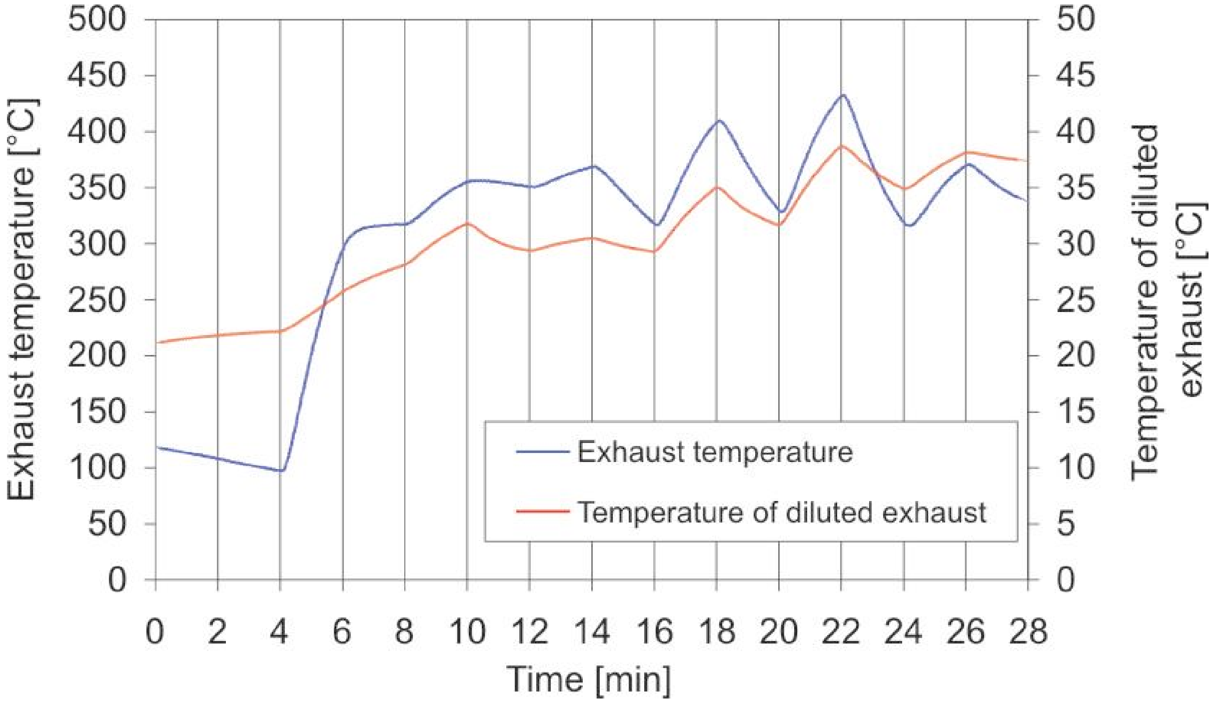

Fig. A-4: Exemplary course of the exhaust gas temperature and the temperature of the diluted exhaust gas in the dilution tunnel (Run Ref118, GTL)

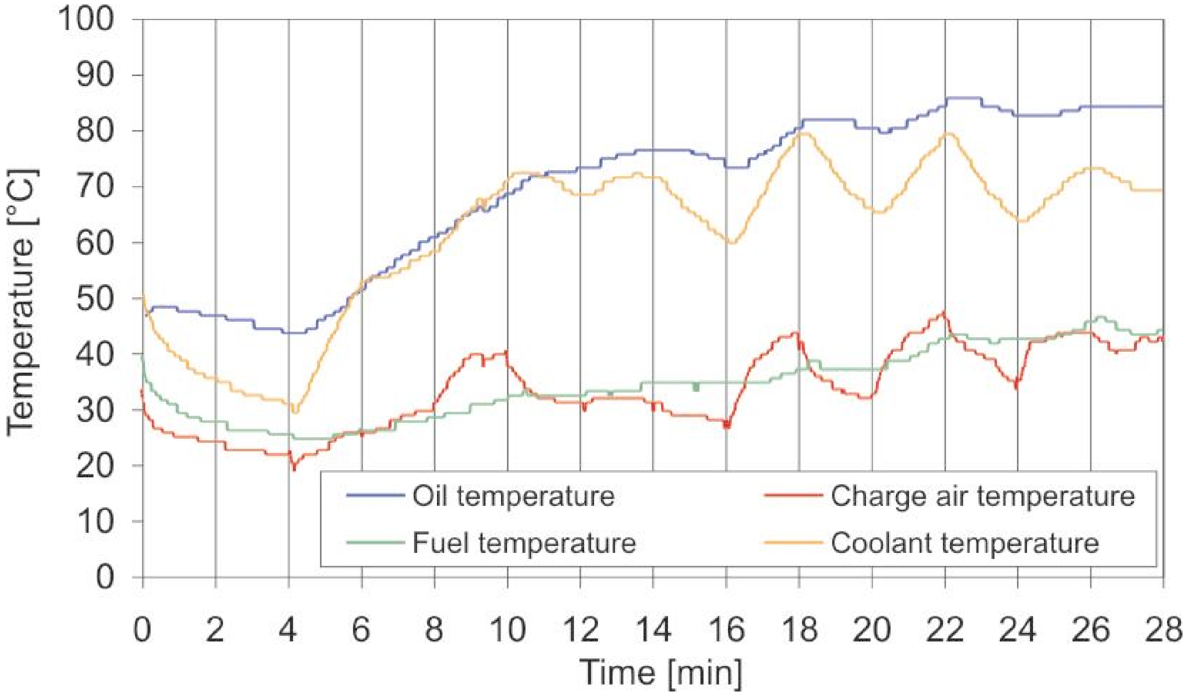

Fig. A-5: Exemplary course of the charge air, coolant, oil and fuel temperatures (Run SMDS23, GTL)

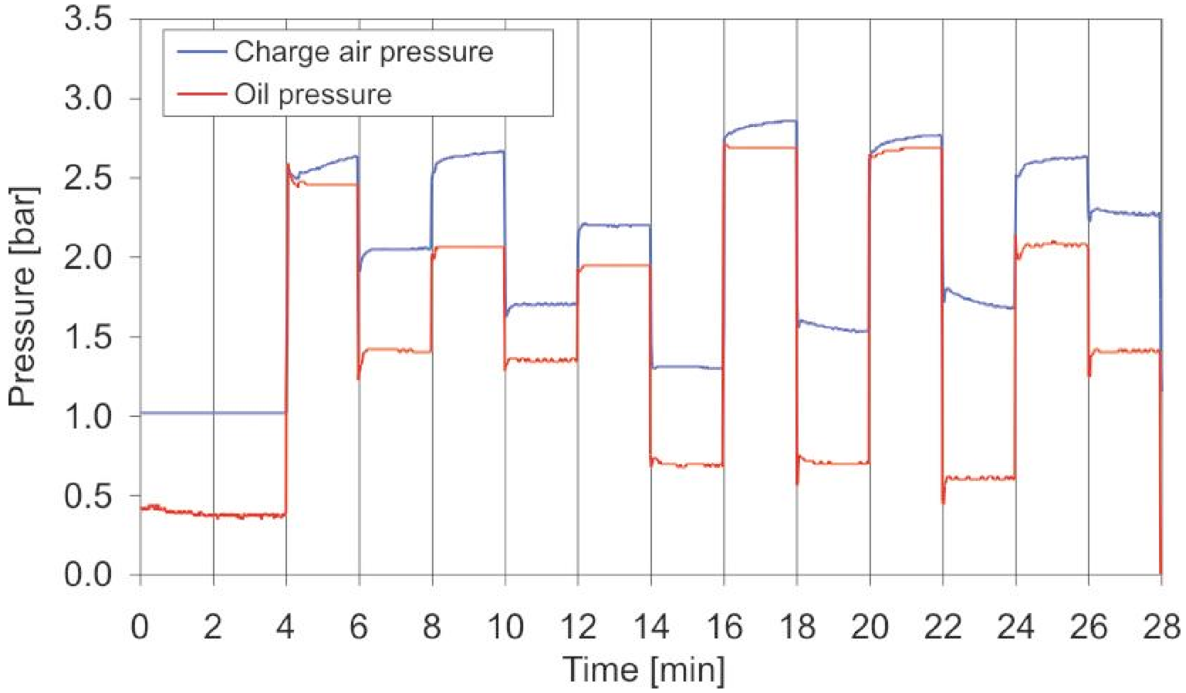

Fig. A-6: Exemplary course of charge air pressure and oil pressure (Run SMDS06, PDF)

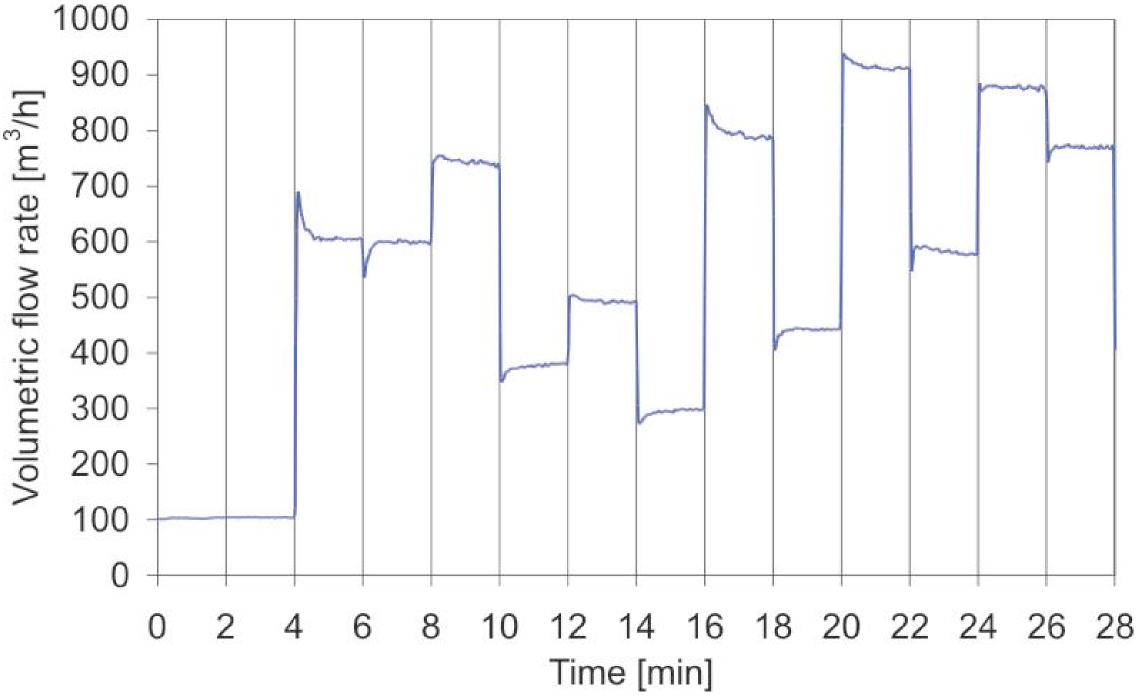

Fig. A-7: Exemplary course of the vacuum volume flow (Run SMDS06, PDF)

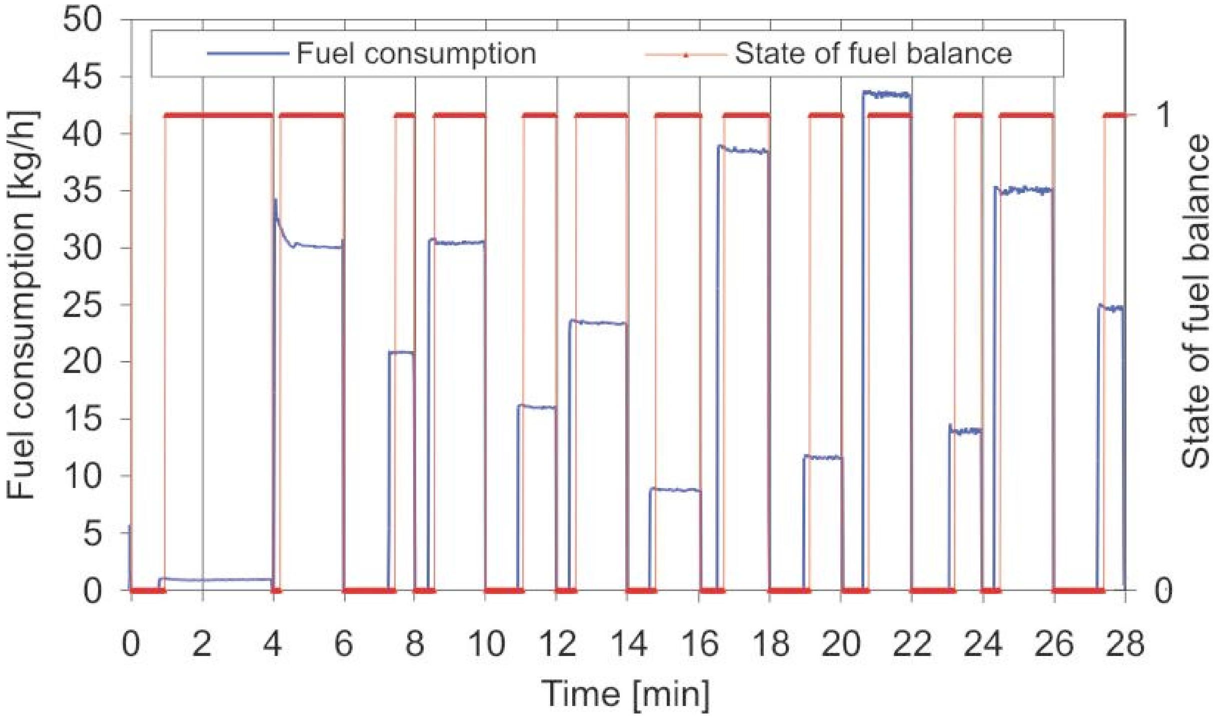

Fig. A-8: Exemplary course of the fuel consumption; measurements only take place during scale status “1,” at status “0” the scale is refilled. (Run SMDS23, GTL)