The Influence of Biofuel Blends

Project No. 6010280

The Influence of Biofuel Blends on Modern Diesel Engines and their Exhaust Gas After-Treatment Systems

Final Report

Abstact

Currently DIN EN 590 stipulates a maximum biodiesel blend rate of 7 % to fossil diesel fuel. According to considerations of the European legislators, in the foreseeable future this percentage shall rise to 10 % at the European level. Provisions of the European Union envisage an increase of the biofuel share to 20 % for the entire fuel and diesel consumption by the year 2020. With this stipulation a 10 % reduction of greenhouse gas is intended. The increase of blend shares with biogenic components involves more frequent variations of the fuel properties. It was the impact of such variations on sophisticated engine technology in practice which was the purpose of this study.

The objective of this report was the investigation of the storage stability of the future blend fuels and their influence on the combustion behaviour as well as the emission process involved. In a long-term study the fuel-carrying components and any influences on the exhaust gas after-treatment system were to be analyzed during engine operation.

It could be shown that the storage stability of the fuel blends was given during the test period of 17 months. No significant influences on the parameters ôviscosityô and ôneutralization numberô could be identified. Just the parameters ôoxidation stabilityô and ôperoxide numberô showed minor changes in the permissible range. The short-term engine tests showed that the influence of the different fuel properties on the combustion behaviour can hardly be detected due to modern and progressive engine management. Merely at high heavy load operation which did not allow for any adjustment of the engine operation (without EGR = exhaust gas recirculation), fuels with HVO content showed reduced ignition delay. In addition, it could be confirmed that the fuelôs FAME content causes a reduction of particle emission. An influence of the fuel blends on the exhaust gas after-treatment system could not be verified in the short-term tests.

The objective of this research project <u>was achieved.</u>

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Index

1 Management Report

The subject of this study was the investigation of five biofuel blends with regard to the storage stability, combustion behaviour as well as formation of emissions. For this purpose test runs were carried out at a EURO VI passenger car diesel engine (four cylinders). The focus of these test runs were six short-term tests and three endurance runs with selected biofuel blends to study their influence on the internal combustion behaviour, on the emission formation and the functionality of the exhaust gas after-treatment system. The following fuels were tested:

I. Diesel fuel B0 (Reference)
II. Diesel fuel with 20 % FAME
III. Diesel fuel with 30 % FAME
IV. Diesel fuel with 30 % HVO
V. Diesel fuel with 7 % FAME and 3 % HVO
VI. Diesel fuel with 7 % FAME and 13 % HVO

Storage Study

The FAME components of the fuels noted above were stabilized by means of antioxidant agents. The biofuel blends were stored at two different temperatures (10 ÁC, Ï 25 ÁC) for 17 months, sampled and analyzed at defined intervals.

No significant changes of the fuel-related properties **'**viscosity**'** and **'**neutralization number**'** were observed throughout the storage period. The parameters of oxidation stability and peroxide value showed minimal deviations from the initial state. The limits of DIN EN 590 were safely maintained throughout the test period. It can be stated that the investigated blends with a high biodiesel content of 30 % can also be stabilized over a storage period of 17 months by specific additivation with antioxidants. For the investigation period of 517 days the storage stability of the blends could be proven.

Engine Short-Term Test

In the short-term engine tests five diesel fuel blends were compared at selected engine operating points. Successful operation with blend fuels could be demonstrated in a EURO VI engine. A shift of operating points under stationary load was observed due to different fuel properties (boiling characteristics; surface tension; calorific value).

The differences in the combustion behaviour and in the engine control values are quantified on the test bench. Higher fuel volumes were injected for identical load points when operating on the oxygen-rich fuels with biodiesel content (at same air mass and engine speed).

The variations of the individual parameters were within 5 % of the specified values for the six fuels investigated. These differences could be compensated in engine control units, if information on the applied fuel is stored in the ECU.

In the high load range a direct influence of the fuels on the combustion behaviour could be observed. The HVO fuels showed a reduced ignition delay. In contrast, the fuel with FAME experienced a longer ignition delay.

The determination of the FSN and the particle number confirmed that the FAME content in the fuel causes a reduction of particulate emissions. The reason for that is the oxygen bound in FAME molecules. On the other hand fuel blends containing HVO led to a higher number of particles (100 % more) whereas FSN remained the same as for diesel fuel. The reason for that lies in the finer atomization of the HVO. Consequently, engine operation with an HVO blend leads to the emission of smaller particles.

The influence of fuel blends on the exhaust gas after-treatment system could not be proven in the short-term tests. The particle reduction of the diesel particulate filter was about 99 %. In the engine operation range which is relevant for emission certification the SCR reduces

the nitrogen oxides by 90 %. Over the whole engine map, a nitrogen oxide reduction of over 40 % was measured.

Engine Endurance Runs

In the engine endurance runs fuels ÷DF + 7 % FAMEô, ÷DF + 30 % FAMEô and ÷DF + 30 % HVOô were tested in the engine for 500 h each. The findings of the short-term tests could be confirmed, i.e. the shift of operating points as well as the emission behaviour.

Furthermore, the engine components injector, turbocharger, cylinder head and throttle showed no different signs of wear compared to engine operation on standard fuel over the same period.

When operating on FAME blends less soot deposits were found on the EGR coolers; which correlates with the particulate emissions.

In all three endurance runs the engine lubricating oil showed the same behaviour as typically found for engine operation on standard diesel fuel. For all three test fuels there were no differences between the oils with regard to the parameters of viscosity, TBN and wear metal content. A sharp increase of the neutralization number, even exceeding the limit, was detected in endurance runs two and three. This was probably caused by the increase to 4.5 % of the FAME content in the lubricating oil in endurance run two.

Outlook

It should be noted that fuel-related differences, as known from earlier engine applications, could not be detected for the examined EURO VI engine. This is especially true for the typical increase in nitrogen oxide emissions caused by FAME-containing fuels. Fuel-related limitations of engine operation could not be found in both the short-term tests and the endurance runs.

It would be desirable to adjust the engine control unit by implementing based specific fuel type detection. Thus, for example, the improved EGR potential of fuels with high FAME content could be exploited. Furthermore, the AdBlue dosing could be adjusted to the actual emissions of nitrogen oxides in order to avoid incorrect dosing.

2 Introduction and Objectives

Presumably for yet another 20 years, liquid mineral fuels made of crude oil will play a dominant role in the transport sector. In addition, alternative fuels such as biodiesel, bioethanol and synthetic diesel fuels will gain in importance. The reasons for that are the increasing shortage of fossil energy sources, environmental aspects including the demands for the reduction of critical green-house gas emissions and last but not least the implementation of EU Directive 2009/28/EG, with which the market share of biogenic fuels shall be increased to about 10 % in different steps by the year 2020. Bearing in mind these goals of the European Union as described before, the implementation of fuel blends (mixed fuels) will gain more and more in importance. So far diesel fuel standard DIN EN 590 covers a blend rate of 7 % (V/V) of biodiesel according to DIN EN 14214 to the mineral oil based basic fuel.

The current legislation at European level claims a blend rate of 10 % of renewable energies in the transport sector (directive 2009/28/EG). As a consequence, in the first place the blend component determines the fuel properties and secondly the deviation range of the fuel properties increases significantly. The latter can be attributed to the fact that though admixture is allowed it is not obligatory for every batch. As a result some fuel properties (e.g. density, viscosity, oxidation stability, coking tendency [CCR], temperature behaviour) have a relatively wide range.

The objective of this research project was the systematic analysis and assessment of the impact of biofuel blends on the operation of a common-rail car diesel engine, the make of which complies with the current exhaust gas standards (EURO VI). Apart from the influence of the biofuel blends on the combustion management and the raw emissions generated, the effects on the complex exhaust gas after-treatment systems were to be assessed in detail for the first time.

For that, a test engine of the category mentioned above was operated with various biofuel blends on an engine test bench. The impact of the changed fuel properties on the combustion management and the emission behavior was determined by means of short-term measurements at selected operating points within the engine map. Subsequently three 500-h long-term tests were carried out, in order to compare the efficiency and reliability of the exhaust gas after-treatment systems (consisting of DOC, *diesel oxidation catalyst* ï DPF, *diesel particulate filter* ï SCR, *selective catalytic reduction*) for the operation on standard-conform reference fuels and biofuel blends.

The engine tests were paralleled by systematic analyses of lubricants to determine the influence of biofuel blends on the ageing of the oil. Furthermore, the stability of the fuel-carrying elements with regard to the biofuel blends used was monitored.

3 Approach

To illustrate the approach, all the work packages are introduced and described in this chapter.

Work package 1: Procurement and Analysis of the Blend Components

In the first work package possible sources of supply for the blend components were sought, the relevant fuel components were purchased and analyzed. The required blend components were RME (rapeseed oil methyl ester) and SME (soybean oil methyl ester) according to DIN EN 14214 as well as HVO (hydrogenated vegetable oil).

At the beginning of the test runs the fuel components supplied as well as the blends made thereof were subjected to standard fuel analytics (caloric value, density, hot properties, cold properties, coking tendency [CCR], lubricity). The results were evaluated and assessed with regard to standard conformity and/or deviations.

During the course of this project the following fuel blends were made and used for storage and engine tests:

I. Diesel fuel B0 (reference fuel)
II. Diesel fuel with 20 % FAME
III. Diesel fuel with 30 % FAME
IV. Diesel fuel with 30 % HVO
V. Diesel fuel with 7 % FAME and 3 % HVO
VI. Diesel fuel with 7 % FAME and 13 % HVO

This resulted in the elegibility and selection of the fuel blends for the engine test runs. Based on this analysis data, first indications of the expected deviations concerning the engineôs performance could be gained.

Work package 2: Procurement of Reference Diesel Fuel and Development of the Fuel Supply

In work package 2 diesel fuel according to DIN EN 590 without any FAME (B0 diesel fuel) was purchased and analyzed as reference fuel. Furthermore, an additional fuel supply system was fitted to the engine test bench (service tank with fuel pump and relevant stop valves) to enable a speedy exchange of the fuel variant implemented with minimised purging.

Work package 3: Long-term Study on the Storage Stability of the Blend Fuels

Two samples were made of the above mentioned fuel blends to be able to monitor the storage stability. One was stored at 10 ÁC, the other at an increased temperature (25 ÁC on average) to be able to make a concrete statement with regard to the influence of the storage temperature.

Selected parameters of the relevant biofuel blends were eventually analyzed at determined intervals.

Work Package 4: Test Bench Tests – Short – Term Runs ‚Blends‘

Basis for the projectôs scheduled short-term runs on an engine test bench was a partially open control unit with serial application for standard-conform diesel fuel. The biofuel blends were not modified or adapted with regard to the serial application setup for B0. For each of the blends implemented 30 engine operating points were considered and measured. Those

engine operating points result from the engine speed at 1500, 2000, 2500, 3000 and 3500 min^{-1} and the torque steps of 50 Nm each (see figure 10).

Work Package 5: Assessment of the Measuring Data Obtained in Work Package 4

The measuring data gathered in work package 4 was systematically evaluated. The evaluation focused mainly on the analysis of the influence of fuel blends on the combustion management. Based on the recorded data of pressure indication, the burning velocity, focal point of heat release and combustion function of the main combustion were determined.

The results of the exhaust gas emissions were expressed dependent on the fuel implemented and related to the identified changes in the combustion management. The focus of the emission analysis lay on nitrogen monoxide and particle emissions.

The function and efficiency of the exhaust gas after-treatment systems (DOC, *diesel oxidation catalyst* ï DPF, *diesel particulate filter* ï SCR, selective catalytic reduction) during engine operation with different biofuel blends was based on the raw emissions. The aim was to assign determined deviations to the changed raw emission process and to the possibly chanced operational conditions of the exhaust-gas after-treatment systems.

Work Package 6: Assessment of the Condition of the Exhaust Gas After-Treatment Components

On completion of the short-term measurements using the different biofuel blends, the influence of the blends on the condition of the exhaust gas after-treatment components was assessed.

The first step was the assessment of the exhaust gas after-treatment systems (DOC, DPF, SCR) by means of the emission and operation data of work package 4 (emission data before and behind after-treatment, Δt via DOC, pressure loss in DPF, NH_3 slip after SCR) with regard to any possible occurrence of premature ageing, contamination or other changes.

Work Package 7: Test Bench Endurance Runs

Subject of this work package were three endurance tests of 500 operating hours each on an automated test bench. A simplified step cycle based on the AMA cycle was programmed and retraced. The following fuels were implemented in the endurance test:

1. Endurance run 1: DF + 7 % FAME
2. Endurance run 2: DF + 30 % FAME
3. Endurance run 3: DF + 30 % HVO

After every 100 operating hours of the endurance runs the following measurement readings were gathered at 10 measuring points of the engine map:

- Air streams (air, fuel, exhaust gas) including pressure and temperature data
- Gaseous exhaust gas components (CO_2, CO, O_2, NO, NO_X, THC) in the raw exhaust gas and following exhaust gas after-treatment
- Filter Smoke Number in the raw exhaust gas

Furthermore, at the beginning and the end of the test runs the pressure in the combustion chamber was measured at the defined measuring points.

Work Package 8: Stability of Components

Upon completion of the individual endurance run, relevant components (injectors, EGR valve, EGR cooler, EGT (exhaust gas turbocharger), air intake system, combustion chamber,

etc.) were inspected with regard to their stability/resistance to the biofuel blend. The results of the optical inspection were recorded.

Work Package 9: Stability of Exhaust Gas After-Treatment Components, Provision of Engine Components for Intensified Analytics

A more intensive inspection of the exhaust gas after-treatment components followed when the endurance runs were completed.

A first measure was the assessment of the exhaust gas after-treatment systems (DOC, DPF, SCR) based on the emission and operational data obtained with the endurance test (emission data before and following exhaust gas after-treatment) with regard to any possible occurrence of premature ageing, contamination or other changes.

The DPF systems were analyzed by *Johnson Matthey* in England.

Work Packgage 10: The Influence on Lubricants by Blends/Blendfuels

In order to monitor the quality of the lubricants, periodical analyzes and comparative assessment of the lubricants were conducted both during the short-term and the endurance runs.

Here the following samples were taken:

- Short-term runs: one sample each upon completion of each blend variant of work package 4
- Endurance runs: a sample each at the beginning and after 100, 200, 250, 300, 350, 400, 450 and 500 operating hours

The aim was the determination of the lubricantõs stability in the presence of the blend components, especially with regard to polymerisation and/or impermissible dilution. The following lubricant properties were analyzed: viscosity, oligomer formation, wear metals, total base number, neutralization number, fuel content, soot content.

4 State-of-the-Art Knowledge

4.1 Fuels

Fuels serve as energy sources the chemical energy of which is converted into thermal and mechanical energy by means of combustion. With a percentage of more than 20 % Germany is the biggest fuel consumer within the European Union. Merely 2 % of the European Union's fuel consumption can be covered by its own resources, which indicates a strong dependence on the oil exporting countries. Due to the increasing shortage of resources and the ensuing price increases for Otto and diesel fuels as well as growing environmental awareness, a new tendency is noticeable in the automotive trade. Biofuels gain in importance more and more. In addition, there is a multitude of biogenic fuels providing alternatives as energy sources. Particular environmental compatibility is not necessarily given, though. Since the Biofuel Quota Act took force on 1 January 2007, in Germany a minimum content of renewable resources in fuels intended for transport purposes is required. Figure 1 illustrates the aforementioned proportions since the introduction in 2007. The implementation of the quota obligations can be achieved by blending of biogenic fuels to conventional Otto and diesel fuels or by marketing pure biofuel.

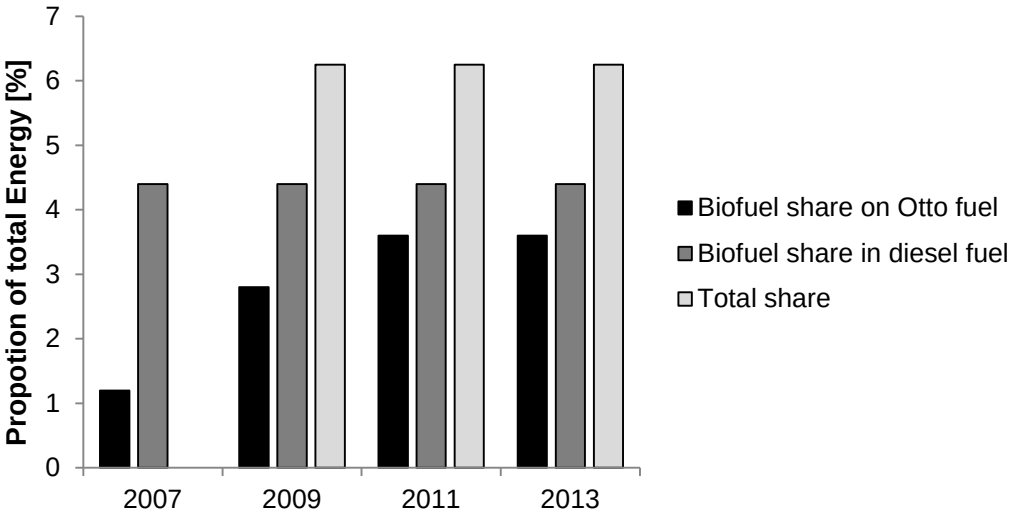


Figure 1: Legally Stipulated Biofuel Proportion in Fuels According to the BioKraftQuG (*Biofuel Quota Act*).

The emission behaviour of the engine can be significantly influenced by the selection of the fuel and its additives.

4.1.1 Diesel Fuel

Diesel fuel is almost exclusively produced from crude oil. It is a mixture of different light middle-distillates which are generated during the refining process of crude oil in the medium boiling range of 150 ÁC to 390 ÁC. The proportion of the individual components has a significant influence on the engine behaviour. In addition, various additives are added to the diesel fuel for the improvement of its properties and/or environmental compatibility. In contrast to Otto engines, which may suffer from engine damage due to the use of fuels with insufficient knock resistance, diesel engines also run on minor fuels, although to a restricted extent. In order to assure sound performance and to limit the exhaust gas emissions, DIN EN 590 stipulates the quality criteria for fossil diesel fuel available in Europe. Some of the relevant properties of diesel fuel are dealt with in the following paragraphs.

The combustibility of the fuel is characterised by its cetane number. The higher the cetane number (CN) the more easily the fuel is combustible and the lower is the ignition delay. A long ignition delay entails a high formation of thermal NO_x; however, it counteracts the formation of soot particles.

Since carbon is a mixture of different hydrocarbons it has ï unlike pure hydrocarbon ï a boiling range rather than a boiling point. For diesel fuel the range is between 180 ÁC and 380 ÁC. The location at the upper part of the boiling range is of particular interest. If the boiling point of the fuel is too high it can lead to unburnt hydrocarbons and thus to increased soot formation. An additional consequence is the coking of injectors and valves which is also described by the Conradson carbon residue (CCR).

Both the performance and the soot emission of the engine increase as a consequence of the rising fuel density and the energy content resulting thereof. It is important to use fuels with a low density spread in order to observe the emission limits and performance specifications of the engine because the injected fuel volume is added volumetrically.

Viscosity is a measure for the fluidity. The essential lubrication of movable parts of the injection system is reduced if the viscosity is too low. If too high and in case of stipulated injection pressure the viscosity causes an increase of the droplet size of the fuel spray which results in inferior combustion as a consequence of insufficient carburetion as well as an increase of soot emissions. Those aspects call for a small viscosity range.

Basically the oxidation stability ï also called ageing stability ï is a measure for the shelf life of fuels. If stored for a lengthy period of time fuels can react with oxygen and polymerise. The oxidation products thus formed induce filter plugging and/or deposits in the fuel system. Consequently, the diesel fuel standard (DIN EN 590) stipulates the minimum requirements with regard to oxidation stability. One possible method for the determination of the oxidation stability is the so-called Rancimat method according to DIN EN 15751. However, this test method can only be safely applied for fuels with a minimum FAME content of 2 % (V/V). Otherwise the method according to DIN EN ISO 12205 must be implemented.

During the refining process diesel fuel is already desulphurized by hydrogenation in order to prevent the emission of toxic sulphur dioxide. However, in the course of that process polar fuel components with good lubrication properties are also extracted. For compensation reasons the implementation of adequate additives (e.g. lubricity additives) is essential for the improvement of the lubrication so as to avert any needless wear on pumps and injectors. Other than diesel fuels without any FAME content, FAME-containing fuels show improved lubrication properties due to their molecules containing oxygen atoms and so the implementation of such additives can be dispensed with.

Apart from water the fuel may contain solids. Their amount is restricted by the total contamination. Included are sand, rust and undissolved organic components. Undissolved impurities promote the erosive and abrasive wear of the injection systems which may cause leaking or increased particle emission (Reif 2010, Mollenhauer and Tschº ke 2007).

4.1.2 Biofuels

As mentioned before the implementation of biogenic fuels produced from fast growing feedstock is continuously gaining in importance with regard to economic and environmental aspects. However, due to their limited availability they are generally not offered in their pure form but just as blend components to conventional diesel fuel. Their admixture can bring about essential property improvements. Separate quality directives apply for biofuels. In case of their blending with diesel fuel, the quality criteria of DIN EN 590 must be fulfilled nonetheless.

Fatty Acid Methyl Ester (FAME)

The á10. BImschVô(German Emission Act) also authorises fatty acid methyl ester according to DIN EN 14214 to be called á biodieselô as which is its more generally known. In Germany

rapeseed oil is the main feedstock basis and so it is often also called rapeseed oil methyl ester (RME). However, other vegetable oils or animal fats can also be the basic material.

The quality requirements for FAME are stipulated by DIN EN 14214. FAME can be implemented in its pure form as B100 or as blend component with fossil diesel fuel. The currently in Germany available standard B7 diesel fuel contains a FAME content of up to 7 % according to fuel standard DIN EN 590. The implementation of a higher biodiesel proportion requires the release by the engine manufacturers. Biodiesel is not hazardous for the engine itself but it has increased solvent properties than conventional diesel fuel. Therefore, rubber and plastic parts must be resistant. During normal engine operation the ingress of fuel into engine oil permanently occurs. In contrast to fossil diesel fuel, biodiesel does not escape from the engine lube oil. As a consequence the viscosity decreases and thus minimises the lubricating effect of the engine oil. To prevent excessive wear the oil change intervals given by the manufacturers must be observed. Due to its reduced caloric value one litre of biodiesel substitutes 0.92 l of conventional diesel fuel (Machhammer 2007), (Mollenhauer and Tschºke 2007).

Hydrogenated Vegetable Oils (HVO)
Basic materials for hydrogenated vegetable oils are oils freed of solids and dehydrated. By catalytic reaction with hydrogen (hydration) and decarboxylation, vegetable oils pure are converted into hydrocarbons. There are two different methods for the production of HVO. They can be either hydrated jointly with fossil crude oil in the conventional refinery hydration process, or they are processed óstand aloneô in specific vegetable oil plants.

The products properties depend on the oils implemented. HVO is free of sulphur and aromatics; it does not contain any oxygen and is hardly water soluble. Compared to conventional diesel fuel its density is somewhat lower, yet its cetane number is considerably higher. The cold property of HVO can be adjusted by changing the atom arrangement of a molecule, thus by isomerisation. The properties of the hydrocarbons formed thereby resemble those of fossil diesel fuel. Therefore, hydrogenated vegetable oils can be used in conventional diesel engines in combination with diesel fuels or in their pure form. By adding HVO to diesel fuel an improvement can be achieved due to the higher cetane number. Mixing ratios of significantly more than 10 % are technically feasible. The only limit is the lower density of the hydrogenated vegetable oils, and so dependent on the diesel fuel used, there is a certain value when DIN EN 590 cannot be observed any longer (Burgmer and Meyer 2008).

4.2 Combustion in Diesel Engines

Combustion in diesel engines is characterised by an internal carburetion and self-ignition. To ensure that ignition is initiated, ignitable fuels, considerable pressure and temperature must prevail. High compression (compression ratio 12 < Ů < 21) and a possible air heating by means of a bulb assure the energy release by the combustion process. Shortly before the top dead point the fuel is generally introduced directly or indirectly (pre-chamber method) into the main combustion chamber by means of high pressure. Due to the self-ignition of the fuel at the hot compressed air, fast injection and good atomisation or surface extension are important for an intensive and speedy carburetion; that way total and extensive combustion is enabled. For the diesel process, the adjustment of various load conditions is achieved by varying the fuel amount. Compared to the Otto engine operating at ə = 1 here a higher efficiency can be spoken of due to quality management (Mollenhauer and Tschºke 2007), (Merker and Stiesch 1999).

Numerous influencing factors determine the quality of the combustion and the exhaust gas composition resulting thereof. Constructive measures such as the order of the injectors or the construction/design of the combustion chambers are in combination with the fuel parameters responsible for the composition of the mixture.

4.2.1 Common Rail Method

In the diesel process the common rail method has become the prevailing technology compared to other methods with direct injection because of its efficient fuel consumption, low

exhaust gas and reduced noise emissions. Due to its advantages this injection technology is meanwhile fitted in high quantities in all types of modern diesel engines of serial deployment (Mollenhauer and Tschöke 2007).

The Unit Injector (UI) System, deemed competition for a long time, could also inject under high pressure. However, due to the pressure controlled fuel injection it is inferior to the hub/time-controlled direct injection. The advantage of the method resulting thereof is characterised by the separation of high pressure from fuel injection independent of load and engine speed throughout the entire engine map. A central high pressure pump induces the permanently prevailing storage pressure which enables the engine control system to assure a flexible fuel supply with regard to frequency, position and quantity by the during every combustion cycle. The quantity injected is dependent on the height of the rail pressure and the pitch time of the fuel injectors. For that the injector body consists of a jet nozzle and a control valve; the valve is adjusted by a magnet (also called piezo actuator) which guarantees the possibility of multiple injections at high efficiency. An intended pilot injection reduces the ignition delay for the main injection and the accompanying pressure gradient in the combustion chamber. A short ignition delay safeguards the reduction of noise and nitrogen oxide emissions as well as a reduced component load. However, a post-injection immediately following the main injection can have a reducing effect on the formation of soot and unburned hydrocarbons (UHC) (Mollenhauer and Tschöke 2007).

The exact tuning of those features for implementation purposes and ways of use enables a high development potential and in combination with appropriate exhaust gas after-treatment systems it is a guarantee for the compliance with present and future emission standards. Increasing storage pressure and the improvement of engine components involved in the fuel and exhaust gas system will also provide potential concerning the innovation of the common rail injection system in the future.

4.2.2 Diesel Fuel Emissions

Incomplete combustion of diesel fuel leads to the formation of a variety of residues. In case the engine is cold, directly noticeable exhaust gas components are hydrocarbons in the form of partly or non-oxidized droplets, white or blue smoke or odour-intensive aldehydes. Apart from gaseous pollutants, diesel engines also emit dust-like matter with the exhaust gas which has been intensively discussed in public under the general term of ôparticlesô The exhaust gas of diesel engines contains several components which must be assessed in a differentiated way with regard to any detrimental effects on the environment and the publicôs health as illustrated in figure 2.

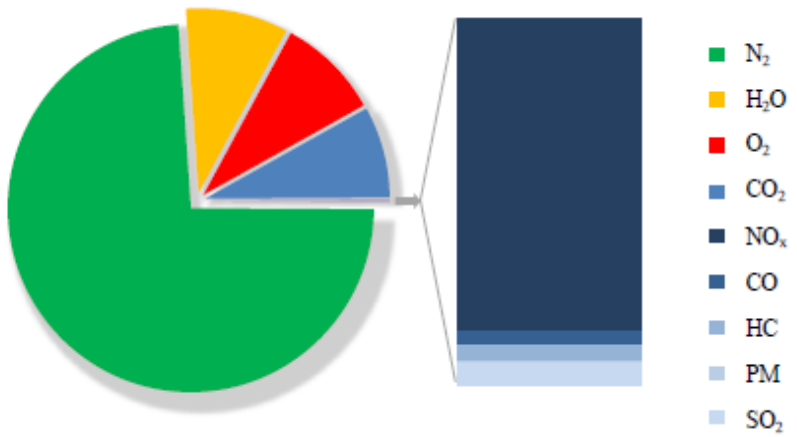


Figure 2: Composition of the Exhaust Gas Resulting from Diesel Engine Combustion (Mollenhauer and Tschöke 2007).

The main components of the emissions are the unhazardous combinations nitrogen, oxygen and water. With increasing concentrations carbon dioxide is considered one of the causes for the greenhouse effect. Other emission pollutants are carbon monoxide, hydrocarbons, sulphur oxide, nitrogen oxides and soot particles.

All solid and liquid matter formed by abrasion, comminution, erosion, condensation or incomplete combustion is considered particles. Those processes generate particles of different shapes, sizes and structures. Since they are generally so small that they hover in gases, by nature they are air pollutants which can potentially cause harm to living organisms.

Moreover, during the combustion process of a diesel engine soot particles are formed; microscopic agglomerates with a diameter of up to 0.05 εm. They basically consist of pure carbon to which various hydrocarbon compounds, metal oxides and sulphur absorb; some of those hydrocarbon compounds are categorized toxic and cancerogene and thus rated as potential health hazards. The exact composition of the soot particles depends on the engine technology, the implementation and the fuel. The formation of soot particles depends on the individual elements of the combustion process of a diesel engine such as air supply, injection as well as flame spread and additionally from the fuel quality. There is a correlation between the combustion quality and the quality of the mixture of air and fuel. In some areas of the combustion chamber, the mixture can be too rich due to an insufficient amount of oxygen which results in incomplete combustion and the formation of soot particles. The volume and the number of soot particles principally depend on the quality of the engineœs combustion.

The number of pollutants can be minimized ether by measures inside the engine ï such as exhaust gas recirculation (EGR) or by specific variation of the injection timing and therefore of the combustion. EGR is a method for the reduction of NO_x emissions. The main share of the NO_x emissions is formed by thermal NO_x. By implementing the EGR the heat capacity of the working gas is generally increased while the O_2 share in the combustion chamber is reduced. As a result the flame spread is slowed down, the combustion time is increased and therefore the top pressures and temperatures are reduced. Another aspect is the inert gas or dilution effect. Since the EGR is no longer sufficient to meet the EURO-VI Standard other exhaust gas after-treatment systems must be implemented like diesel oxidation catalytic converters with diesel particulate filter and a DeNOx unit (e.g. NO_x storage catalyst or SCR) (Mollenhauer and Tschºke 2007).

5 Fuels Used and Test Set-up

5.1 Fuels Used

For this research project the following three initial fuels were used for the production of relevant test fuels:

- Reference diesel fuel (B0)
- Fatty acid methyl ester: 70 % (*V/V*) of rapeseed oil methyl ester (RME) plus 30 % (*V/V*) of Soybean Oil Methyl Ester (SME)
- Hydrogenated vegetable oil (HVO)

To assure the storage stability of the FAME components, the oxidation stability at 110 ÁC was increased to at least 10 hours by additivation with antioxidants. Here BHT (see figure 3: 2,6-Di-*tert*.-butyl-p-hydroxytoluol) was implemented for the stabilisation of RME and Bisphenol (see figure 4: 6,6ôDi-*tert*.-butyl-2,2ômethylen-bis-p-hydroxytoluol) for that of SME.

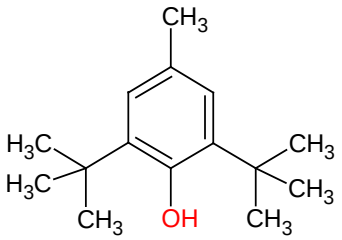


Figure 3: Chemical Structure of BHT

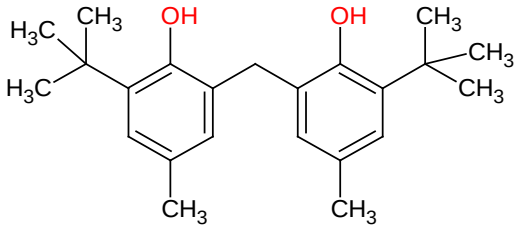


Figure 4: Chemical Structure of Bisphenol

The necessary concentrations were determined by previous tests. The applicable values of the oxidation stability of the individual FAME components before and after stabilisation are listed in tables 1 and 2.

Table 1: Oxidation Stability of Rapeseed Oil Methyl Ester before and after Additivation

BHT added [mg/kg]	Oxidation Stability of RME [h]
0	7.5
1000	11.9
2000	14.0

Table 2: Oxidation Stability of Soybean Oil Methyl Ester before and after Additivation

Bisphenol added [mg/kg]	Oxidation Stability of SME [h]
0	3.4
1000	7.4
2000	10.5

Based on these results the entire stocks of RME and SME were stabilized with 1000 mg/kg of BHT (RME) and 2000 mg/kg of Bisphenol (SME).

To avoid ónozzle foulingôthe addition of a detergent was stipulated. According to that FAME was mixed with 100 mg/kg of an additive of the polyisobutylene succinimide category (PIBSI, see figure 5). By doing so practical conditions could be simulated because according to the mineral oil industry blend fuels without any additivation are not offered within the European Union.

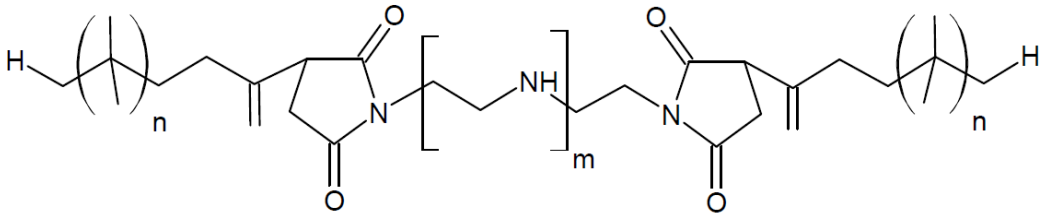


Figure 5: Chemical Structure of the PIBSI Detergent.

The chemical-physical parameters of the FAME components are listed in Table 3:

Table 3: Chemical-Physical Parameters of the FAME Components (limits according to DIN EN 14214)

Parameter	Unit	RME[1)]	SME[1)]	FAME[2)]	Limit
Ester Content	%	98.5	98.2	n.d.	min. 96.5
Density at 15 ÁC	kg/mį	884	886	884	875 - 900
Kinematic Viscosity at 40 ÁC	mmĮ/s	4.4	4.2	4.41	3.50 ï 5.00
Flash Point	ÁC	>120	>120	166	min. 120
CFPP	ÁC	-16	-7	-10	max. -10
Sulphur Content	mg/kg	< 10	< 10	n.d.	max. 10.0
CCR	%	< 0.3	< 0.3	0.30	max. 0.30
Cetane Number	-	> 51	> 51	52	min. 51
Ash Content	%	< 0.02	< 0.02	< 0.01	max. 0.02
Water Content	mg/kg	216	174	240	max. 500
Total Contamination	mg/kg	5	5	3	max. 24
Copper Strip Corrosion	-	1	1	n.d.	max. 1
Oxidation Stability (DIN EN 14112)	h	8.3	6.3	14	min. 6
Acid Number	mg KOH/g	0.14	0.33	0.28	max. 0.50
Iodine Number	g J_2/100g	115	133	121	max. 120
Content of Linolenic Acid Methyl Ester	%	11	10	n.d.	max. 12
Content of Fatty Acid Methyl Ester Ó4 Double Bonds	%	< 1	<1	n.d.	max. 1
Methanol	%	0.03	0.01	n.d.	max. 0.20
Monoglycerides	%	0.63	0.71	n.d.	max. 0.80
Diglycerides	%	0.12	0.12	n.d.	max. 0.20

Triclycerides	%	0.02	0.02	n.d.	max. 0.20
Free Glycerol	%	< 0.01	0.01	n.d.	max. 0.02
Total Glycerol	%	0.18	0.21	n.d.	max. 0.25
Alkali Content (Na + K)	mg/kg	0.76	0.44	< 1.0	max. 5.0
Earth Alkali Content (Ca + Mg)	mg/kg	0.02	0.01	< 1.0	max. 5.0
Phosphorus Content	mg/kg	0.4	0.5	< 4.0	max. 10.0

[1)] According to Certificate by ADM Hamburg
[2)] Analysis following complete additivation
CFPP - Cold Filter Plugging Point; CCR - Conradson carbon residue (from 10 % distillation residue);
n.d. ï not determined

The reference fuels and five biofuel blends were used for the storage and engine tests:

I. Diesel Fuel B0 (Reference Fuel)
II. Diesel Fuel with 20 % FAME
III. Diesel Fuel with 30 % FAME
IV. Diesel Fuel with 30 % HVO
V. Diesel Fuel with 7 % FAME and 3 % HVO
VI. Diesel Fuel with 7 % FAME and 13 % HVO

The chemical-physical parameters of the initial blends are summarized in tables 4 and 5.

Table 4: Fuel Parameters of the Biofuel Blends, Part 1

	Density at 15 °C	**Viscosity at 40 °C**	**Calorific Value**	**C**	**H**	**CFPP**
Unit	**kg/m³**	**mm²/s**	**kJ/kg**	**%**	**%**	**°C**
Limit [1)]	**820.0 – 845.0**	**2.00 – 4.50**	**-**	**-**	**-**	**-**
DF	831.3	2.44	42676	84.42	13.74	-4
DF + 20 % FAME	847.2	2.81	41464	84.41	12.36	-7
DF + 30 % FAME	851.7	2.96	40862	83.75	12.48	-8
DF + 30 % HVO	820.6	2.57	42944	82.15	12.75	-12
DF + 7 % FAME + 3 % HVO	839.9	2.63	42174	85.70	12.43	-7
DF + 7 % FAME + 13% HVO	833.7	2.61	42344	85.78	12.50	-7

[1)] According to DIN EN 590

Table 5: Fuel Parameters of the Biofuel Blends, Part 2

	HFRR	NN	PV	OS at 110 °C	OS at 140 °C	CCR	CN
Unit	**µm**	**mg KOH / g**	**meq/kg**	**h**	**min**	**% (m/m)**	**-**
Limit	**< 460**	**2.0**	**-**	**≥ 20**	**-**	**< 0.30**	**≥ 51**
DF	346	0.06	2.4	-	52	0.00	52
DF+20% FAME	163	0.09	2.8	30.9	87	0.15	51
DF+30% FAME	162	0.11	3.1	26.7	79	0.19	51
DF+30 % HVO	398	0.06	1.7	25.2	68	0.03	59
DF+7 % FAME + 3 % HVO	168	0.09	2.6	38.0	94	0.08	51
DF+7 % FAME + 13 % HVO	172	0.08	3.7	41.0	98	0.09	52

HFRR - High-frequency reciprocating rig; lubricity; corrected ãwear scar diameteró(wsd 1,4) at 60 ÁC; NN ï Neutralization Number; PV - Peroxide Value; OS ï Oxidation Stability; CCR ï Conradson Carbon Residue (from 10 % distillation residue); CN ï Cetane Number

The above parameter data proves that the biofuel blends comply with requirements of DIN EN 590 except for two. The limit for density at 15 ÁC was merely exceeded by the samples ôDF + 30 % FAMEôand ôDF + 20 % FAMEô As anticipated, the fuels with a FAME proportion showed a lower calorific value (see table 4) and improved lubrication properties (see HFRR, table 5) compared to FAME-free fuels. The increased cetane number (see table 5) of the HVO-containing fuel must be pointed out in particular. The addition of 30 % HVO to the diesel fuel led to improved ignition quality of the fuel.

5.2 Set-up and Management of the Storage Tests

The determination of the long-term stability of the biofuel blends was carried out during a period of 17 months. For that the samples were stored at cool 10 ÁC as well as at an increased temperature of 25 ÁC on average (accelerated ageing). Table 6 summarizes the relevant storage conditions.

Table 6: Storage Conditions of the Storage Study

Temperature	10 ÁC	35 ÁC, 8 h daily (average 25 ÁC)
Storage Containers	Glas Bottles	Glas Bottles
Quantity Stored	2 liters	2 liters
Storage Conditions	dark, covered, no airtight sealing	dark in a heated cabinet, 35 ÁC, 8 h daily, covered, no airtight sealing
Storage Time	17 months, sampling after 0, 2, 4, 6, 9, 12, 17 months	
Storage Start	8 July 2010	
Storage End	6 December 2011	
Parameters Analyzed	Visuell evaluation, viscosity, oxidation stability (Rancimat/PetroOxy), acid number, peroxide number, polymers	

Figure 6 shows fuel samples stored in the heated cabinet.

Figure 6 : Test Set-up of the Storage in the Heated Cabinet.

The individual samples were analyzed according to the test methods listed in table 7.

Table 7: Parameters of the Fuel Analytics

Parameter	Test Method
Density at 15 ÁC	DIN EN ISO 12185
Kinematic Viscosity at 40 ÁC	ASTM D 7042
Calorific Value	DIN 51900-3
Cold Filter Plugging Point	DIN EN 116
Lubricity at 60 ÁC (wear scar diameter 1.4)	DIN EN ISO 12156-1
Oxidation Stability at 110 ÁC (Rancimat Test Method)	DIN EN 15759
Oxidation Stability at 140 ÁC (PetroOXY Test Method)	ASTM D 7545 / EN 16091
Coke Residue (from 10 % distillation residue)	DIN EN ISO 10370
Cetane Number	DIN EN ISO 5165
Neutralization Number	DIN 51558, part 1
Peroxide Number	DIN EN ISO 3960
Polymer Content	E DIN EN ISO 16931

5.3 Set-up and Measuring Technology of the Engine Tests

For the engine tests a regular Volkswagen production engine (CR car diesel, EURO VI) was operated on the test bench with different biofuel blends. The technical data of the test engine is listed in table 8.

Table 8: Technical Data of the Test Engine

Hub	95.5 mm
Drill Hole	81.0 mm
Exhaust Gas After-Treatment	DOC ï DPF ï SCR
Engine Make	4 cylinders ï 16 valves
EGR	Cooled high pressure EGR
EGT	With VTG
Engine Capacity	2.0 Liter / 1968 cmį
Nominal Power	103 kW at 4200 min^{-1}
Max. Torque	320 Nm at 1750 ï 2500 min^{-1}

Figure 7 illustrates the specific fuel consumption during diesel fuel operation in the engine map. It corresponds to the expectations regarding an optimized EURO-VI engine.

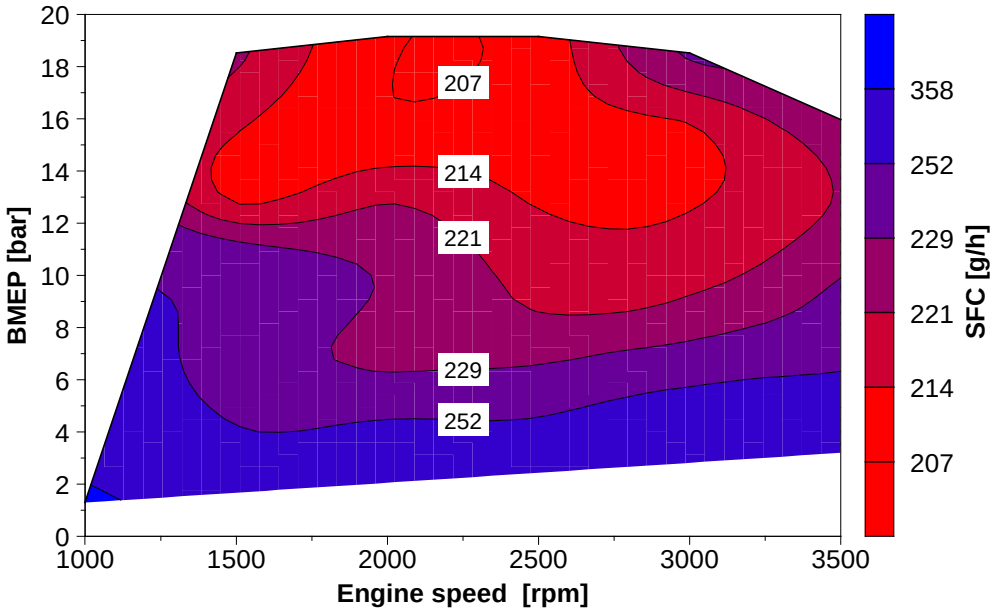


Figure 7: Consumption Characteristics/Map of the Test Engine Operated on Diesel Fuel.

A total of three PCs were necessary for monitoring and controlling the test bench and recording the measurements (as illustrated in figure 8). The test bench control was executed by PC1 with MORPHEE II, a computer programme by *D2T*. Furthermore, the thermal elements and pressure sensors installed in addition (see figure 9) were integrated into the control system and their measurements were recorded.

PC 2 worked on the ÷NDI-Setôsoftware by software company *AVL*. The signals of crank angle and pressure in the combustion chamber were synchronized and recorded by the quartz crystal via a charge amplifier. For evaluation purposes the pressure in the combustion chamber was determined during the course of 100 work cycles. The combustion process was calculated by means of a one-zone model with the pressure determined in the combustion chamber.

The control unit used for this test was ãpartly openõ, which means that it was only permissible to read out labels (data) released by the manufacturer. The write access to the engine control unit (e.g. to change labels or values with regard to the combustion) or readout of other labels was prohibited. The required obligatory regeneration of the DPF could be achieved manually by the research group with the regeneration switch. The readout of the released label/data was supported by the interface module ÷ETAS ES 591.1ô(serial number 2223295). To enable the data transfer it was connected to the CAN bus interface of the engine control unit and for the evaluation using software ÷NCAô to the third test bench PC (see figure 8).

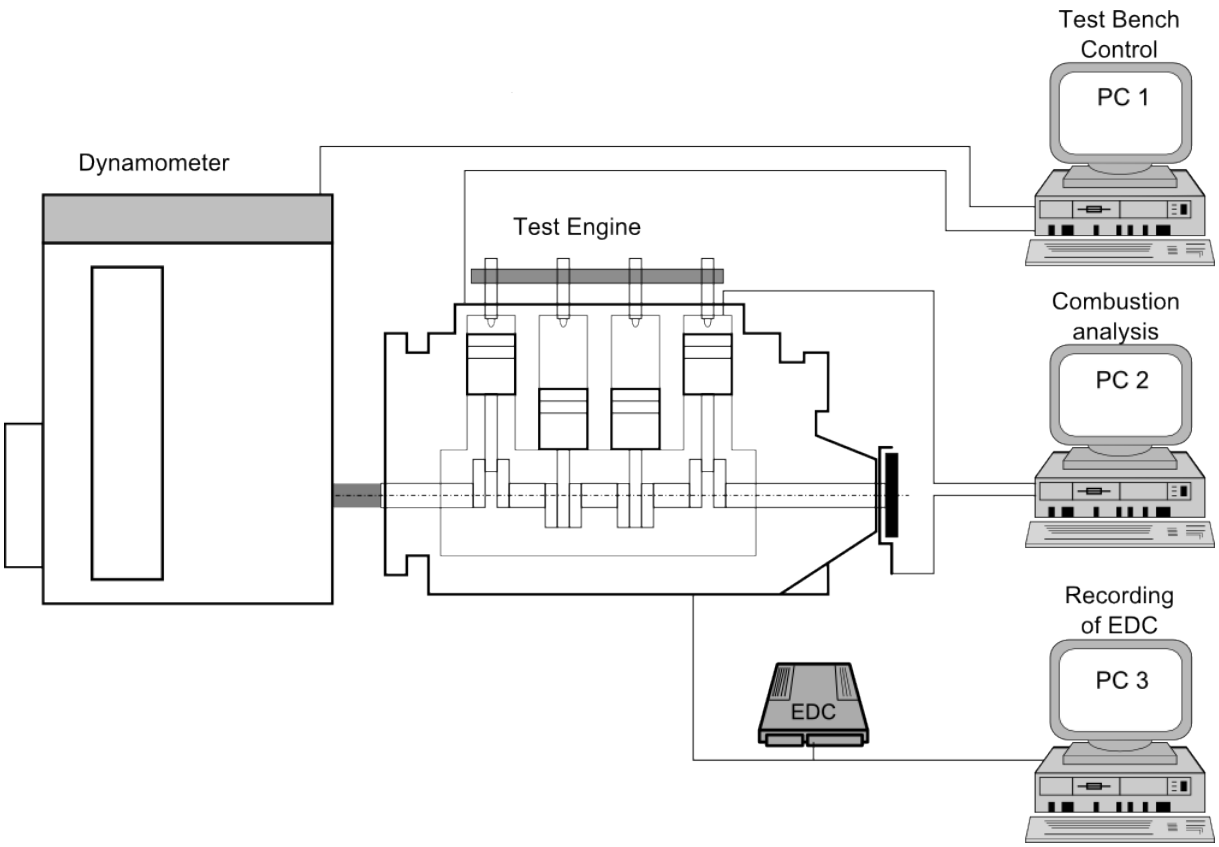


Figure 8: Diagram of the Test Bench Set-up Including Measuring and Control Technology.

The engine set-up including the relevant pressure and temperature sensors as well as the exhaust gas sampling point is illustrated as follows in figure 9.

It is easy to see that exhaust gas samples were taken before and after the DPF (diesel particulate filter) as well as after the SCR (selective catalytic reduction).

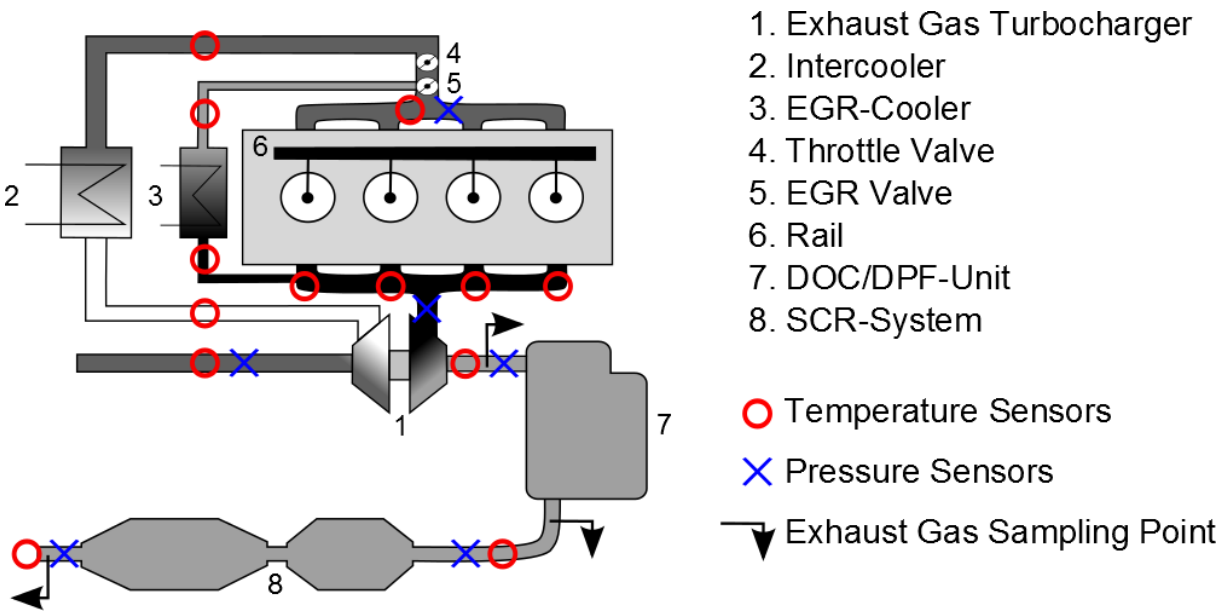


Figure 9: Engine Set-up with Measuring Points for Pressure and Temperature as well as Exhaust Gas Sampling Points.

The determination of gaseous exhaust gas components was carried out with an exhaust gas analyzer by *ABB*, type AO2020. The device comprises various measuring methods which were summarized to a so-called function block, see table 9.

In addition, soot content and particle number in the exhaust gas were determined. The determination was carried out with the aid of the *AVL* ôParticle Counter 489ô and ôSmoke Meterô

Table 9: Exhaust Gas Components and their Appropriate Analyzers.

Measuring Unit	Analyzer (Module)	Measuring Method
O_2	ABB AO2020 (Magnos 106)	Magneto mechanic oxygen analyzer
CO/CO_2	ABB AO2020 (Uras 14)	Non-dispersive infrared adsorption
HC	ABB AO2020 (FID)	Concentration measurement
NO/NO_2	ABB AO2020 (CLD)	Photoemission
NO	ABB AO2020 (Limas 11)	Wavelength comparison
Particle Number	AVL Particle Counter 489	Light-scattering method
FSN	AVL Smoke Meter	Optical smoke measurement on filter paper

5.3.1 Short-term Test Runs

The effects of the changed fuel properties on combustion management and emission performance were determined by means of short-term measurements at selected measuring points of the engine map (see figure 10). In addition, data of the engine control unit was recorded and evaluated. For that purpose a selected point during operation was approached and maintained for 10 minutes to assure stationary engine performance. Afterwards the parameter values obtained were recorded.

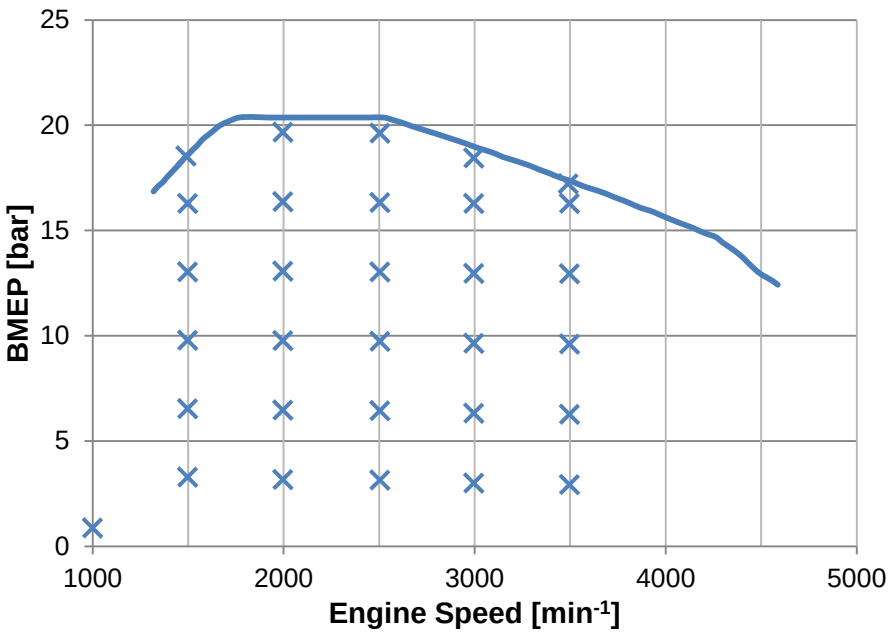


Figure 10: Selected Measuring Points on the Engine Map.

Measuring the particle number in the exhaust gas was part of the short-term runs. As framework conditions four stationary operating points and a load step were defined (see table 10 and figure 11). The sampling points are marked in figure 9 (exhaust gas sampling points). For the step test 10 load steps were recorded and averaged.

Table 10: Measuring Points for Particle Counting.

Measuring Point	Engine speed / min^{-1}	BMEP / bar
1	1875	1.27
2	1500	3.3
3	2000	3.3
4	2000	6.6

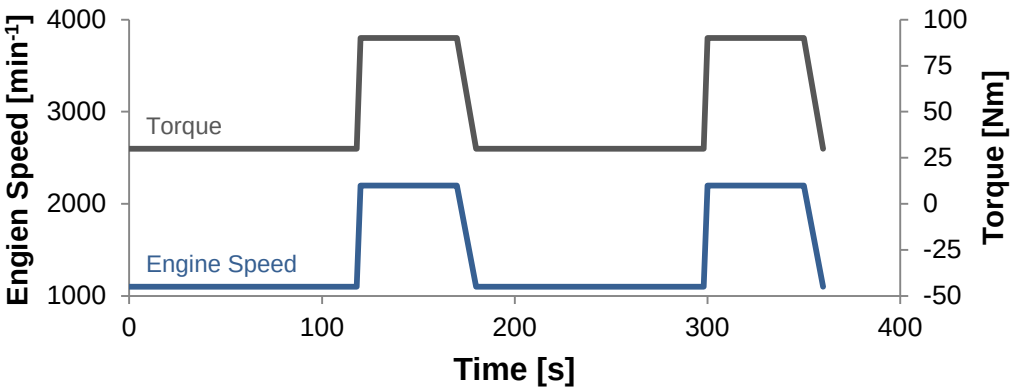


Figure 11: Torque and Speed Curve during the Step Test Measurement.

The synthetic engine lubrication oil implemented was ÷Formula V LongLife 5W-30ô In order to monitor its quality, samples of the lubrication oil were taken after every short-term run and analyzed with regard to the parameters listed in table 11.

Table 11: Selected Parameters for the Analysis of the Lubrication Oil.

Parameter	Unit	Test Method
Kinematic Viscosity at 40 ÁC	mmĮ/s	ASTM D 7042
Total Base Number	mg KOH/g	DIN ISO 3771
Neutralization Number	mg KOH/g	DIN 51558 T1
Soot Content	%	DIN 51452
Fuel Content	%	Infrared Method

The condition of the lubrication oil samples was additionally characterised by the analysis of the wear metals to obtain important information on the corrosive and/or abrasive wear. The wear metals as well as the additive components of the lubrication oil samples were determined directly by emission spectrometry with inductively coupled plasma (ICP-OES) according to DIN EN 51399-1.

Furthermore, the content of dimers and polymers in the lubrication oil was determined by means of HPSEC according to E DIN EN ISO 16931.

The engine lubrication oil was not changed at the end of the relevant short-term run. Following every fuel change, the fuel and lubrication oil filters were exchanged for new ones.

5.3.2 Execution of the Endurance Runs

In order to be able to compare the efficiency and reliability of the exhaust gas after-treatment systems (consisting of DOC, DPF and SCR) operating on standard-conform reference fuel and biofuel blends, three endurance tests were run of 500 hours each. These engine tests were paralleled by systematical lubrication oil analyzes (see table 11) for the determination of the impact of biofuel blends on the oil ageing during the engine operation.

For the endurance tests the engine was operated daily for 24 hours from Sunday 4.00 p.m. until Friday 24:00 (midnight). The endurance run was interrupted for a short time to sample the lubrication oil. The operational cycle implemented is illustrated by figure 12.

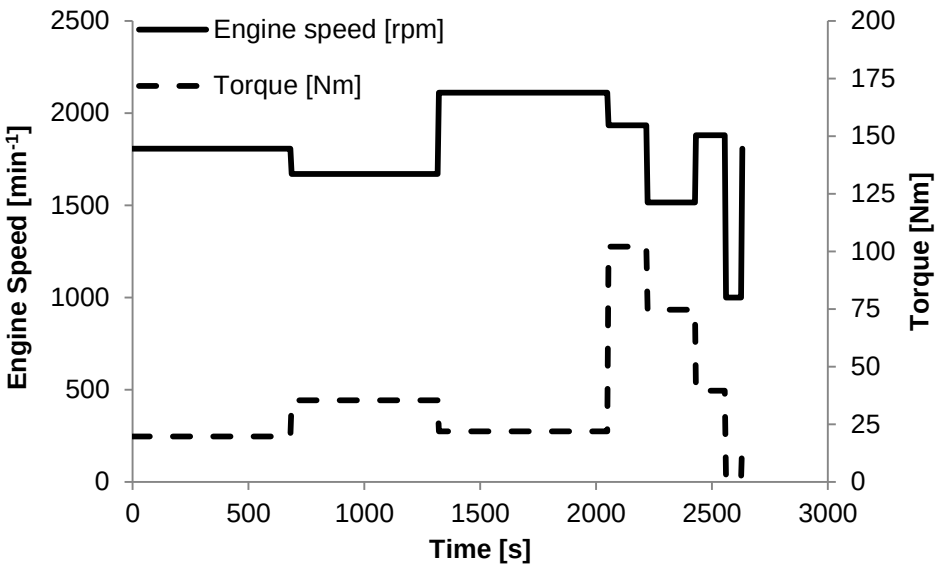


Figure 12: Torque and Speed Curve during the Endurance Run Cycle.

The endurance run cycle was based on the AMA cycle. The fuel blends implemented are listed in table 12.

Table 12: Fuel Compositions for the Endurance Runs

Endurance Test Run	Fuel
1	DF + 7 % FAME
2	DF + 30 % FAME
3	DF + 30 % HVO

After every endurance run, the lubrication oil was changed. The particle filter regeneration was arranged automatically according to the algorithm stipulated in the engine control device. There was no forced regeneration by the test bench engineer.

6 Results of the Storage Study

6.1 Analysis of the Initial Fuels

First of all the fuel properties of the relevant biofuel blends were determined to guarantee a safe operation of the engine (see tables 4 and 5). According to that, four of the six samples analyzed fully comply with the requirements of standard DIN EN 590. The fuel samples with a FAME content of 20 % and 30 % slightly exceeded the relevant limit for a density at 15 ÁC. Those deviations could be neglected, however, and a trouble-free implementation of the selected biofuel blends for the intended engine test runs was anticipated.

6.1.1 Surface Tension

If the surface tension is known, important statements can be made on the injection behaviour of a fuel. Minor surface tension leads to improved fuel atomization and thus optimum combustion. In order to obtain information on the evaporation behaviour of the fuel samples dependent on the relevant FAME and/or HVO contents, the tests included the determination of the surface tension of the selected samples by means of the ôTensiometer TD1ô(by *Lauda*) according to DIN EN 14210 (Ring Test Method).

As follows in figure 13, the surface tension of the diesel fuel/FAME blends dependent on the temperature is illustrated. The repeatability of the method was 0.2 mN m^{-1}.

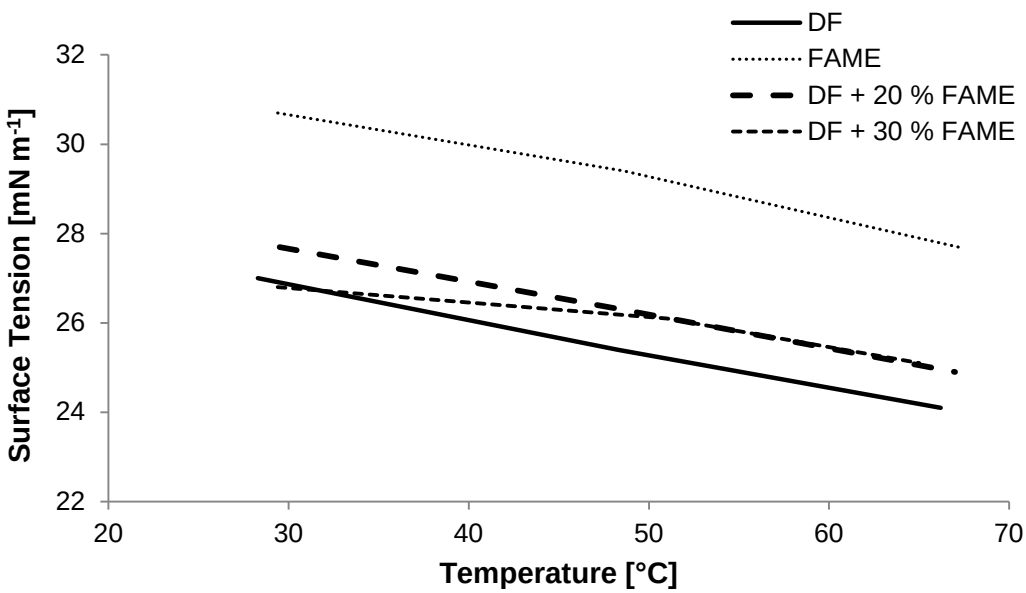


Figure 13: Surface Tension of the Diesel Fuel/FAME Blends Dependent on the Temperature.

The expectations that the surface tension of the samples declines as the temperature rises are confirmed by the results. It is also noticeable that increasing polarity leads to higher surface tension.

So due to the moleculeôs polarity the measuring results for FAME are significantly higher than those of pure diesel fuel. As expected, if the FAME content in diesel fuel is increased the surface tension rises. In analogy to the evaporation behaviour this means that FAME-containing fuels show inferior evaporation ability compared to diesel fuel. The increased surface tension causes the formation of larger fuel droplets in the combustion chamber which do not evaporate and burn as well as smaller droplets due to small surface/air ratio. Therefore, compared to the reference diesel fuel, differences in the combustion behaviour and higher exhaust gas emission must be expected if FAME-containing blends are implemented.

The results of the surface tension of the biofuel blends dependent on the HVO concentration are illustrated in figure 14 as follows:

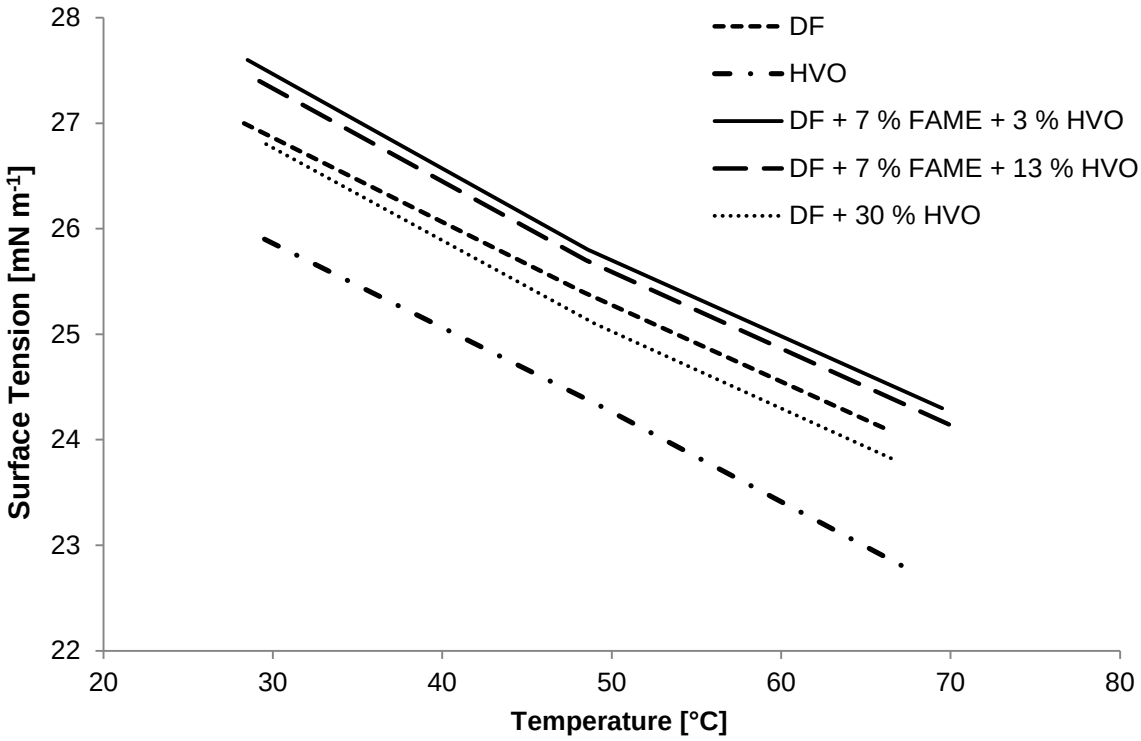


Figure 14: Surface Tension of the Diesel Fuel/HVO Blends Dependent on the Temperature.

The curves indicate that pure HVO has a significantly lower surface tension than diesel fuel. The measuring results for the fuel samples containing 30 % HVO are within the same range as the reference diesel fuel. The results of the relevant biofuel blends with FAME and HVO slightly exceed those of the diesel fuel which can be attributed to the higher surface tension of the FAME contained.

In conclusion it can be stated that pure HVO as well as the sample with an HVO content of 30 % show better evaporation behaviour in the combustion chamber. The reduced surface tension of the fuel causes smaller droplet sizes which results in a big relationship between the fuel surface and volume. That way evaporation and combustion are improved which thus results in the reduction of exhaust gas emissions.

6.1.2 Distillation Characteristics

Additional information on the evaporation and cold start behaviour of a fuel is obtained due to the distillation characteristics. As part of this project the boiling characteristics of the fuels were recorded according to DIN EN ISO 3405 with the *Petrotest* distillation unit, model ADU4. Here the boiling curve was recorded, i.e. the determination of the dependency of the condensed volume [%] from the relevant boiling temperature [ÁC]. It generally applies to hydrocarbons that the boiling temperature increases as the chain lengths increase.

The distillation characteristics of diesel fuel, FAME and the relevant diesel Fuel/FAME blends are summarized in figure 15 as follows:

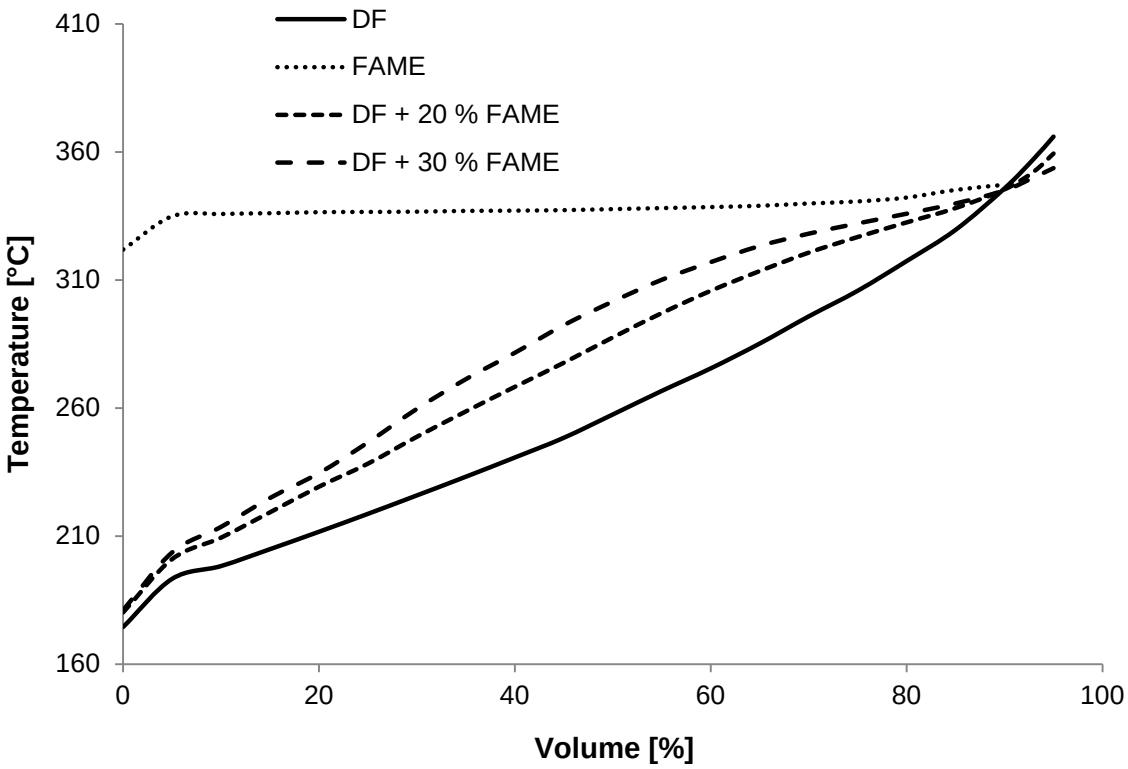


Figure 15: Distillation Characteristics of the Diesel fuel/FAME Blends.

The results presented illustrate the significant difference between FAME and fossil diesel fuel with regard to their boiling behaviour. Due to the fact that diesel fuel is a mixture of a number of hydrocarbons with different chain lengths, a steady rise of the boiling curve can be registered. The individual components evaporate at the relevant boiling temperature dependent on their chain lengths. Diesel fuel starts to evaporate at about 170 ÁC.

FAME fuel has a differing boiling range, however. It is noticeable that its homogene composition leads to a very narrow boiling range. Another striking aspect is that it begins to boil at significantly higher temperatures (>310 ÁC). So FAME shows inferior evaporation and cold start behaviour compared to diesel fuel.

The boiling ranges of biofuel blends with FAME contents of 20 % and 30 % resemble that typical of diesel fuel.

As follows in figure 16, the distillation characteristics of diesel fuel, HVO as well as DF-HVO-blends are illustrated in comparison.

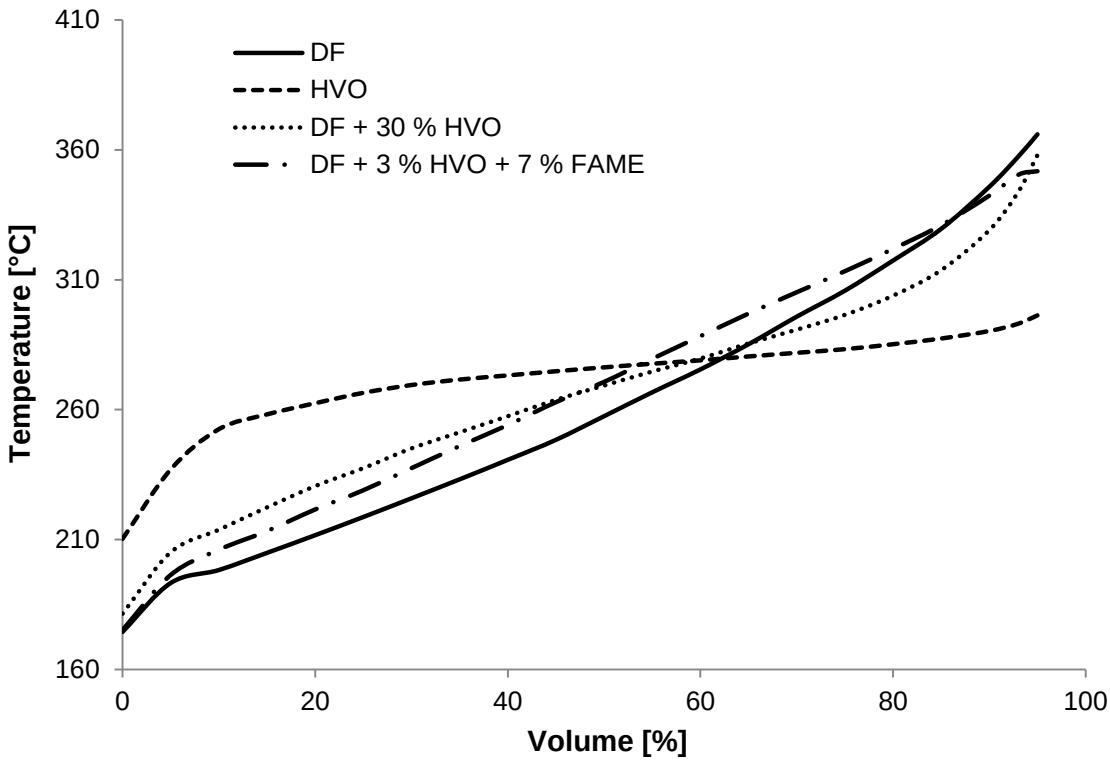


Figure 16: Distillation Characteristics of the Diesel Fuel/HVO Blends.

The curves illustrate that HVO ï compared with diesel fuel ï has a relatively narrow boiling range (210 ÁC ï 300 ÁC). HVO starts boiling later and stops boiling earlier than diesel fuel. Finishing the boiling process earlier has a positive effect on the combustion behaviour. When HVO is implemented the danger of fuel ingress diluting the lubrication oil is reduced compared with the implementation of diesel fuel.

6.2 Storage Stability of the Biofuel Blends

To examine their long-term stability the biofuel blends were stored for 517 days under the conditions described before (see table 6) and sampled at defined intervals. Table 13 provides an overview of the results of the visual evaluation of the samples stored at 10 ÁC at the beginning (t = 0 d) and the end (t = 517 d) of the storage study. The designation ôlittle sedimentô corresponds to the total contamination of Ò8 mg/kg (analysis result of the reference diesel fuel).

Table 13: Visual Evaluation of the Samples Stored at 10 °C.

	Initial Sample (t = 0 d)			Final Sample (t = 517 d)
Fuel	**Appear-ance**	**Colour**	**Sediments**	**Remarks**
DF	clear	yellow, slightly green	little	white layer on bottom, otherwise unchanged
DF + 20 % FAME	clear	yellow, light amber colour	little	white layer on bottom, otherwise unchanged
DF + 30 % FAME	clear	yellow, light amber colour	little	layer on bottom, otherwise unchanged
DF + 30 % HVO	clear	yellow-green	little	layer on bottom, otherwise unchanged
DF + 7 % FAME+ 3 % HVO	clear	yellow, slightly greenish	little	layer on bottom, otherwise unchanged
DF + 7 % FAME + 13 % HVO	clear	yellow, slightly greenish	little	layer on bottom, otherwise unchanged

Due to visual evaluation no relevant differences could be identified after a storage period of 17 months at 10 ÁC. The appearance of the samples stored at an average temperature of 25 ÁC did not show any significant changes either.

The results of the analysis methods dependent on storage temperature and time are presented as follows.

6.2.1 Oxidation Stability

For this project, the oxidation stability of the biofuel blends was analyzed by means of two separate methods which are based on different measuring principles.

The Rancimat method according to DIN EN 15751 induces the thermal ageing of the samples by air supply (10 l/h) at 110 ÁC and the secondary oxidation products are finally detected by continuous conductivity measurements. So the formation of volatile, electrically conductive components is imperative for this method, which is only suitable for FAME and FAME blends with diesel fuel according to the standard. As a result the so-called PetroOXY method (ASTM D 7545 ï EN 16091) was implemented for the analysis of the reference diesel fuel as well as for additional tests of the biofuel blends. According to this method the sample is heated to 140 ÁC in an oxygen atmosphere (7 bar). Incurring oxidation reactions lead to a pressure decrease within the system which is directly related to the oxidation stability. In the following section the individual results of the methods are presented.

6.2.1.1 Rancimat Method

As reference sample pure FAME fuel was integrated additionally into the storage study. It was to be assumed that this sample were the most likely to show significant oxidation reactions. Generally it was stated that pure FAME showed the lowest and the samples with FAME and HVO contents (DF + 7 % FAME + 3 % HVO; DF + 7 % FAME + 13 % HVO) the highest oxidation stability.

As is illustrated in table 17, for some of the samples stored at an average temperature of 25 ÁC, significant changes were identified during the course of the storage time which applied

to the reference sample (100 % FAME) as well as the two blends with a FAME content of 20 % and 30 %.

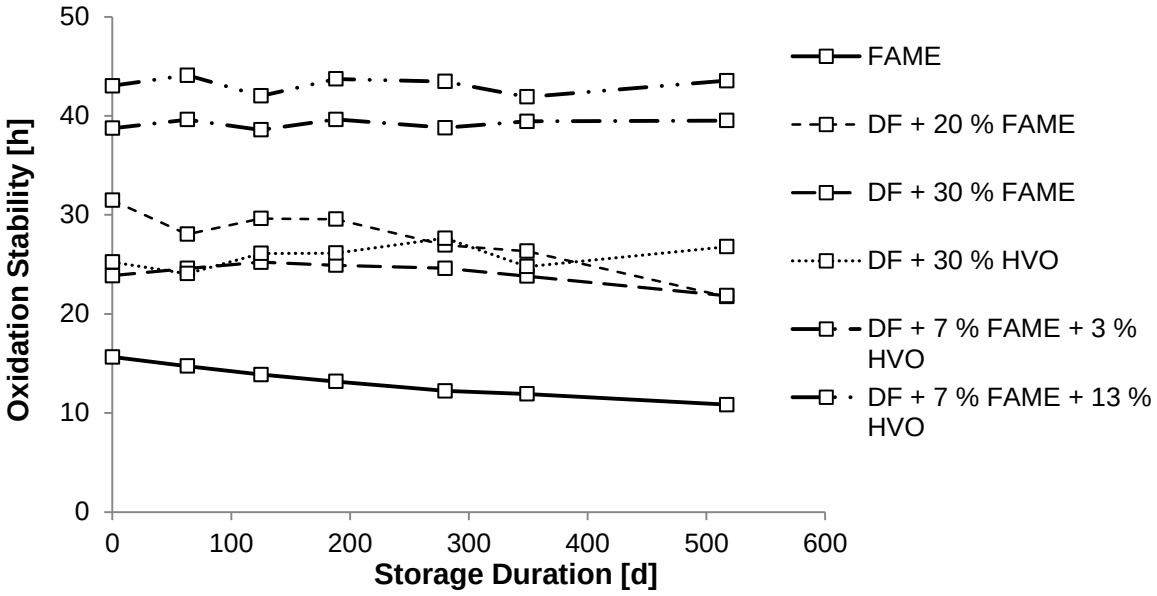


Figure 17: Oxidation Stability of the Biofuel Blends at 110 °C (Rancimat) Dependent on the Storage Time at 25°C.

The oxidation stability of the reference sample (FAME) dropped from 15.7 h at the beginning of the storage study to 10.8 h after a total of 517 days. These results illustrate that the Rancimat method is generally suitable for the monitoring of the oxidation stability; however, the other biofuel blends did not show any significant changes.

Figure 18 shows the oxidation stability at 110 ÁC of the biofuel blends dependent on the storage time at 10 ÁC as follows:

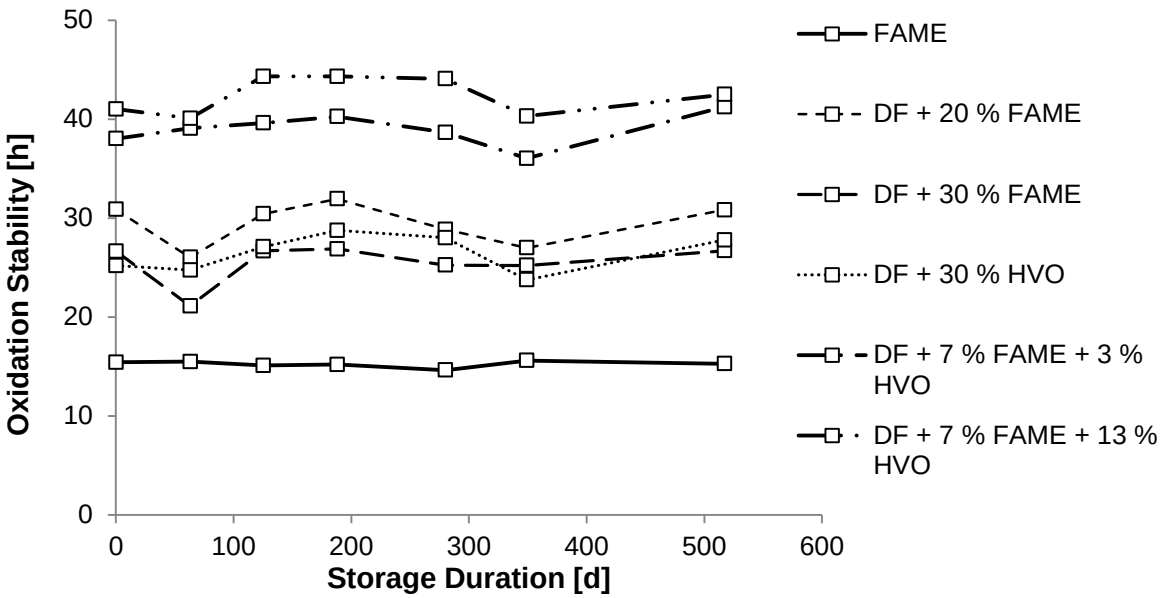


Figure 18: Oxidation Stability of the Biofuel Blends at 110 °C Dependent on the Storage Time at 10 °C.

Looking at the curves reveals that there are no significant changes between the initial and the final oxidation stabilities of the biofuel blends tested. The deviations incurred were within the methodôs repeatability r = 0.22027 + 0.04344 x. Thus no correlation was identified between the oxidation stability and the storage time at 10 ÁC.

6.2.1.2 PetroOXY Method

Figure 19 shows the oxidation stabilities at 140 ÁC dependent on the storage time at 10 ÁC as follows:

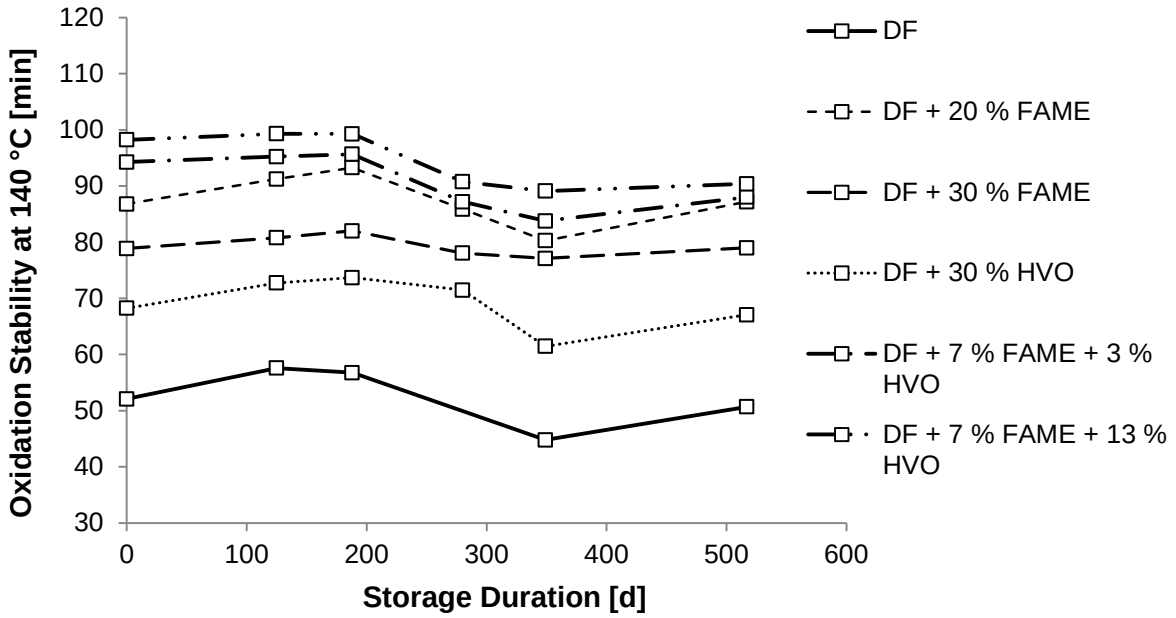


Figure 19: Oxidation Stability of the Biofuel Blends at 140 °C (PetroOXY) Dependent on the Storage Time at 10 °C.

It is apparent that the diesel fuel shows the lowest oxidation stability during the entire test period. This surprising fact could not be resolved during the course of this project. Higher oxidation stability had been expected for the reference diesel fuel (B0) without any FAME content had since it did not contain any components easily prone for oxidation. In comparison, the samples containing FAME showed higher oxidation stability due to their prior additivation with antioxidants.

The highest oxidation stability was measured for the sample ôDF + 7 % FAME + 13 % HVOô. In addition, it was determined that none of the biofuel blends showed any significant changes dependent on the storage time; the deviations of the analysis results were within the range of the repeatability of the measuring method (6 %).

The development of the oxidation stabilities of the biofuel samples stored at 25 ÁC is illustrated in figure 20. As anticipated, an influence of the increased storage temperature on the resulting oxidation stability can be noticed. Therefore, significant changes could be identified for all samples.

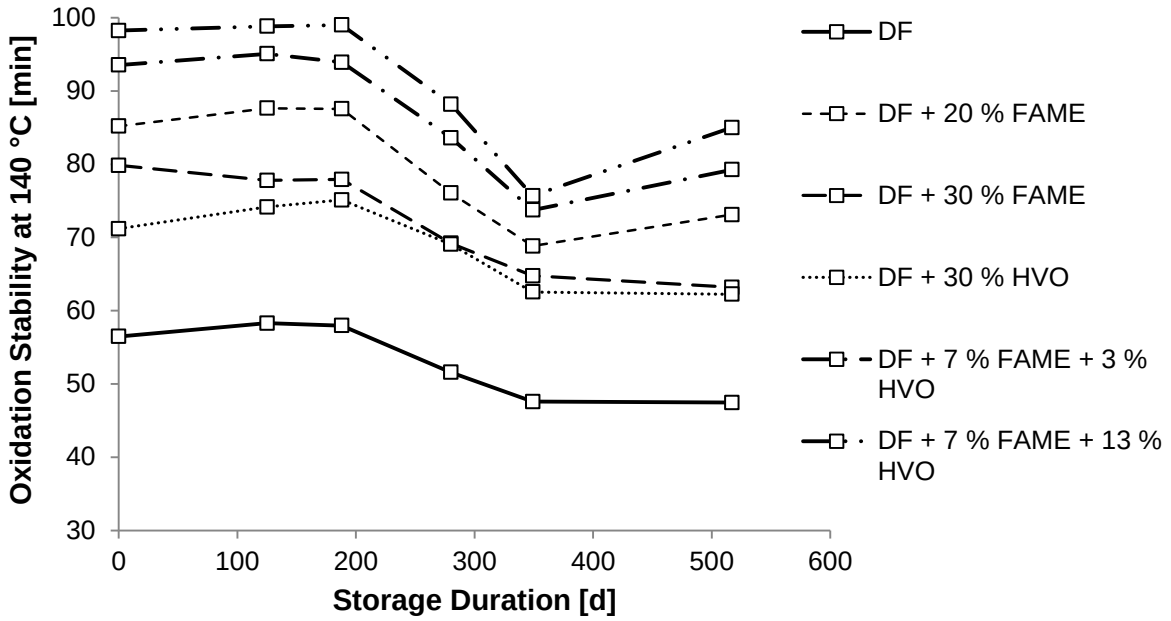


Figure 20: Oxidation Stability of the Biofuel Blends at 140 °C (PetroOXY) Dependent on the Storage Time at 25 °C.

During the course of this project no correlation could be found between the two methods for the determination of the oxidation stability. By means of the PetroOXY method significant changes were found whereas the Rancimat results did not show any dependence from the storage period. The reason for that is that with the PetroOXY method the beginning of the oxidative decline of the sample is detected by the relevant pressure decline within the system. In contrast to that the Rancimat measuring principle records the secondary oxidation products which only form at the end of the induction period, thus at a later time of the sample ageing process. Due to their differing measuring principles the results of the two test methods are not directly comparable.

6.2.2 Neutralization Number

The neutralization number is an indicator for the content of acidic components of a sample. If FAME is degraded by oxidation, free fatty acids form for example which lead to a dramatic deterioration of the quality. Therefore, a high neutralization number is an indicator for fuel ageing. The biofuel blends stored at an average temperature of 25 ÁC are discussed as follows (see figure 21):

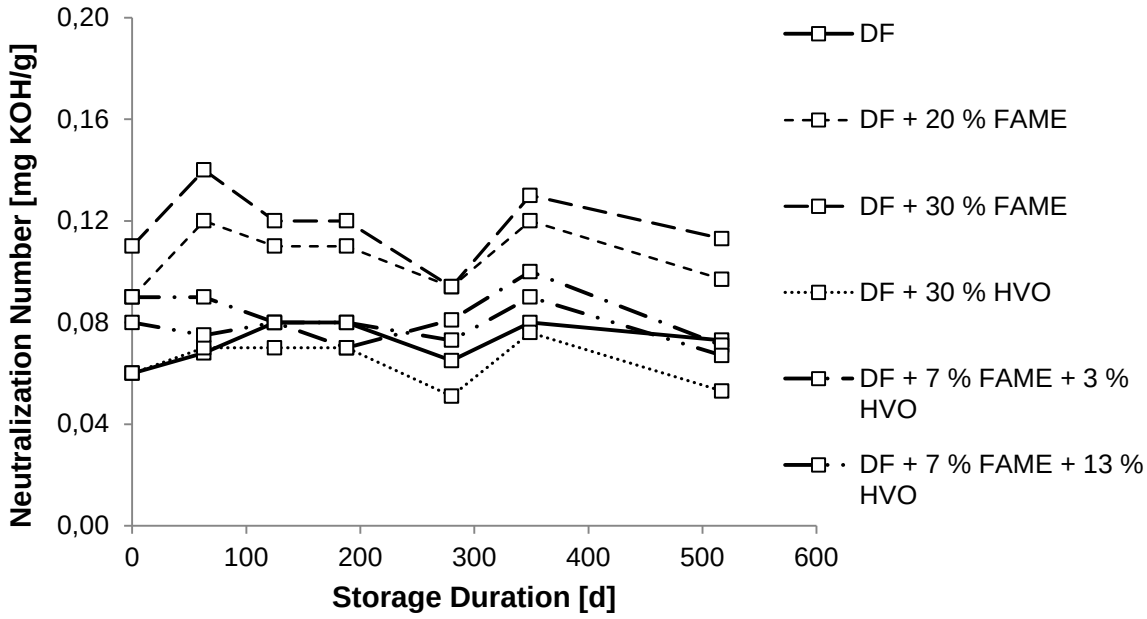


Figure 21: Neutralization Number of the Biofuel Blends Dependent on the Storage Time at 25 °C.

As anticipated, the FAME containing fuels showed the highest neutralization number compared to the other biofuel blends. The higher the FAME content of a sample, the higher the neutralization numbers resulting therefrom; whereas the lowest measuring results were those of the ÷DF + 30 % HVOô sample.

The samples stored at 10 ÁC show a similar development (see figure 22).

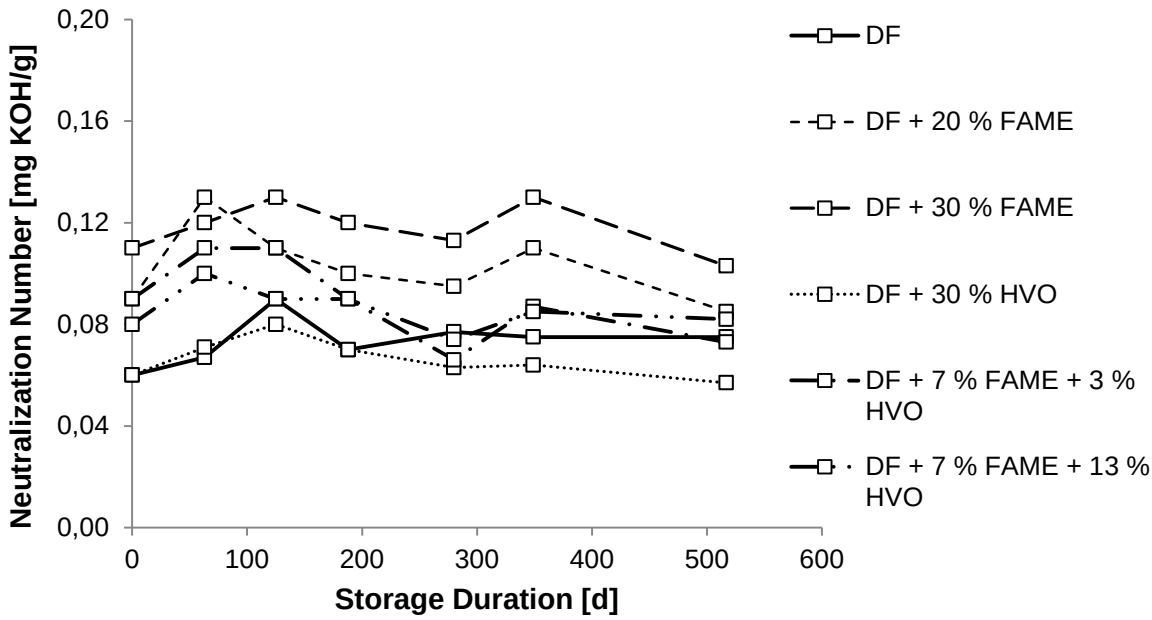


Figure 22: Neutralization Number of the Biofuel Blends Dependent on the Storage Time at 10 °C.

The curves illustrate that during the test period of 517 days no significant changes of the neutralization number occurred dependent on storage time and temperature.

6.2.3 Viscosity

The kinematic viscosity was determined at 40 ÁC according to ASTM D 7042. Figure 23 shows the measuring results of the individual biofuel blends dependent on the storage time at 25 ÁC as follows:

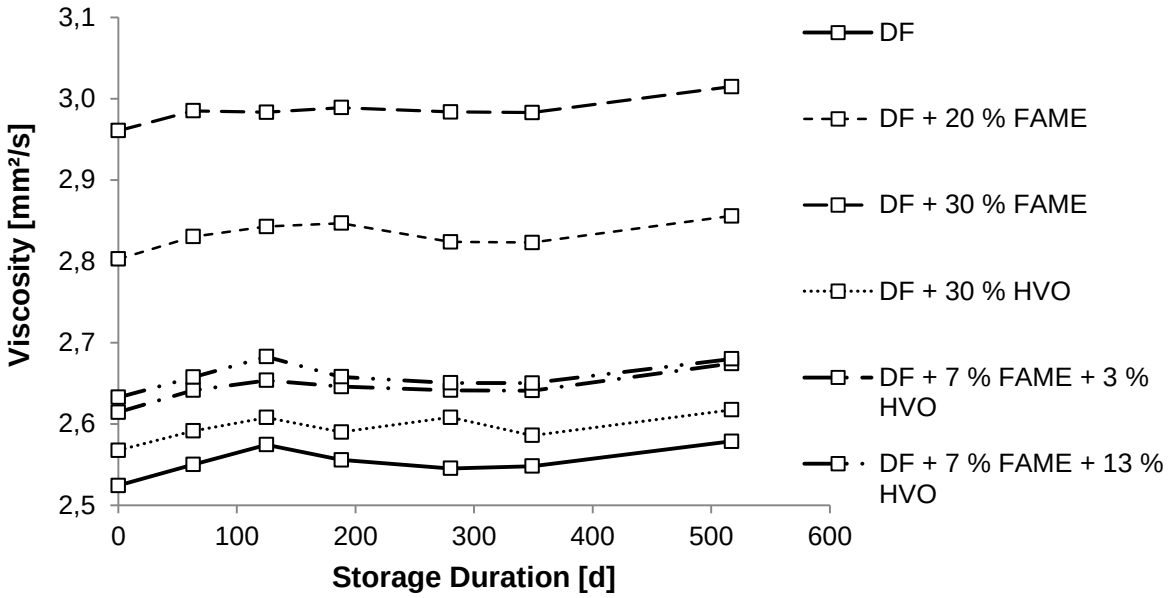


Figure 23: Kinematic Viscosity of the Biofuel Blends Dependent on the Storage Time at 25 °C.

The viscosity of the fuel samples stored at 10 ÁC showed a very similar development (see figure 24). No significant changes of the viscosity of all fuels tested were measured during a storage period of 17 months.

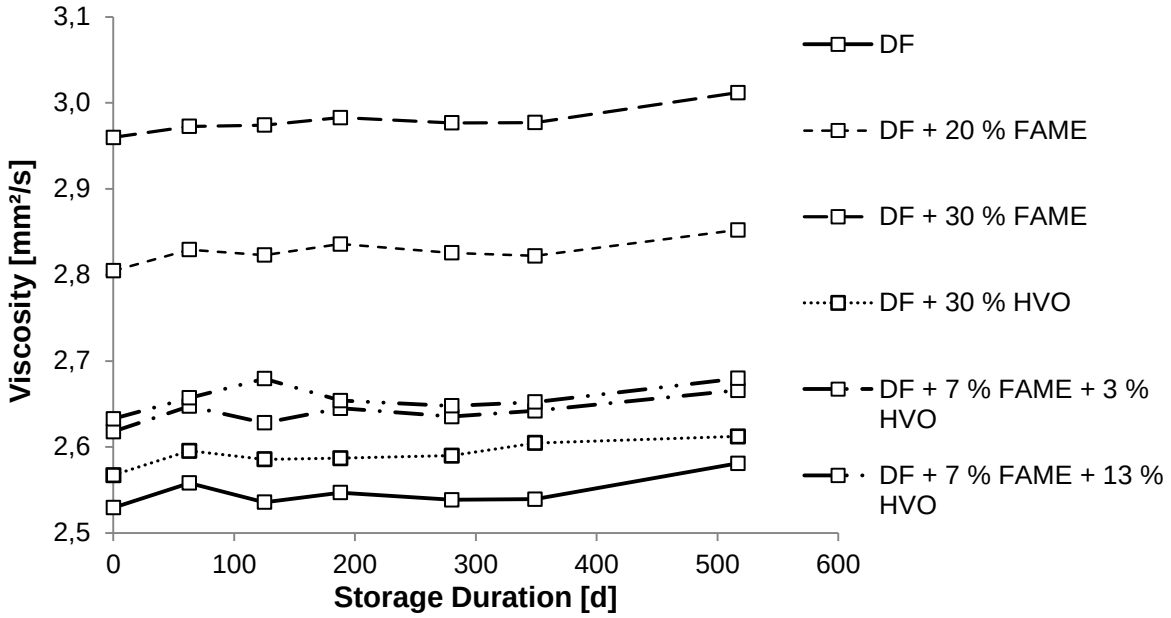


Figure 24: Kinematic Viscosity of the Biofuel Blends Dependent on the Storage Time at 10 °C.

6.2.4 Peroxide Value

The peroxide value (according to DIN EN ISO 3960) is another indicator for the possible monitoring of the ageing of biofuels due to oxidation. It indicates the amount of oxygen chemically bound as peroxide and/or hydroperoxide. During the degradation of the bio components (FAME) due to oxidation, at first hydroperoxides form which finally react to become secondary oxidation products; i.e. the content of hydroperoxides decreases again as the ageing progresses. So the result of the peroxide value highly depends on the changes the sample undergoes with time. The peroxide value of the biofuel blends stored at 25 ÁC is illustrated in figure 25 as follows:

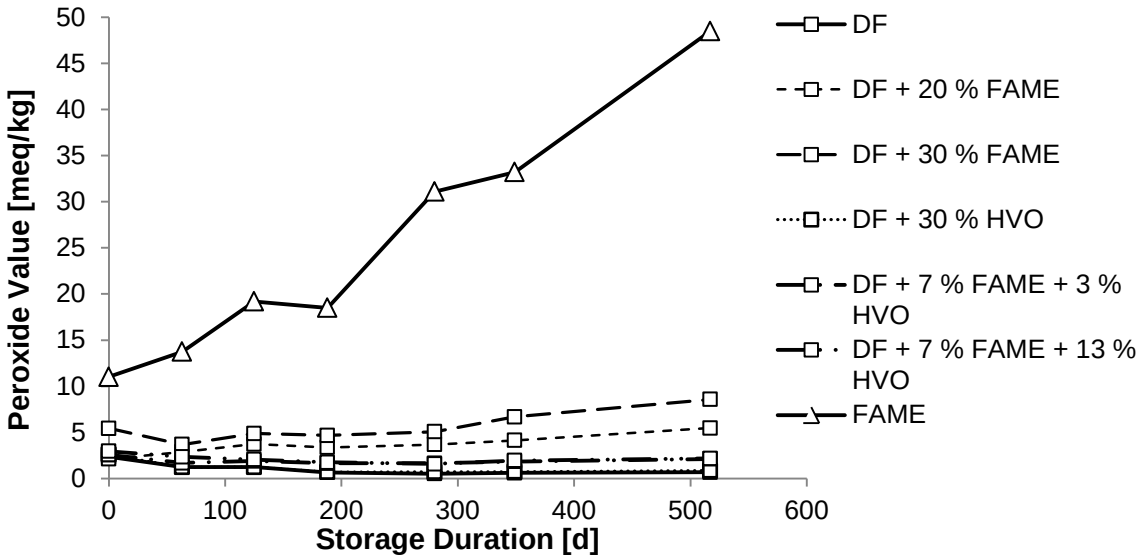


Figure 25: Peroxide Value of the Biofuel Blends Dependent on the Storage Time at 25 °C.

The results illustrate that the reference sample (FAME) showed a high increase of the peroxide content during the storage time at 25 ÁC. The basic usefulness of the method could thus be confirmed. However, it is necessary to mention that this method shows significant deficits concerning the endpoint determination (visual) and the reproducibility. Both methods for the determination of the oxidation stability (Rancimat, PetroOXY) as described before are much more suitable for the determination of oxidative ageing.

As expected, no significant changes of the biofuel blends stored at 10 ÁC could be identified dependent on the storage time as is illustrated in figure 26 by the results of the analysis.

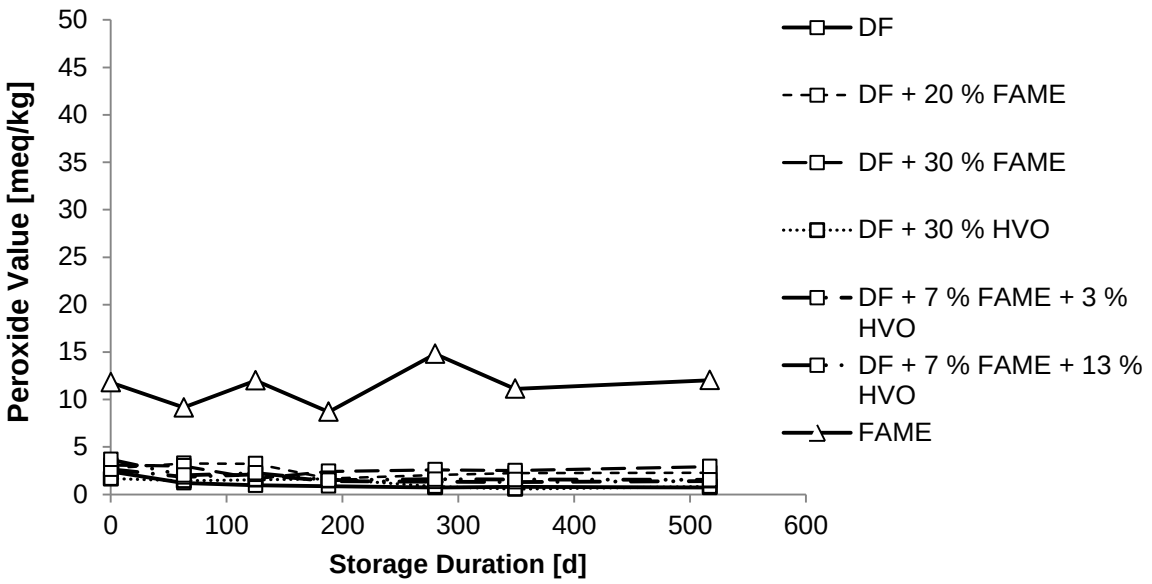


Figure 26: Peroxide Value of the Biofuel Blends Dependent on the Storage Time at 10 °C.

6.2.5 Polymer Content

Another method to assess any quality deterioration of the biofuel blends is the determination of the polymerised proportion which is a result of the ageing of the fuel components. Oligomers and polymers contained in the fuel samples can be analyzed by means of high-performance size-exclusion chromatography (HPSEC). The separation of the individual sample components is achieved by gel permeation chromatography (GPC) according to their molecular sizes. According to E DIN EN ISO 16931 all HPSEC measurements were executed with selected samples in a Merck-Hitachi unit with a refractive index detector.

Since a significant rise of the oligomer and/or polymer components dependent on the storage time at increased temperature was considered most likely for the FAME reference sample, figure 27 shows the HPSEC elugrams of the FAME sample stored at 25 ÁC at the beginning and the end of the storage study as follows.

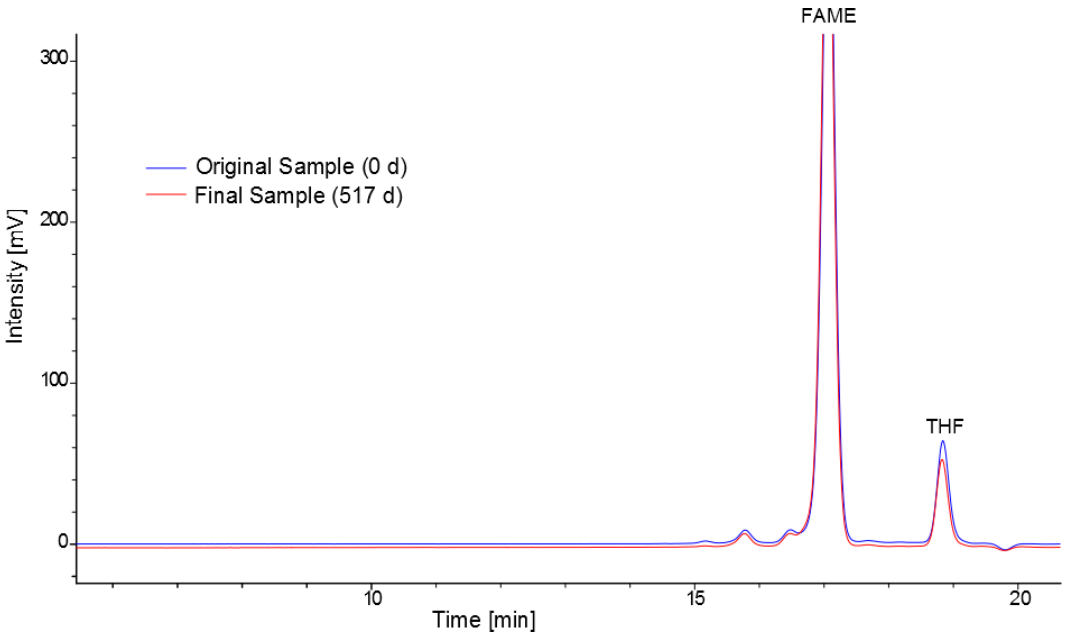


Figure 27: HPSEC Anlaysis of FAME Dependent on the Storage Time at 25 °C.

Due to their higher molecular mass, HPSEC analysis detects oligomer/polymer components first, i.e. at shorter retention periods (< 10 min) compared to those of the relevant monomer FAME components.

Accordingly ï as shown above in figure 27 ï no oligomer and/or polymer components could be verified for the FAME sample stored for 517 days at an average temperature of 25 ÁC. Although the oxidative decomposition of the FAME could be verified due to the decreasing oxidation stability (see figure 17), the oxidation products formed were yet no polymerization products.

The results for diesel fuel samples stored at 25 ÁC obtained by HPSEC analytics both before and at the end of the storage study are given in figure 28 as follows.

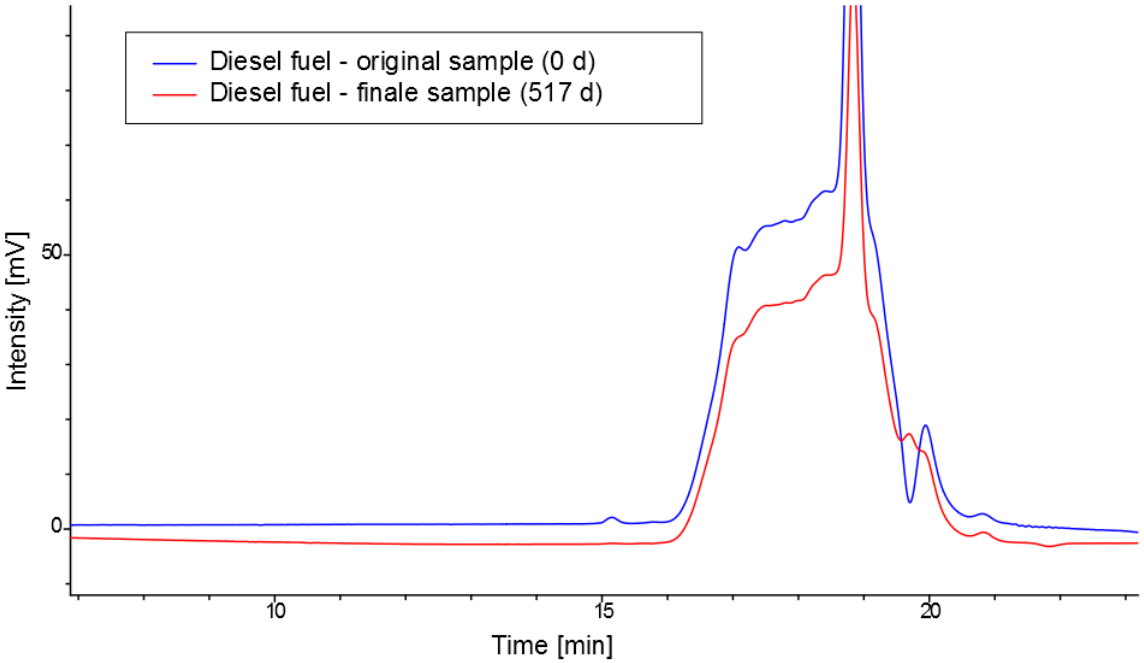


Figure 28: HPSEC Anlaysis of Diesel Fuel Dependent on the Storage Time at 25 °C.

The elugramms given here clearly illustrate that both samples only showed the expected diesel fuel peak (retention time: 16 min) and/or the eluent signal (tetrahydrofuran, retention time: 20 min). Thus no major structures were detected for retention times of <10 min. This means that during the test period no oligomer and/or polymer components were formed in the diesel fuel sample.

The results of the HPSEC analysis for HVO-containing fuel (DF + 30 % HVO) are given in figure 29 as follows.

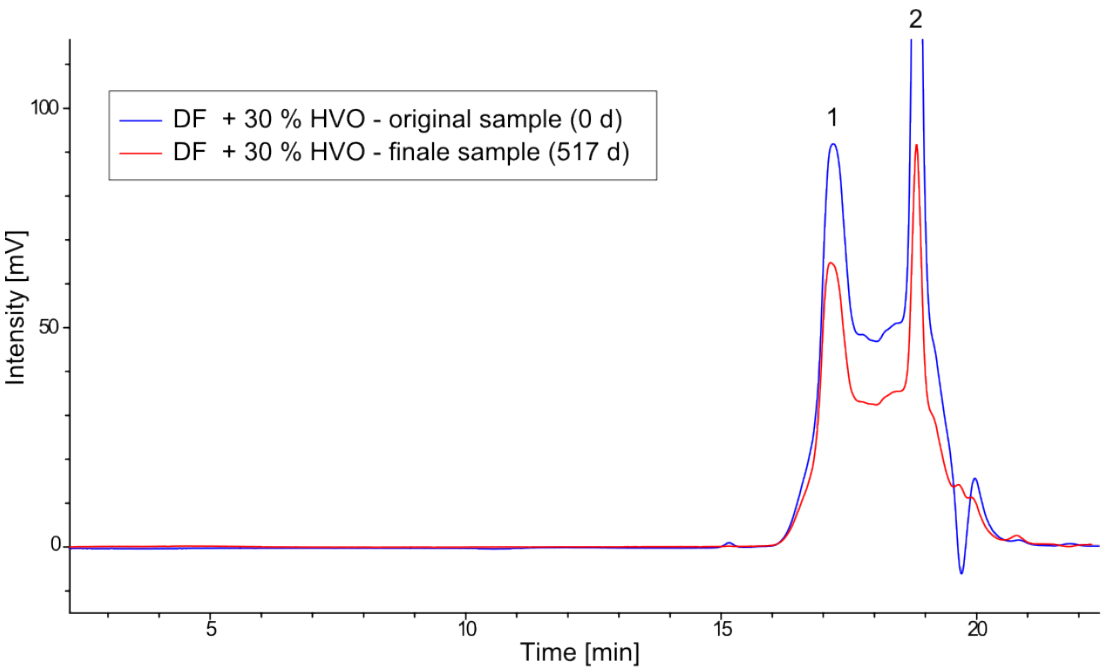


Figure 29: HPSEC Analysis of the 'DF + 30 % HVO' Sample Dependent on the Storage Time at 25 °C.

The above elugrams illustrate that for both the initial and the final samples only two peaks could be detected for the two main components HVO (peak 1) and diesel fuel (peak 2). Oligomer and/or polymer components could not be determine in the sample.

After the storage time of 17 months HPSEC analysis could not determine any polymers in the other biofuel blends either, indepentent of the storage temperature.

7 Results of the Short-term Test Runs

The short-term measurements were conducted with different fuel blends (see figure 10) at 30 operating points of the engine map. The results of representative operating points are illustrated and discussed as follows. The operating points addressed in detail are one without EGR at high engine load at n = 3500 min^{-1}, one with EGR at n = 2000 min^{-1} and the idle point.

7.1 Influence of the Fuel Blends on the Engine Control Unit

The adjustment of the test engineôs torque momentum with regard to the required torque momentum was achieved by adjusting the gas position via the test bench control. The differing calorific values of the fuels were thus taken into account during the test runs. The current-flow times for the injectors were not directly accessible. By changing the external variable ógas positionô the control unit variable ófuel quantity injectedô was changed, i.e., in the test runs a different quantity to be injected was stipulated for every fuel. Since the control unit variable ófuel quantity injectedô is used as reference variable in many engine maps, minor changes of the operating points could be identified in the map of the engine control unit for different fuels.

Exemplary data obtained at a constant speed of 2000 min^{-1} are illustrated as follows:

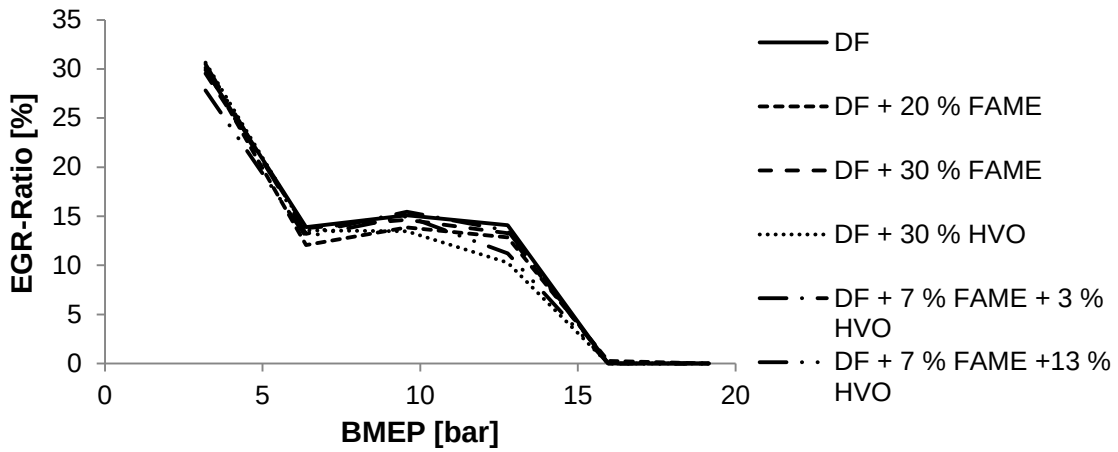


Figure 30: EGR at Increasing Load and Constant Speed of n = 2000 min^{-1}.

Figure 30 illustrates the EGR ratio at the mean effective pressure and a constant speed of 2000 min^{-1}. The EGRôs nominal value is a function of the reference variable ófuel quantity injectedô which depends on the type of fuel as explained before. The average EGR deviation between the blend fuels and the refererence fuel resulting thereof was 3.9 %. The average value shows that the fuels óDF + 30 % HVOô and óDF + 7 % FAME + 13 % HVOô induced an EGR reduction of 6.2 % resp. 5.8 %.

As mentioned before, EGR is a method to reduce NO_x emissions. NO_x emissions are chiefly produced by thermal NO_x. The implementation of the EGR generally reduces the O_2 proportion in the combustion chamber. As a result the flame spread is decelerated, the combustion time is increased and thus top pressure and temperature are reduced. Additional aspects are the inert gas or dilution effect and increased specific heat capacities of water and carbon dioxide. The control range of the EGR is given in figure 31.

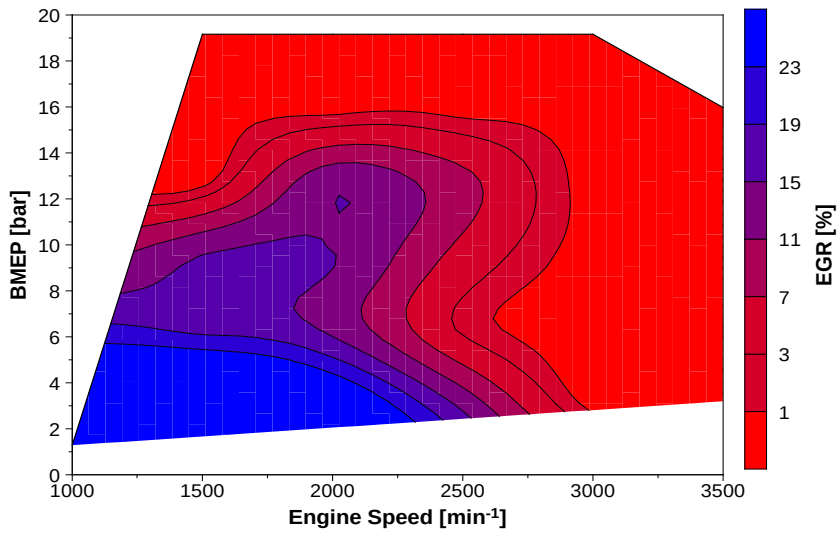


Figure 31: EGR in the Engine Map when Operated with DF.

Quite clearly the EGR ranges in a rev band from idle point to 2500 min^{-1} and in a load range from 0 to about 14 bar BMEP.

Influenced by the slightly different EGR ratios the Lambda values move up by about 2 %. The reason for that is that the share of the inert gas is substituted by the intake air. Figure 32 conprises the Lambda values dependent on the engine performance**.** It is well noticeable that the Lambda values drop with increasing load until the EGR is switched off at BMEP = 12.6 bar. At the operating point without EGR at BMEP = 15.9 bar the Lambda values rise again and then drop afterwards with increasing load as expected.

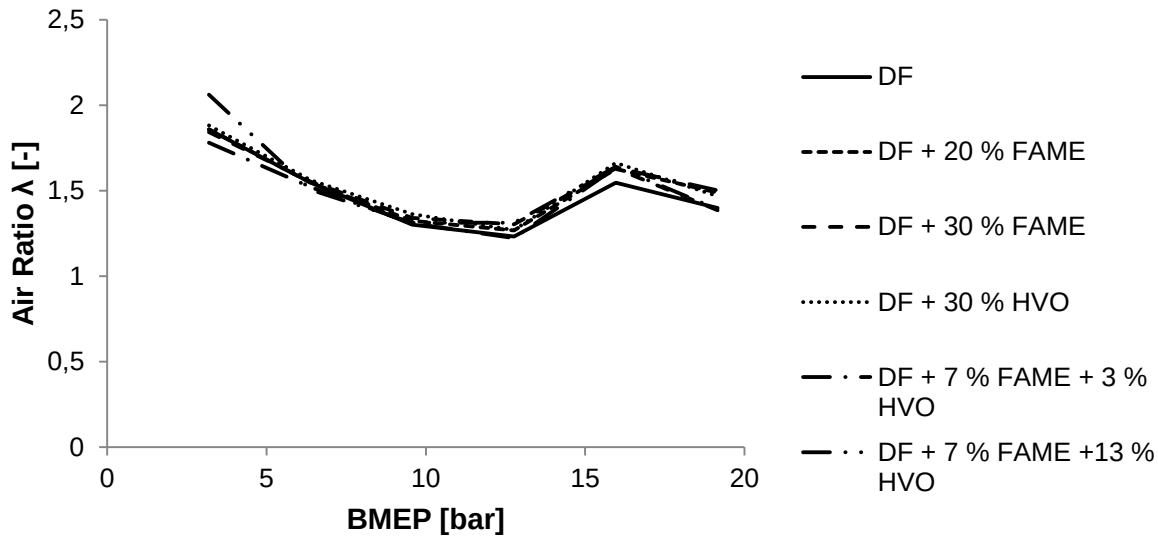


Figure 32: Air Ratio λ at Increasing Load and Constant Speed of n = 2000 min^{-1}.

7.2 Influence of the Fuel Blends on the Combustion Behaviour

The direct effect of the fuel properties on the combustion behaviour can only be identified during operation without EGR (high load range) because the complex influence (charge air pressure; EGR, EGR temperature, VNT) of the control unit significantly superimposes the influence of the fuel.

Figure 33 shows the pressure in the combustion chamber and the combustion behaviour at operating point n = 3500 min^{-1} and BMEP = 9.6 bar.

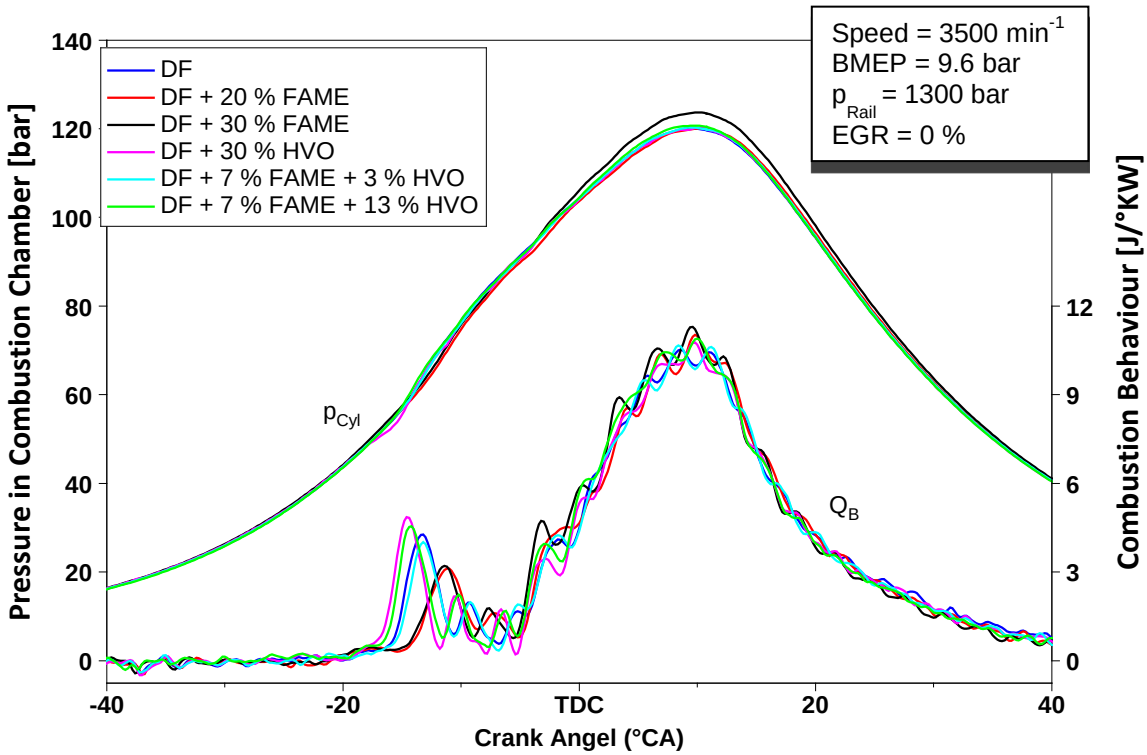


Figure 33: Pressure in Combustion Chamber and Combustion Behaviour at n = 3500 min^{-1} and BMEP = 9.6 bar.

A distinctive pre-combustion (pilot combustion), resulting from pre-injection, is noticeable at this operating point. The tests confirmed that for all six fuels tested pre-injection has a stabilizing effect on the main combustion.

During the pre-combustion process (figure 34) the influence of the fuel becomes clearly apparent. An early ignition and combustion of fuels with HVO proportion can be observed. The optimum evaporation behaviour due to the chain lengths of the hydrocarbons contained in the HVO proportion of the fuel noticeably promotes the combustion. From the location of the pre-combustion it can be seen that those fuels have a reduced ignition delay (see figure 35). Their high cetane number and low evaporation temperature guarantee an early ignition of the fuel-air-mixture.

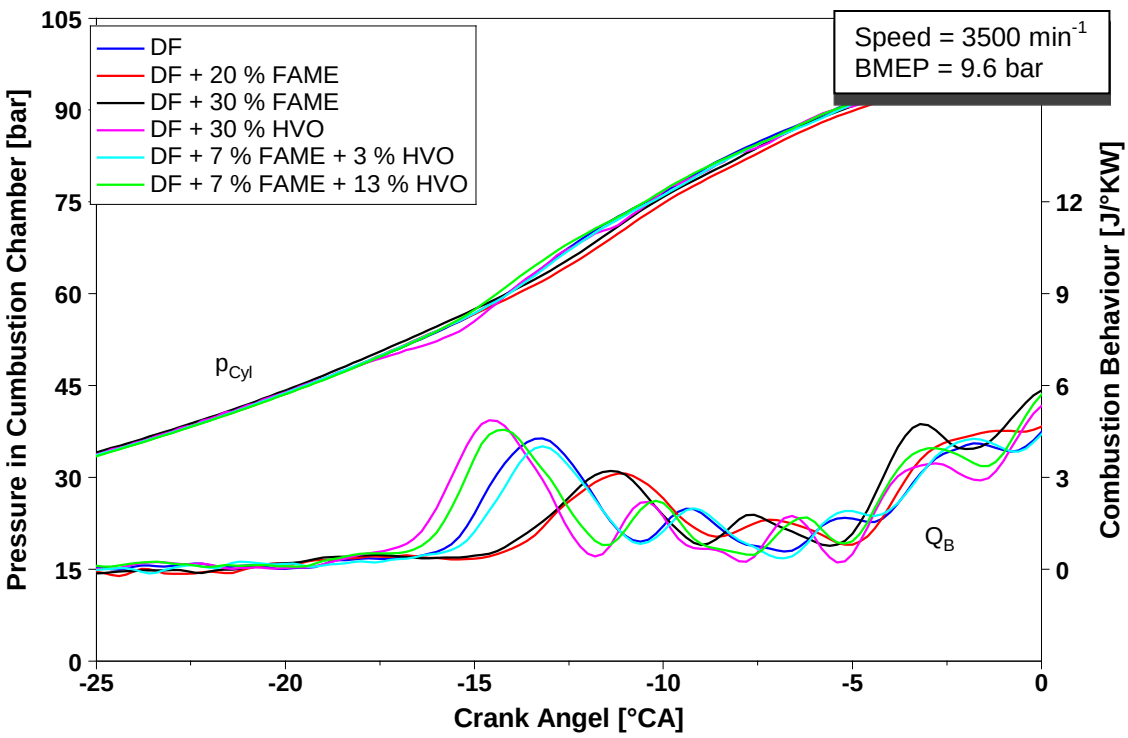


Figure 34: Combustion Behaviour of the Precombustion at n = 3500 min^{-1} and BMEP = 9.6 bar.

The order in which the fuels initiate pre-combustion is also distinctly visible. The pre-combustion of DF with 30 % HVO and DF with 13 % HVO starts earlier releasing more energy. Next in the line of later combustion initiation is the reference DF followed by all blends with gradually decreasing cetane numbers and calorific values.

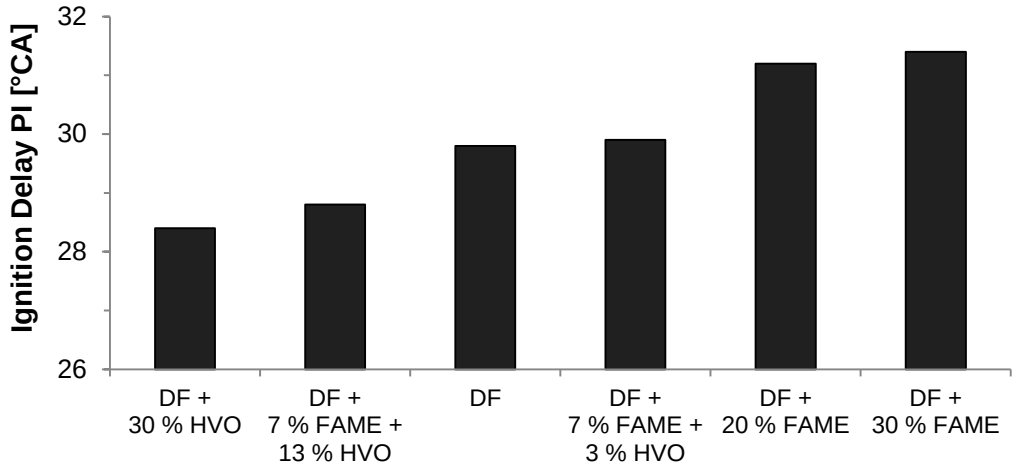


Figure 35: Ignition Delay dependent on the Fuel at n = 3500 min^{-1} and BMEP = 9.6 bar.

This table shows that increasing FAME proportions impair the fuel quality and influence the combustion in a slightly negative way. The delayed ignition of the pre-combustion is paralleled by a restricted energy release.

The initiatition of the pre-combustion at a later point in time combined with a significant reduction of the burning velocity (see figure 36) may be a reason for the decreasing NO_x emissions. For all six fuels the initiation of the combustion and the burning velocity of the main combustion are identical within the measuring precision.

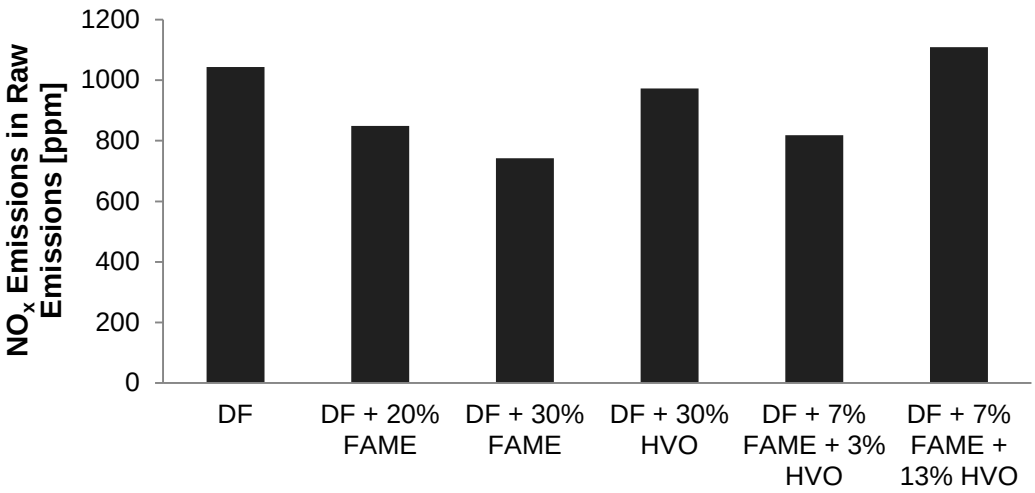


Figure 36: NO_x Emissions in Raw Emissions at n = 3500 min^{-1} and BMEP = 9.6 bar.

An influence of the various fuel properties cannot be recognized in the low-load range (idle speed) because due to the development of the combustion method of the EURO VI engine, the process temperatures are high.

Within the conventional diesel engine the combustion air ratio is significantly above 4 in the idle speed range. For this ôEURO-VIôcombustion concept the combustion air ratio is reduced to 2.3 due to the implementation of an uncooled EGR ratio of 40 %. The oxygen concentration is still sufficient to produce low filter smoke numbers; however, it also results in a significant increase of the process gas temperatures and as a consequence thereof in higher compression temperatures. Thus the prevailing ignition conditions are very good and enable a fast ignition independent of the fuel (see figure 37). At the same time the emission temperature is increased (reduced exhaust gas flow as compared to EURO-VI applications, for example); that way the improved function of DOC and SCR can be guaranteed.

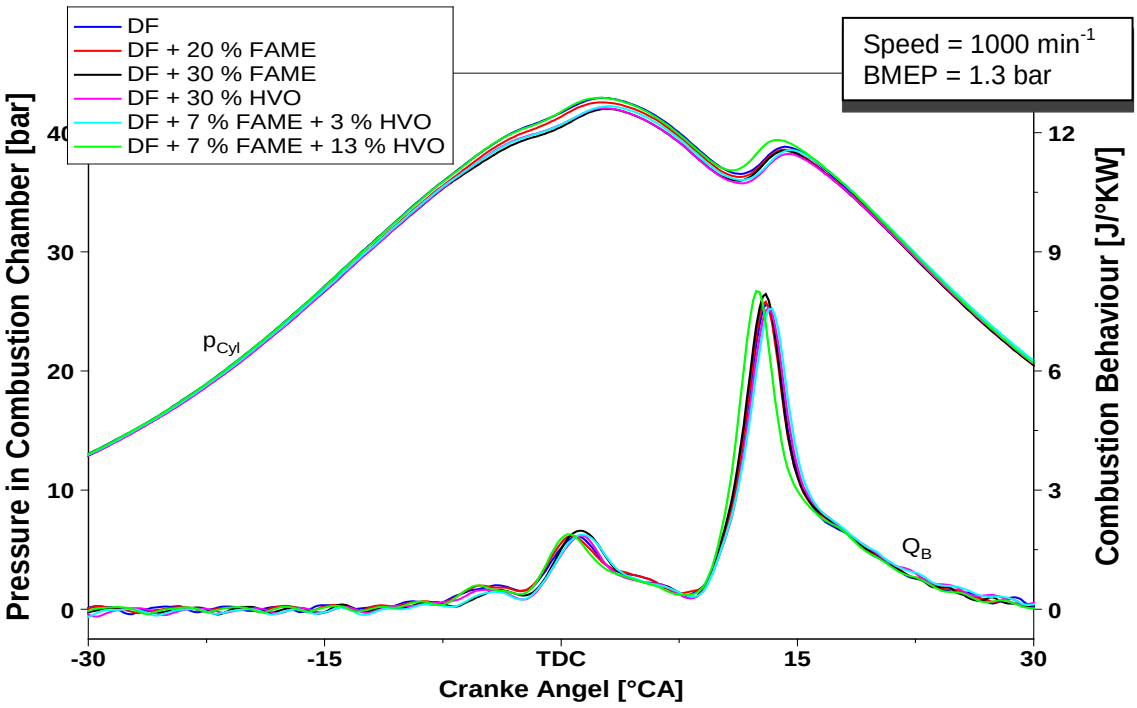


Figure 37: Pressure in Combustion Chamber and Combustion Process at n = 1000 min^{-1} and BMEP = 1.3 bar.

Figure 38 illustrates the pressure in the combustion chamber and the combustion behaviour at a speed of n = 2000 min^{-1} and an effective pressure of BMEP = 9.6 bar.

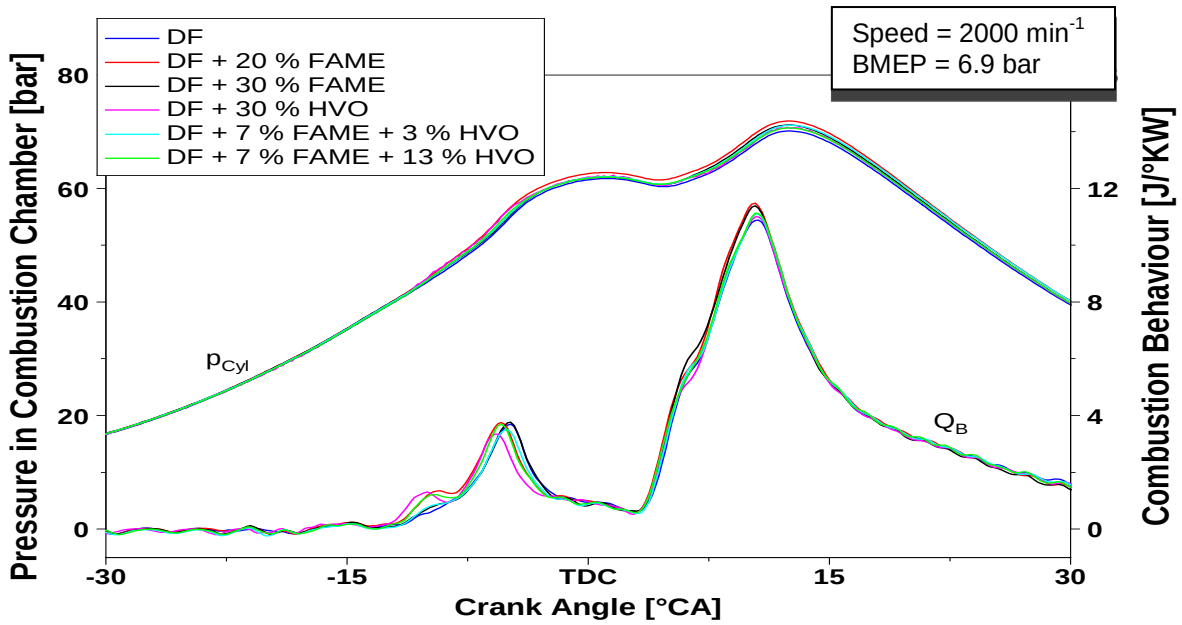


Figure 38: Pressure in Combustion Chamber and Combustion Process at n = 2000 min^{-1} and BMEP = 6.9 bar.

The measurements of this operating point also confirm that pre-combustion has a stabilising effect on the main combustion. However, it must be noted that during partial load range the fuel properties hardly influence the combustion process since the influence of the adjustment options of the engine control (EGR and VNT actuator) is more effective.

7.3 Influence of the Fuel Blends on the Emission Behaviour

The EGR directly influences the formation of nitrogen oxide emissions as can be clearly seen in the following figure 39 because of the division of the diagram. In the operational area of the engine typical for passenger cars, internal engine measures of the EGR induce the reduction of nitrogen oxide. In the high load range, which is rarely used during real engine operation, there is no NO_x reduction by the EGR.

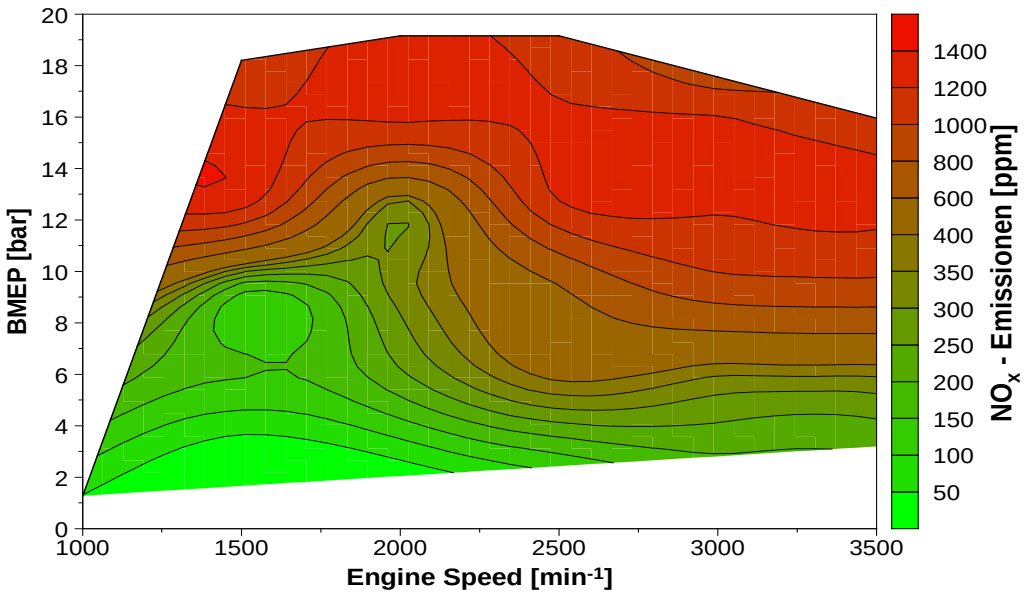


Figure 39: NO_x Emissions in the Map for Diesel Fuel.

Figure 40 shows that the level of NO_x emissions is very low within the EGR controlled range (3.3 < BMEP < 12.6). When the EGR is switched off, the NO_x emissions increase to values of above 1200 ppm.

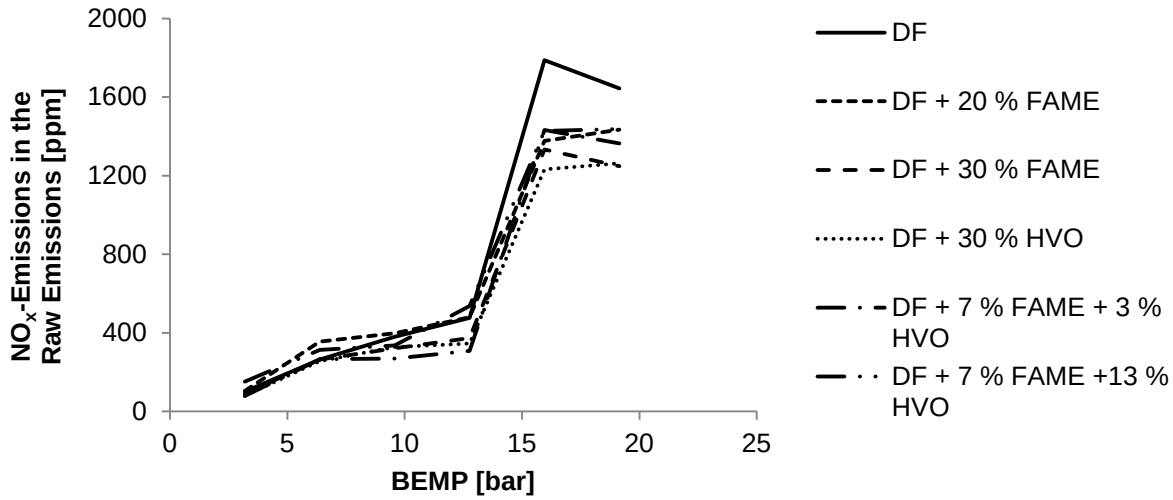


Figure 40: NO_x Emissions at Increasing Load and Constant Speed of n = 2000 min^{-1}.

It can be noted that by achieving values of more than 90 % within the range relevant for the emission test, the exhaust gas after-treatment system (SCR) for the NO_x conversion operates very effectively (see figure 41). The blend fuels did not cause any increased engine emissions within approval-relevant range (after exhaust gas after-treatment). It could be stated additionally that the NO_x conversion in the upper load range was more than 45 %.

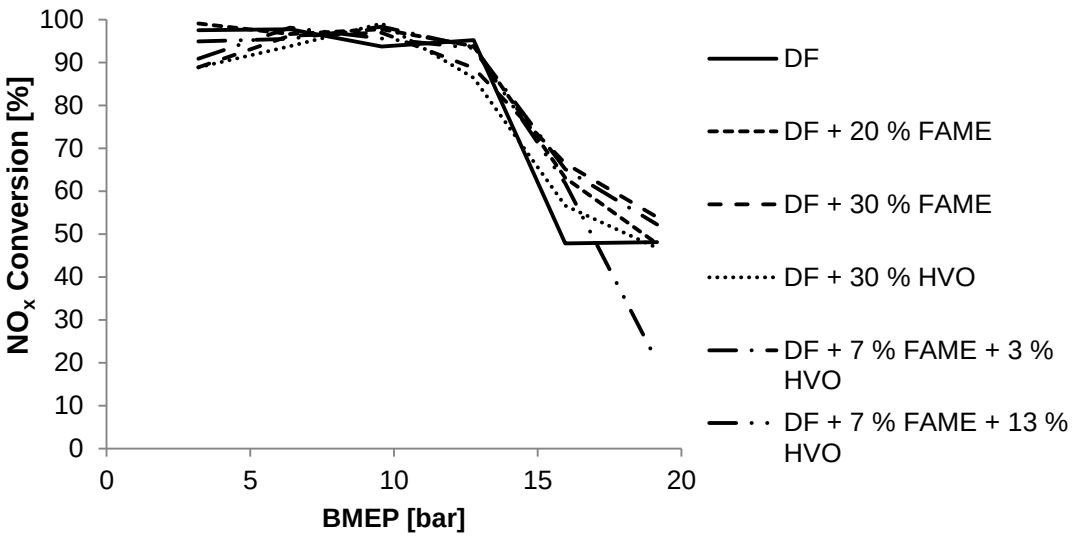


Figure 41: NO_x Conversion at Increasing Load and Constant Speed of n = 2000 min^{-1}.

The filter smoke number (FSN), being an equivilant for the soot concentration, is illustrated in figure 42 at increasing load and constant speed of 2000 min^{-1}.

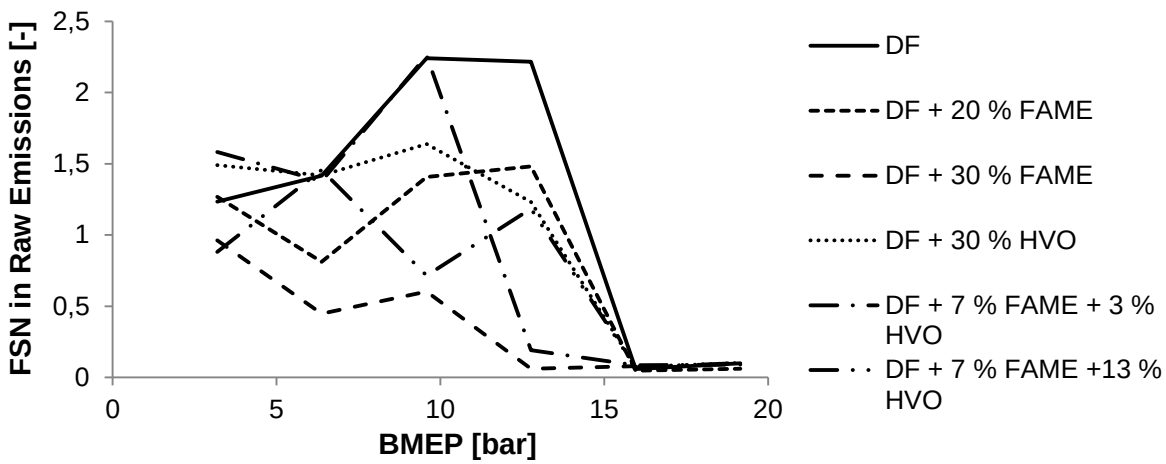


Figure 42: FSN in the Raw Emissions at Increasing Load and Constant Speed of n = 2000 min^{-1}.

It is striking that compared to the reference DF fuels with higher FAME content have a low FSN. The reason for that is that FAME improves the oxygen supply and thus a reduction of the lack of O_2 is achieved in the combustion chamber at the peripheral areas ôdrop-let/combustion airô The formation of particles is thus reduced.

If the EGR is switched off no inert gas, which delays the combustion, is introduced into the combustion chamber. As a result the temperatures in the combustion chamber rise and the formation of thermal NO_x increases. Due to the hotter conditions in the combustion chamber the fuel combustion is optimized which leads to a reduction of the soot concentration and thus results in a decreasing FSN.

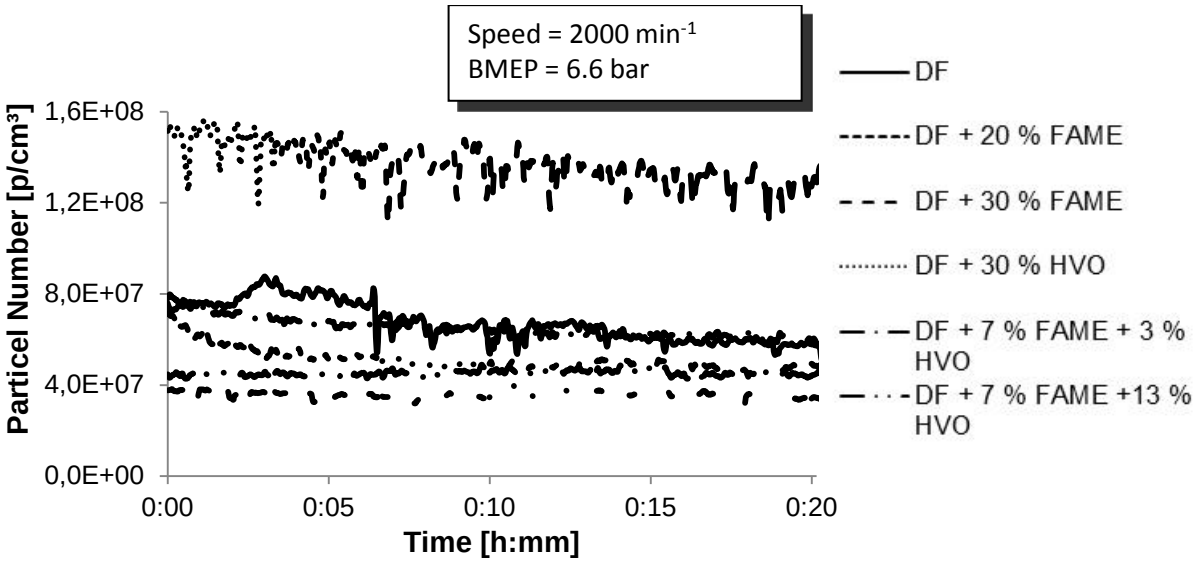


Figure 43: Time Curve of the Particle Number [p/cm³] Dependent on the Fuel.

Figure 44 shows the particle number [p/cmj] at a speed of 2,000 min^{-1} and a BMEP von 6.6 bar. It can be stated that the FAME content of the fuel (DF + 20 % FAME and DF + 30 % FAME) causes a reduction of the particle number. This finding is verified by measuring the FSN (see figure 45).

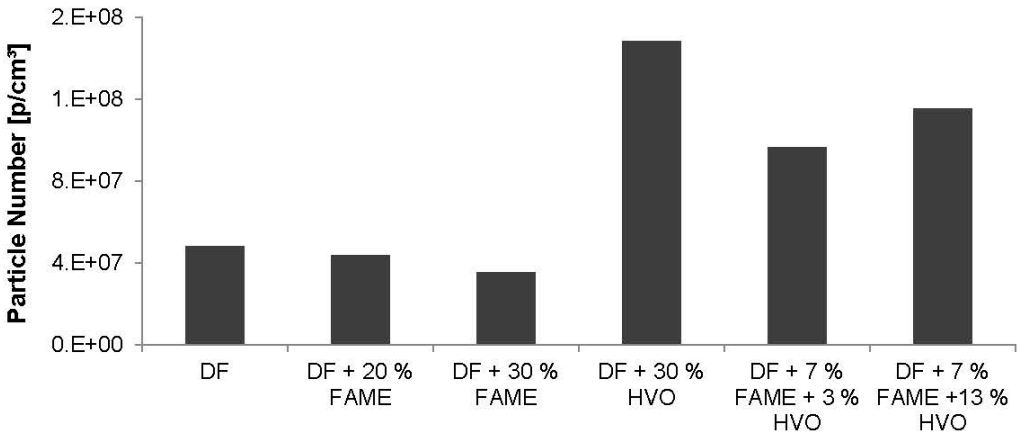


Figure 44: Particle Number [p/cm³] at n = 2000 min^{-1} and BMEP = 6.6 bar.

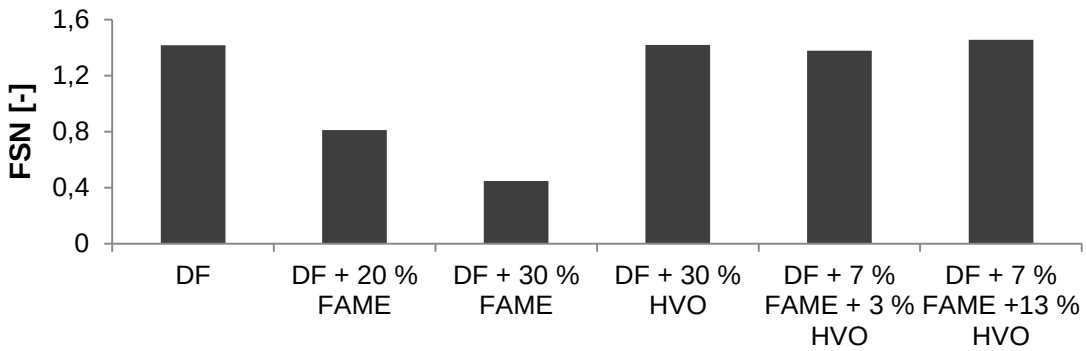


Figure 45: FSN at n = 2000 min^{-1} and BMEP = 6.6 bar.

Due to the bound oxygen, the FAME content of the fuel causes the FSN to be halved at this operating point (n = 2000 min^{-1}, BMEP = 6.6 bar). The fuels containing HVO showed almost identical FSN values compared to diesel fuel; however, in contrast with that, significantly higher particle numbers were measured for HVO-containing fuels. Therefore, the conclusion can be drawn that in this case the average particle size must be smaller.

In addition, the change of the particle number was determined by the DPF (see table 14). It can be stated that in the test range the closed particle filter achieved a reduction of the particle number of more than 99 %.

Table 14: Changes [%] of the Particle Number Due to DPF.

	DF	DF + 20 % FAME	DF + 30 % FAME	DF + 30 % HVO	DF + 7 % FAME + 3 % HVO	DF + 7 % FAME + 13 % HVO
1500 min^{-1} 3.3 bar	100.00	100.00	99.99	99.71	99.99	99.95
2000 min^{-1} 3.3 bar	99.97	99.85	99.93	99.98	98.90	100.00
2000 min^{-1} 6.6 bar	99.89	99.99	99.83	99.81	100.00	99.99
1875 min^{-1} 1.3 bar	99.99	99.88	99.99	99.98	100.00	100.00
Average	99.96	99.93	99.94	99.87	99.72	99.98

As described in section 5.3, an additional measurement of the particle number was made at a load step. Figure 46 illustrates the particle number of 19 subsequent identical load steps when operated with DF.

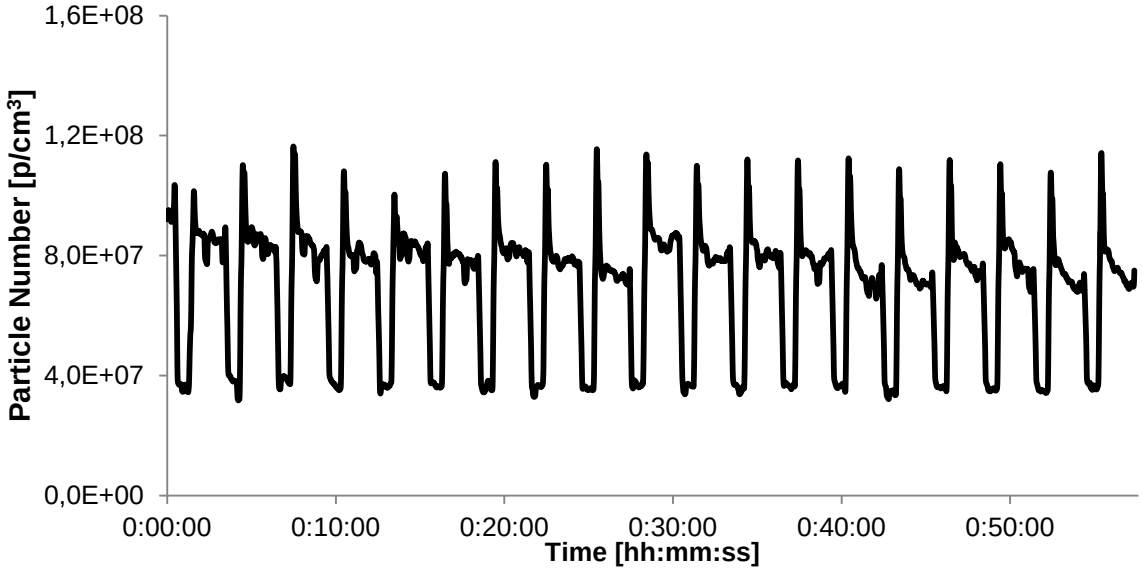


Figure 46: Particle Number [p/cm³] During the Load Step Measurement (Operated with DF).

Figure 47 shows the temporal sychronisation, overlapping and statistical evaluation of the load steps of figure 46.

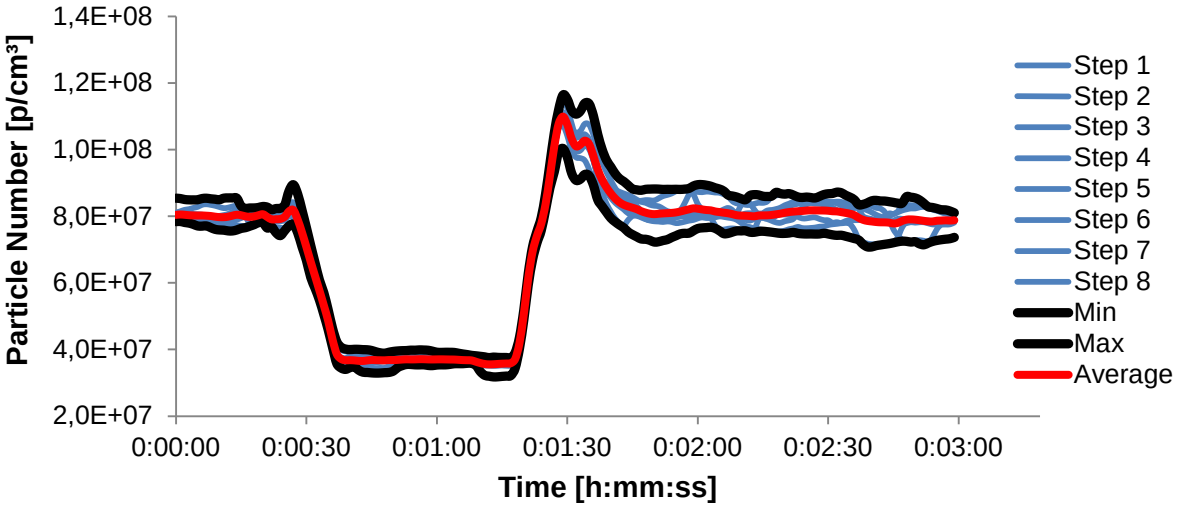


Figure 47: Statistical Evaluation of the Particle Number at Load Step (Operated with Diesel Fuel).

Here it becomes obvious that the particle number decreases with increasing load. The reason is that the temperature in the combustion chamber increases due to the fuel volume injected und thus improved particle post-combustion takes place. Furthermore it can be verified that an oxygen shortage, due to the idleness of the VNT adjustment and the throttle valve during the load step, is responsible for the particle increase. A temporary reduction of the process gas temperature leading to reduced particle combustion and thus higher particle numbers is the result of the load stepping from high to low.

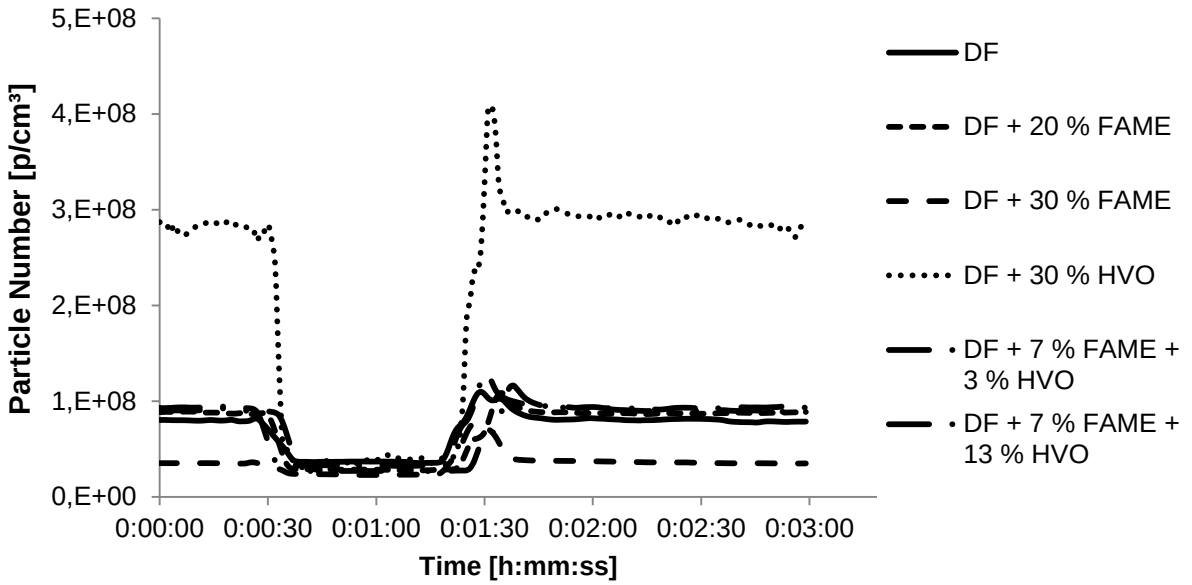


Figure 48: Comparison of the Particle Number at Load Step with Varying Fuels.

Figure 48 illustrates the particle numbers of the different blend fuels with averaged load steps to enable comparision. It is noticeable that in the low load range (n = 1100 min^{-1}, BMEP = 2 bar) fuel ïDF + 30 % FAMEô causes only very low particle emissions; whereas in this operating point the highest particle number was found for ïDF + 30 % HVOô So the measuring results of the particle numbers at the stationary operating points were confirmed.

Additionally it is obvious that the particle number in the high load range (n = 2200 min^{-1}; BMEP = 6 bar) drops. Looking at the particle number the same fuel-related behaviour as for the low load range can be identified (see figure 49). The fuel with a FAME content of 30 % has the lowest particle number and the fuel containing 30 % of HVO has the highest one.

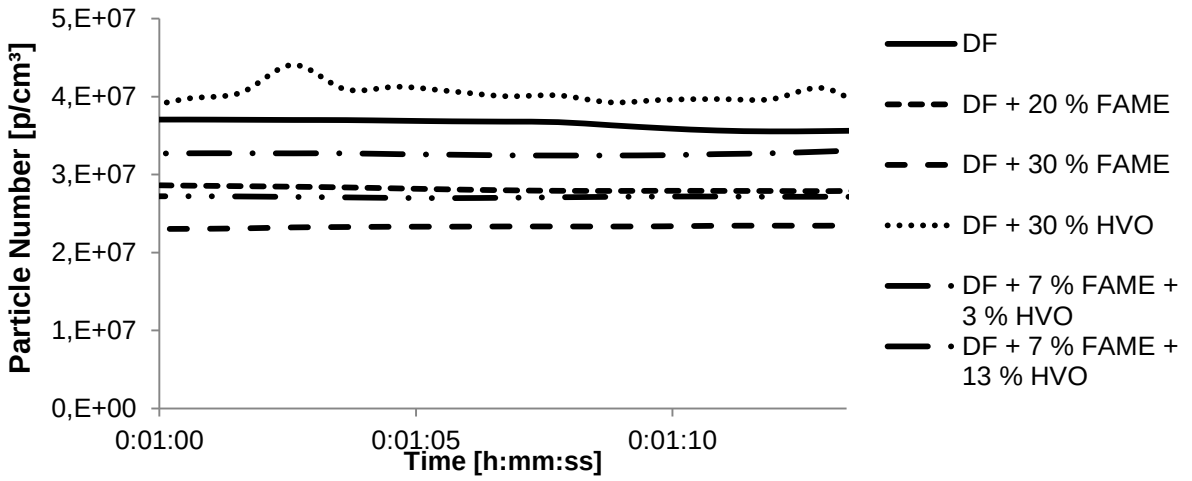


Figure 49: Section of Figure 48 - Comparison of the Particle Number at Load Steps with Varying Fuels.

7.4 Influence of the Fuel Blends on the Engine Lubrication Oil

The quality of the engine oil was monitored by means of various parameters. The parameter values determined after the short-term test runs are listed in table 15.

Table 15: Parameters of the Lubrication Oils after the Short-Term Test Runs.

Fuel	Operating hours [h]	Viscosity at 40 °C [mm²/s]	TBN [mg KOH/g]	Neutralization Number [mg KOH/g]	Soot Content [%]
Reference value	0	73.1	6.0	1.4	0.00
DF	27	71.4	6.2	1.5	0.12
DF + 20 % FAME	22	70.1	6.3	1.9	0.16
DF + 30 % FAME	28	70.4	6.2	1.9	0.20
DF + 30 % HVO	26	70.2	6.2	2.3	0.21
DF + 7 % FAME + 3 % HVO	17	69.6	6.2	2.2	0.24
DF + 7 % FAME + 13 % HVO	18	70.0	6.2	2.2	0.29

The above results of the analyzes illustrate that during the individual operating time with the relevant fuel none of the parameters showed significant changes compared to fresh oil. There were no indications that the quality of the lubrication oil was impaired due to the fuel implemented. So, in none of the cases there was a need to change the engine lubrication oil.

8 Results of the Endurance Runs

8.1 Results of the Control Units During the Endurance Runs

In order to be able to detect any influences of the fuel composition at an early stage, engine test were carried out after every 100 operating hours for the entire duration of the measuring campaign. Beside measurements of the exhaust gas composition the tests also comprised the reading-out of the control unit at 10 operating points. The following is an exemplary elaboration on the control unit data during the course of the endurance runs at the operating point ón = 2000 min^{-1} and BMEP = 6.9 barô

As already described in section 7.1, the torque-forming óinjected volumeôis a reference variable of the engine control unit. For that the volume injected is particularly dependent on the fuelôs density. For comparison the calorific values of the fuels used for the endurance runs are listed in table 16. Viewing the volumetric calorific value, the highest volumetric calorific value can be stated for the reference fuel and lowest one for the FAME-containing fuel.

Table 16: Calorific Values of the Endurace Run Fuels

Endurance Run	Fuel	Density (15 °C) [kg/m³]	Calorific Value [kJ/kg]	Calorivic Value [kJ/l]
1	DF +7 % FAME	836.7	42414	35488
2	DF + 30 % FAME	851.7	40862	34802
3	DF + 30 % HVO	820.6	42944	35240

In the following figure 50 the injected volume at a selected operating point (BMEP = 6.9 bar, n = 2000 min^{-1}) is illustrated comparing endurance runs 1 to 3. It becomes apparent that the low energy density of óDF + 30 % FAMEôhad to be counteracted by increasing the injected volume in order to achieve the same operating point. Compared to the reference fuel, DF + 30 % HVO also required an adaptation with regard to the fuel volume injected. No changes could be observed for all implemented fuels during the operating time.

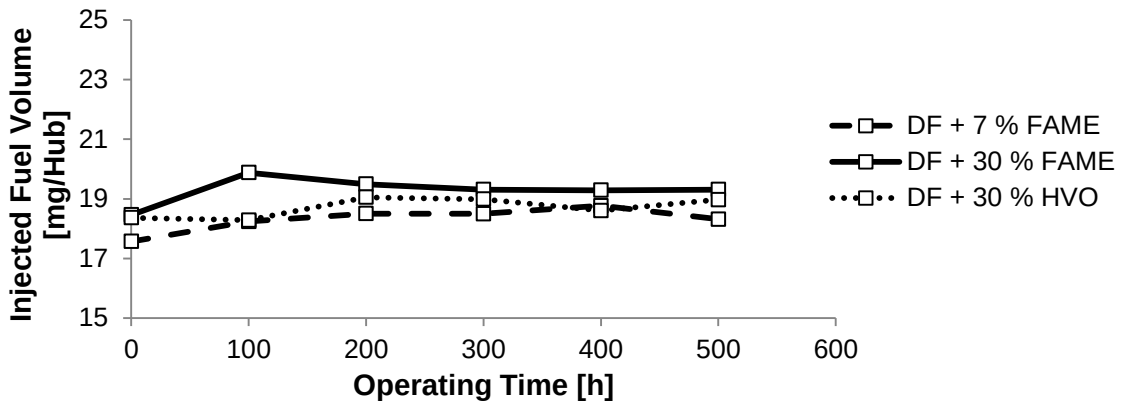


Figure 50: Injected Fuel Volume at BMEP = 6.9 bar and n = 2000 min^{-1} Dependent on the Fuel Implemented and the Operating Time.

The air mass within the engine is controlled with the Lambda nominal value (on file in the control unit) and according to the actual Lambda value (as measured with the Lambda sensor); it is thus directly dependent on the fuel volume injected. As a result the air mass situation during endurance runs 1 to 3 was linked directly to the fuel volume injected and was thus similar for all three (see figure 51).

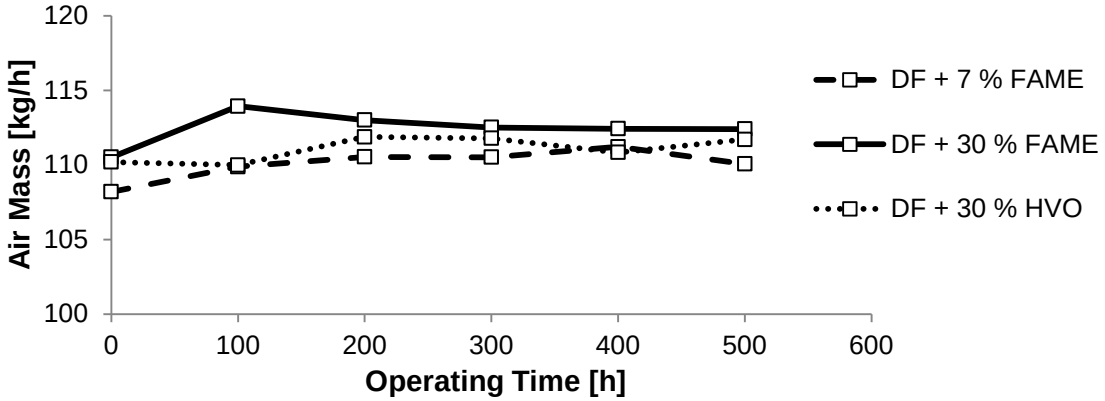


Figure 51: Air Mass at BMEP = 6.9 bar and n = 2000 min^{-1} Dependent on the Fuel Implemented and the Operating Time.

As mentioned before, the EGR is responsible for the inner-engine reduction of NO_x emissions. Figure 52 shows the EGR performance of the three endurance runs throughout the operating hours.

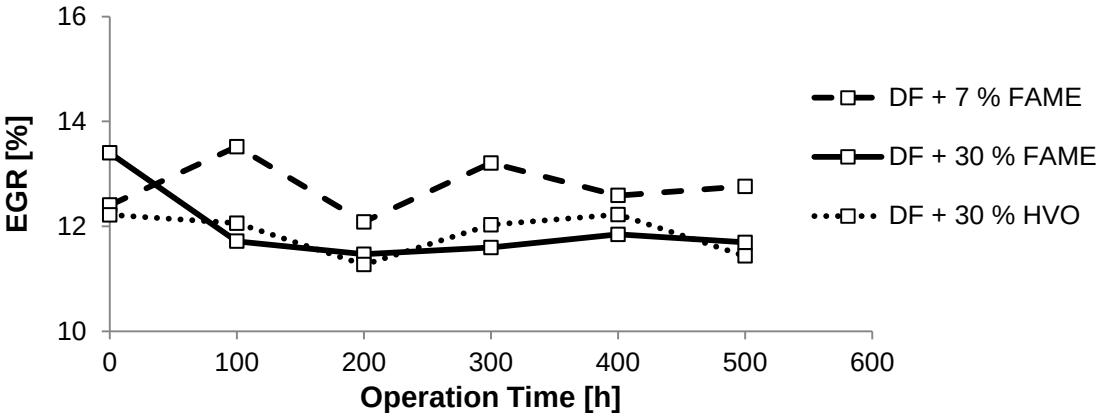


Figure 52: EGR at BMEP = 6.9 bar and n = 2000 min^{-1} Depentent on the Fuel Implemented and the Operating Time.

It can be stated that minor shifting of the operating points within the engine map occurred due to the differing fuel volumes injected. The deviation came to 6 %. The highest EGR showed for ïDF + 7 % FAMEî averaging at 12.7 %. With an average of 11.9 % the EGR for the other fuels was at the same level.

8.2 Emission Behaviour during the Test Period

Figure 53 shows the development of the FSN in endurance runs 1 to 3. The results of the short-term test runs could be confirmed for the same operation point. It turned out that ï compared with the other two runs ï during endurance run 2 the lowest FSN could be measured with a biodiesel content of 30 %. As mentioned before, this is caused by the oxygen bound in the FAME molecule which leads to improved fuel oxidation and thus counteracts soot formation positively.

It can also be demonstrated that the fuel of endurance run 3 containing HVO also showed a lower FSN than that of the reference diesel fuel.

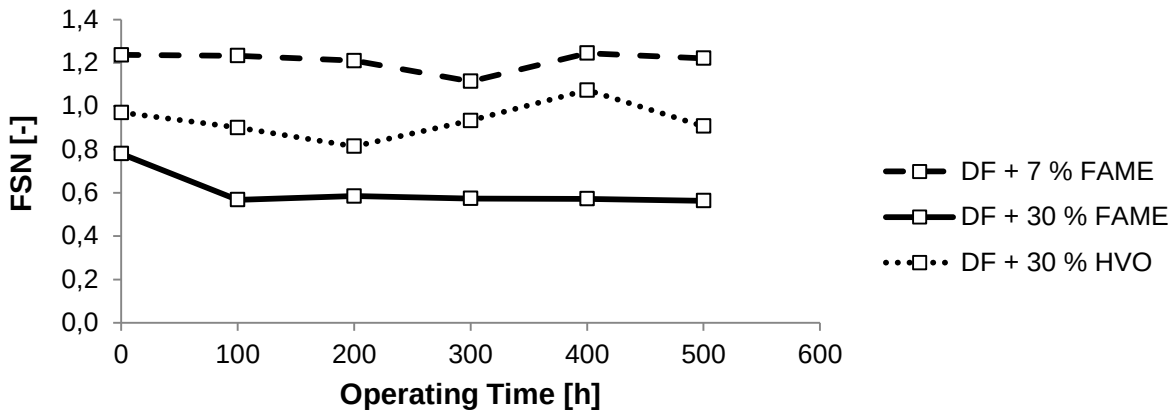


Figure 53: FSN at BMEP = 6.9 bar and n = 2000 min^{-1} Dependent on the Fuel Implemented and the Operating Time.

Figure 54 shows the oxygen content measured in the raw emissions in all three endurance runs dependent on the relevant operating hours.

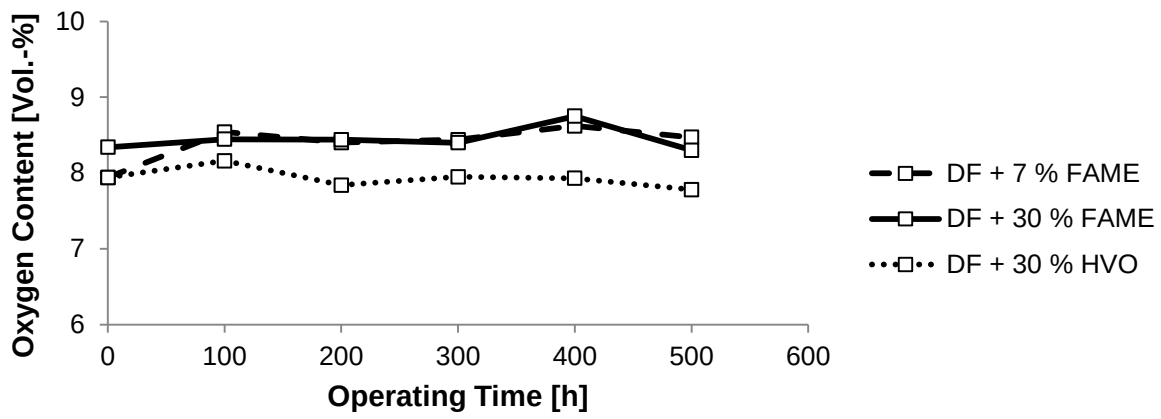


Figure 54: Oxygen Content at BMEP = 6.9 bar and n = 2000 min^{-1} Dependent on the Fuel Implemented and the Operating Time.

Here, with an EGR identical as for a „DF + 30 % HVO“ and „DF + 30 % FAME“ showed a higher oxygen content. On the one hand this is due to the oxygen bound in FAME and on the other hand to the increased air mass required by the shifting of the operational point.

The NO_x emissions determined in the endurance runs are illustrated in figure 55 as follows, dependent on the operating time.

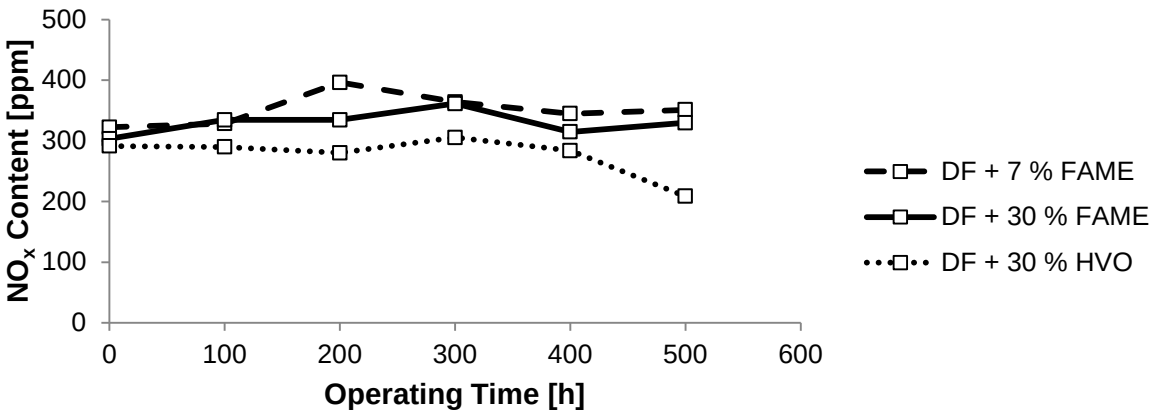


Figure 55: NO_x Emissions at BMEP = 6.9 bar and n = 2000 min^{-1} Dependent on the Fuel Implemented and the Operating Time.

Compared to the other fuels the third endurance run with HVO shows reduced NO_x formation. This fact can be explained by the positive fuel properties of HVO such as low surface tension and a favorable boiling behaviour, for example, which enable an improved carburetion process in the combustion chamber the result of which is a reduced ingnition delay of the pre-combustion and little NO_x formation.

8.3 Optical Inspection of the Engine after the Endurance Runs

After every endurance run an optical inspection of the engine was carried out to be able to assess each engine component. The following engine components were viewed:

- ETL
- EGR Cooler
- EGR Valve
- Throttle Valve
- Injectors
- Air Intake System

The cylinder head was removed for the inspection of the combustion chamber. The elements were visually analyzed and fotographed for documentation reasons. The results for cylinder 2 are illustrated as follows:

8.3.1 Combustion Chamber

The following table compares the liner and the piston tops after endurance runs 1, 2 and 3.

Table 17: Documentation of the Liner and the Piston Top.

	Endurance Run 1	**Endurance Run 2**	**Endurance Run 3**
Fuel	DF + 7 % FAME	DF + 30 % FAME	DF + 30 % HVO
Liner			
Piston			

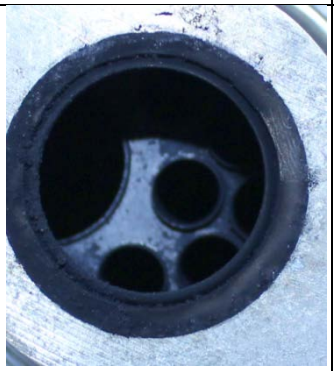
After all endurance runs the hone marks on the liners are in a good condition. Thus no influence of the implemented fuel on the lubrication properties could be detected. The spray pattern was well visible on the piston after all three runs. Thus it can be assumed that no deposits, e.g. by coaking on the injectors, were formed. This assumption was verified by the visual inspection of the injectors.

It must be noted that after the second endurance run white deposits were found on the liner above the first piston ring and the cylinder head. Due to the small amount an additional inspection of those deposits could not be carried out.

8.3.2 EGR Cooler

It is the function of the EGR cooler to reduce the temperature of the exhaust gas which is recirculated into the combustion chamber. Since the untreated raw emissions pass this component, direct influences of the fuel properties can also be noticed here. FAME is known to form little soot which was confirmed by the inspection of the EGR cooler inlet (see table 18). After the second endurance run clearly smaller soot deposits were found. No difference could be determined between deposits due to ÷DF + 7 % FAMEô and ÷DF + 30 % HVOô

Table 18: Documentation of the EGR Cooler

	Endurance Run I	**Endurance Run II**	**Endurance Run III**
Fuel	DF + 7 % FAME	DF + 30 % FAME	DF + 30 % HVO
EGR Cooler Inlet			

8.3.3 Exhaust Gas Turbocharger

The exhaust gas turbocharger was also inspected. Changes dependent on the fuel implemented could not be determined for the compressor or the turbine.

Table 19: Documentation of the Exhaust Gas

	Endurance Run 1	**Endurance Run 2**	**Endurance Run 3**
Fuel	DF + 7 % FAME	DF + 30 % FAME	DF + 30 % HVO
EGT Turbine			
EGT Compres-sor			

8.4 Effect on the Engine Lubrication Oil

During the endurance runs the lubrication oil was analyzed at defined intervals with regard to selected parameters. On completion of each endurance run the lubrication oil was completely discharged at an oil temperature of 80 ÁC. The oil pan was not purged with fresh oil before the next endurance run.

As follows, figure 56 illustrates the dependence of the kinematic viscosity (at 40 ÁC) on the operating time of the three endurance runs.

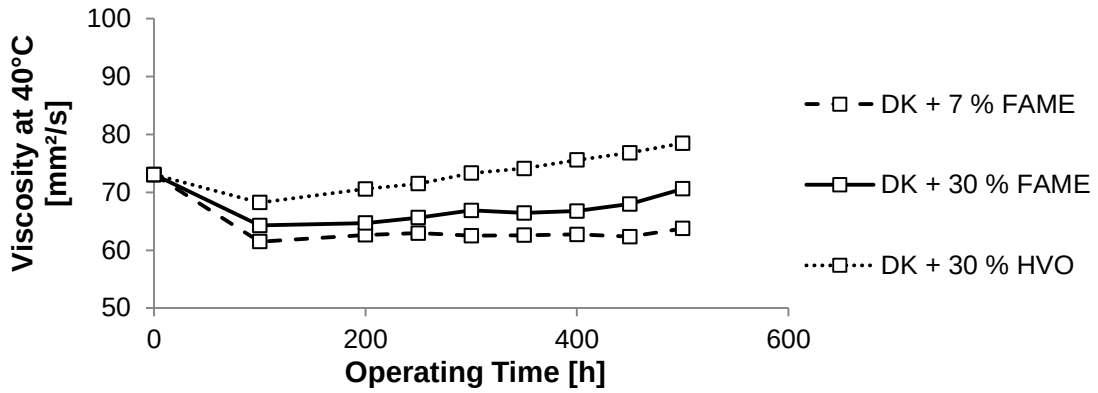


Figure 56: Kinematic Viscosity at 40 °C Dependent on the Implemented Fuel and the Operating Time.

For all three fuels the kinematic viscosity shows the typical development dependent on the operating time, i.e. at first dilution is stated which may be caused by fuel ingress and/or destruction of the VI improver by shearing. Afterwards the viscosity during the first endurance run (DF + 7 % FAME) stays almost constant, whereas a slight increase can be found for the other two endurance runs.

During all three endurance test runs the soot content of the relevant lubrication oil samples was at a very low level and way below the limit of 3 %, as the following results of figure 57 illustrate.

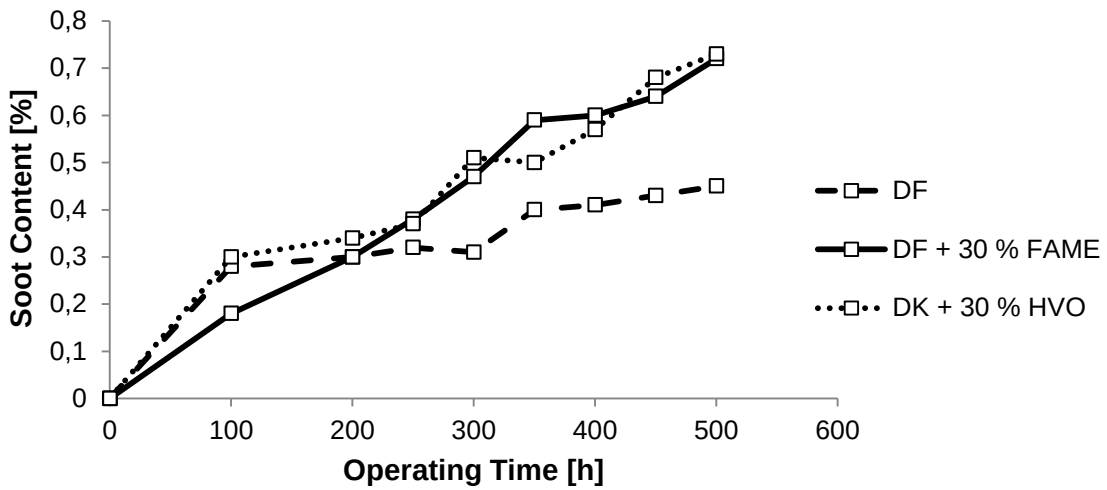


Figure 57: Soot Content of the Lubrication Oil Dependent on the Fuel Implemented and the Operating Time.

The above results confirm the results of the emission behaviour of FAME-containing fuels. According to that it is well-known that fuel with a content of 30 % FAME caused less soot emissions than diesel fuel (see figure 42). Thus during the endurance run with DF + 30 % FAME the soot ingress into the lubrication oil is also lower than that due to the other two fuels.

As follows, figure 58 illustrates the total base numbers (TBN) of the three endurance runs dependent on the relevant operating time.

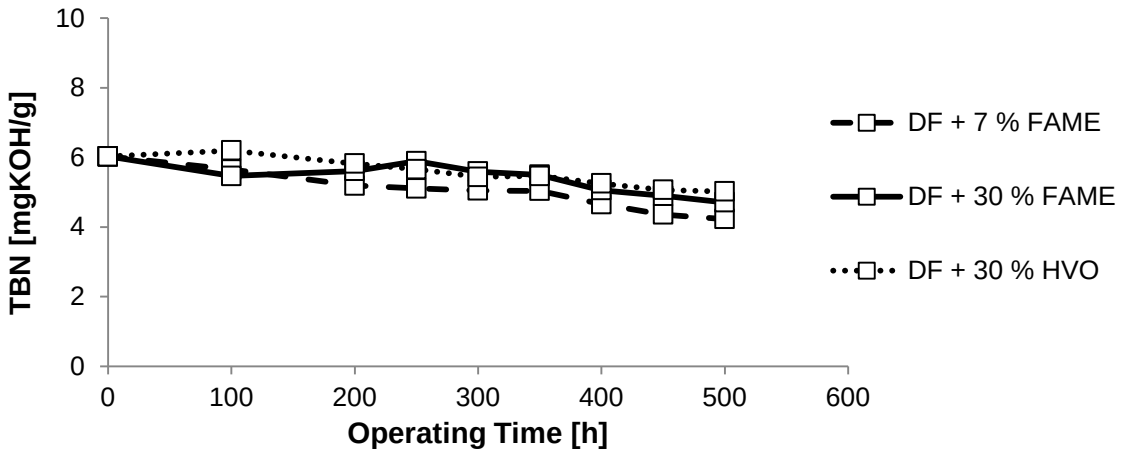


Figure 58: TBN of the Lubrication Oil Dependent on the Fuel Implemented and the Operating Time.

The results explain that during all three endurance runs the total base number of the lubrication oil is reduced as the operation time progresses. When the ageing of the lubrication oil sets in acidic components form which are finally neutralized by lubrication oil additives. As a consequence the total base number drops. However, the limit relevant for an oil change (4 mg KOH/g) is not exceeded in any of the three endurance runs.

Another important parameter of lubrication oil analytics is the neutralization number which informs on the content of free acids which are formed during the ageing process of the lubrication oil. If lubricants with defined biofuel content are used, the increase of the neutralization number precedes an exponential increase of the viscosity; the neutralization number can be used for monitoring the ageing condition of the lubrication oil so that critical oil conditions can be detected at an early stage (see Wichmann et al. 2011). According to results published already an oil change is recommended if the neutralization number rises by significantly more than 4 mg KOH/g. However, the main objective of these tests was the direct comparison of the different fuels during engine operation for the duration of 500 hours under identical engine conditions. Thus all endurance tests were run without a lubrication oil change. The oil was only changed between the endurance test runs on completion of each previous one.

As follows, figure 59 illustrates the development of the neutralization number of the three endurance runs dependent on the operating time.

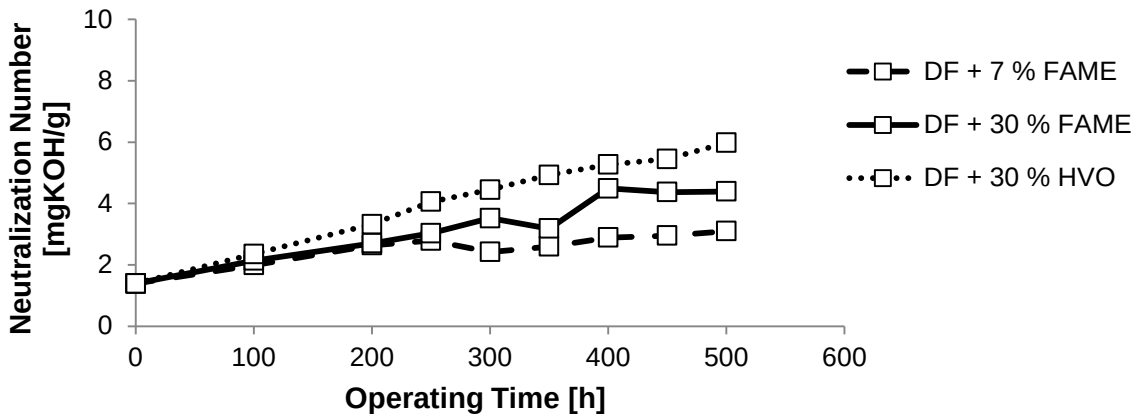


Figure 59: Neutralization Number of the Lubrication Oil Dependent on the Fuel Implemented and the Operating Time.

The neutralization number increased significantly within the oil change intervals given. However, it seems to be worth mentioning that there was obviously no direct correlation between the TBN (see figure 58) and the increase of the neutralization number; that means that not all acids formed can be neutralized by the alkaline reserve.

The results given in figure 59 prove that during the endurance test run with ÷DF + 30 % HVOô there was a strong increase to 6 mg KOH/g which was not expected before for the implementation of HVO. An unintended transfer of FAME-containing lubrication oil (from the first two endurance runs) may be a possible cause.

For additional illustration the FAME contents dependent on the operating time are listed for the three endurance runs in figure 60 as follows:

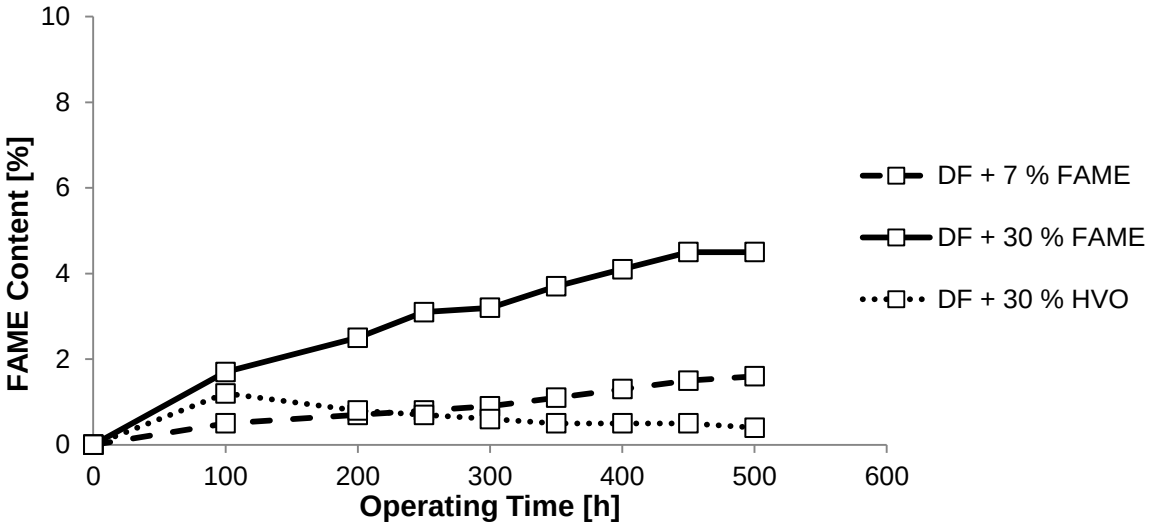


Figure 60: FAME Content of the Lubrication Oil Dependent on the Fuel Implemented and the Operating Time

The above results prove that with up to 4.5 % the lubrication oil of the second endurance run (DF + 30 % FAME) had the highest FAME content. However, that value was regarded uncritical because the limit of 10 % had not been reached.

It is remarkable that a FAME content of 1.2 % was determined in the third endurance run (DF + 30 % HVO) after 100 operating hours. This content indicates a contamination by FAME-containing lubrication oil from the second endurance run. As the endurance run progressed a decrease of the FAME content could be recorded. The FAME residue in the lubrication oil is probably degraded into acid components, which is reflected by a rise of the neutralization number. With the infrared method only those fuel components are recorded which produce a signal in the IR spectrum due to an ester group in their molecules. All acidic components forming in the lubrication oil due to the ageing of FAME are thus not recorded by the IR method.

The lubrication oil samples were tested for any possibly contained polymers by means of HPSEC analysis. Figure 61 shows the elugrams of the final samples of each of the three endurance runs compared to those of fresh oil as follows.

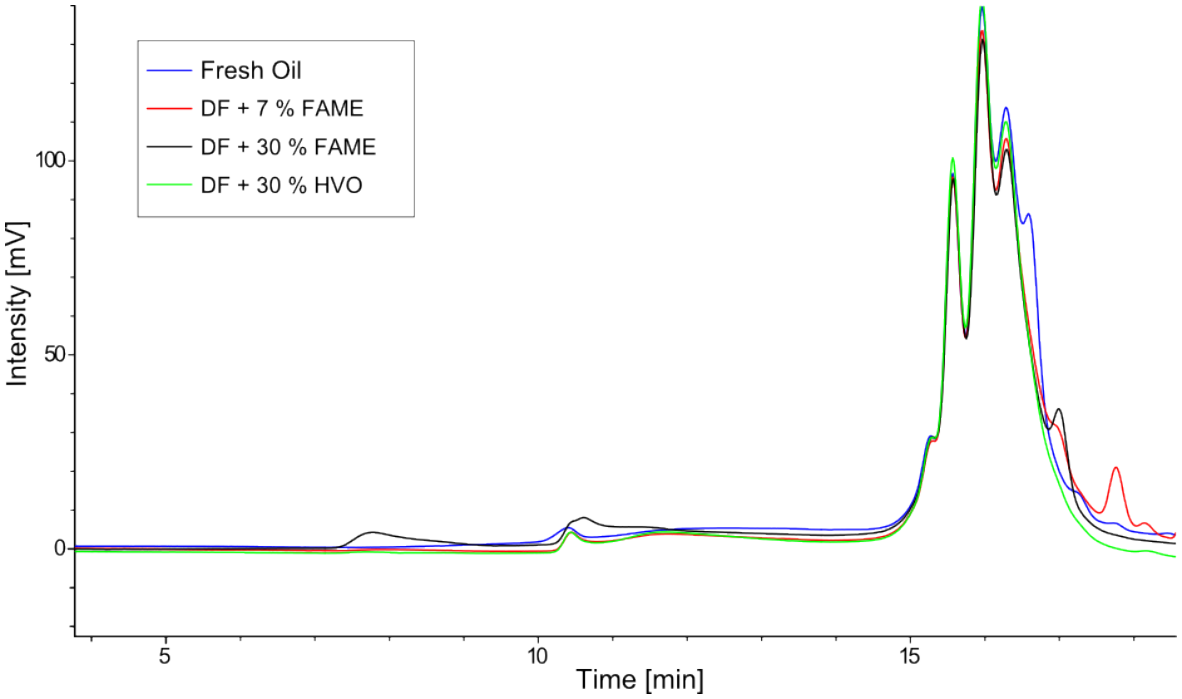


Figure 61: HPSEC Analysis of the Lubrication Oil After 500 Operating Hours Dependent on the Fuel Implemented Compared to Fresh Oil.

The above elugrams illustrate that in the second endurance run (DF + 30 % FAME) at a retention time of 7.5 min and a medium molecular weight of > 100000 g/mol (ca. 2 %) a rise of VI improvers and a slight proportion of polymers were determined. The relevant peak was not detected for the other samples. Still, these polymer components did not have any influence on the viscosity of the sample.

The content of wear metals in the lubrication oil samples inspected was determined by means of ICP-OES. The results thereof are summarised in tables 20 to 22 of the annex. As anticipated, a rising concentration of wear metals was noticeable with increasing operation. In figure 62 the aluminium content is given as an example dependent on the operating time of the three endurance runs.

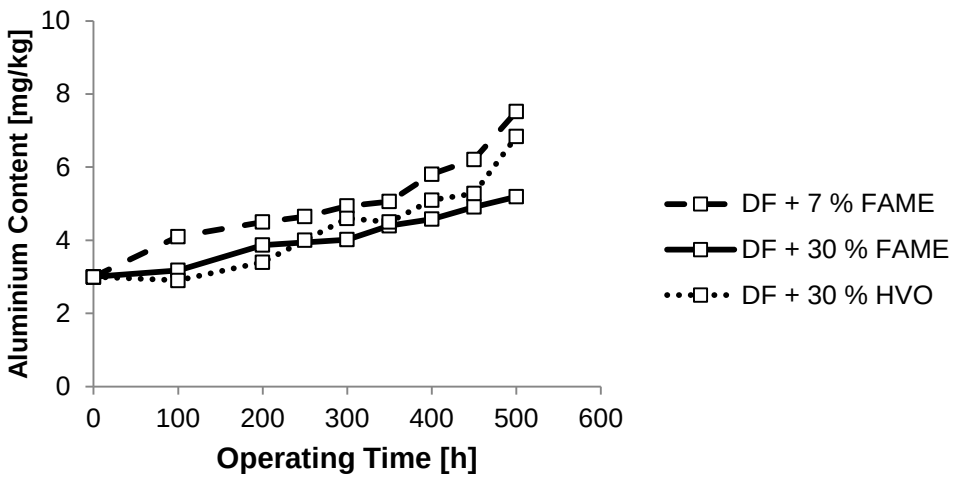


Figure 62: Aluminium Content of the Lubrication Oil Dependent on the Fuel Implemented and the Operating Time.

The increasing aluminium content was assessed as uncritical because it stayed within the permissible tolerance (of between 12 and 55 mg/kg). The levels of the relevant copper and iron concentrations in the lubrication oil were also uncritical (see figures 63 and 64).

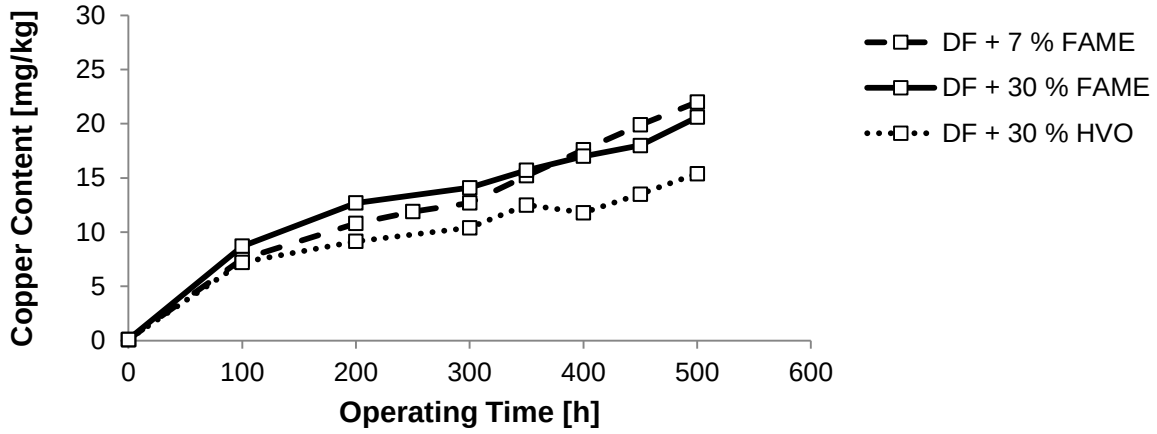


Figure 63: Copper Content of the Lubrication Oil Dependent on the Fuel Implemented and the Operating Time.

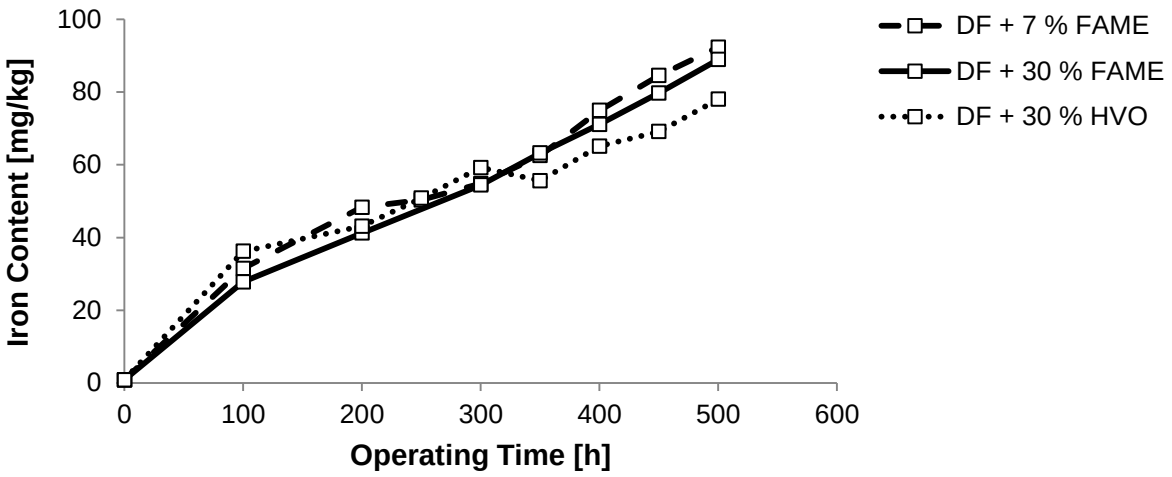


Figure 64: Iron Content of the the Lubrication Oil Dependent on the Fuel Implemented and the Operating Time.

Irregularities concerning metal wear due to the implemented fuel could not be identified.

The contents of additive and contamination components are listed in tables 23 to 25 of the annex. As anticipated, the additive components decreased as the operating time of the lubrication oil in the endurance tests progressed.

Silicon and sodium are considered so-called ócontamination elementsó which can contaminate the engine oil in the form of dust. However, as figure 65 illustrates exemplary with the silicon content the determined concentrations were inconspicuous in every case.

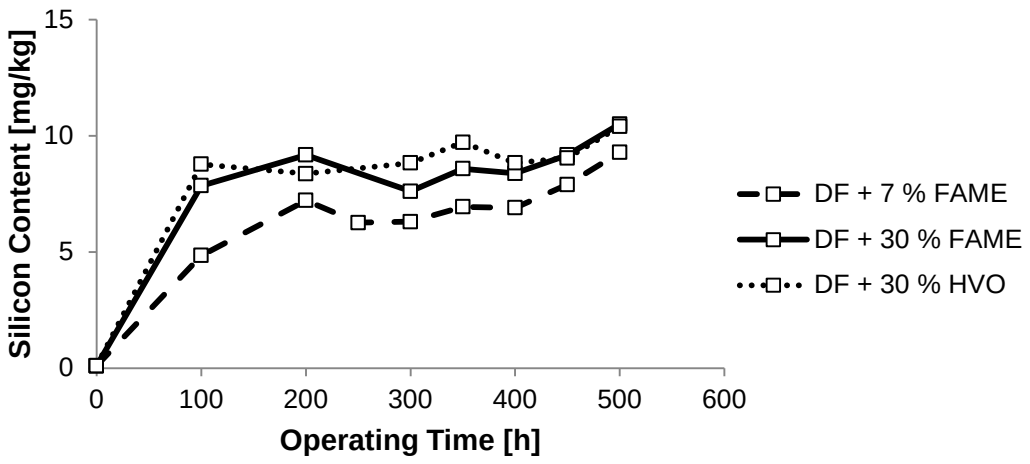


Figure 65: Silicon Content of the the Lubrication Oil Dependent on the Fuel Implemented and the Operating Time.

In conclusion it can be said that during the three endurance runs there was no indication as to any interaction between the wear and additive components and the fuels implemented.

9 Summary

For this project five different biofuel blends were assessed with regard to their storage stability, combustion and emission behaviour. The tests were carried out at a modern 4-cylinder passenger car engine of exhaust gas standard EURO-VI. The test was based on six short-term runs and three endurance runs operated with selected fuel blends with the aim to compare the internal engine behaviour, the formation of emissions and the functionality of the exhaust gas after-treatment system. The following fuels were implemented:

I. Diesel fuel B0 (reference fuel)
II. Diesel fuel with 20 % FAME
III. Diesel fuel with 30 % FAME
IV. Diesel fuel with 30 % HVO
V. Diesel fuel with 7 % FAME and 3 % HVO
VI. Diesel fuel with 7 % FAME and 13 % HVO

Storage Study

Prior to the tests all FAME components of the above fuels werde stabilized by means of antioxidants. The objective was to achieve an oxidation stability of at least 10 hours with the Rancimat test method at 100 ÁC. The next step was the mixing of the biofuel blends consisting of FAME and a B0 Diesel fuel (summer quality) as well as HVO. The biofuel blends were stored at two different temperatures (10 ÁC, Ï 25 ÁC) for the period of 17 months and sampled and analyzed at defined intervals. The fuel properties óviscosityô and óneutralization numberôdid not show any significant changes during the course of the storage time. Minimal deviations compared with the initial condition only occurred for the parameters óoxidation stabilityôand óperoxide valueô The limits of standard DIN EN 590 were safely observed for the entire test period. It can be stated that also test blends with a biodiesel content of as much as 30 % could be stabilized for the entire storage period of 17 months by means of selective additivation with antioxidants.

Engine Short-Term Runs

In the short-term test runs six fuels were compared at selected operational points. It was possible to demonstrate that a failure-free implementation of the blend fuels inspected can be realized for a EURO-VI diesel engine. The shifting of the operational points observed at the stationary load points can be ascribed to the various fuel properties (e.g. boiling behaviour, surface tension, calorific value).

Deviations in the combustion behaviour and the functions of the engine control unit are quantifiable at the test bench. For the operation with oxygen-rich fuels containing biodiesel the injected fuel volume was increased at identical load points (constant air mass and speed).

For the six fuels tested, the variations of their individual parameters were less than 5 % below the nominal values. If necessary, the engine control units of future engine generations could handle such differences if the relevant information on the fuel implemented was programmed beforehand.

In the high-load range the direct influence of the fuels on the combustion behaviour could be observed. Fuels with HVO content showed reduced ignition delay during pre-combustion whereas a longer ignition delay was recorded for fuels with FAME content. Pre-combustion had a stabilizing effect on the main combustion.

The results regarding FSN and particle number confirm that the FAME content in the fuel causes a reduction of the particle emission which can be ascribed to the oxygen bound in the FAME molecule. In contrast HVO-containing fuels produced higher particle numbers (about 100 % more) whereas the FSN was not different from that of the reference diesel fuel. Thus the implementation of fuels containing HVO leads to the emission of smaller particles.

During the short-term test runs, an influence on the exhaust gas after-treatment system due to the blend fuels could not be established. The particle reduction induced by the diesel particulate filter came to 99 %. With the implementation of the SCR, NO_x emissions could be minimized to a percentage of up to 90. For the entire engine map, NO_x reduction of more than 40 % was determined.

Engine Endurance Runs

In the endurance runs the test engine was operated with test fuels ôDF + 7 % FAMEô, ôDF + 30 % FAMEô and ôDF + 30 % HVOô for 500 operating hours each. The findings of the short-term test runs could be confirmed, e.g. with regard to the shifting of the operating points and the emission behaviour.

Furthermore, it could be demonstrated that the engine components ãinjectorõ, ãexhaust gas turbocharger (EGT)ô, ôthrottle valveô and ócylinder headô did not show any noticeable metal wear compared to the operation with diesel fuel. Soot deposits on the EGR cooler were identified after the operation with FAME-containing fuels which correlates to the results of the particle emissions.

With regard to the engine oil condition, the lubrication oils did not differ between the endurance runs concerning their parameters óviscosityô, ôTBNô and ómeal wear contentô regardless of the fuel implemented. However, during endurance runs 2 and 3 a strong increase of the neutralization number past the limit value was strinking. Possible causes may be that at the end of the second endurance runs the FAME content in the lubrication oil increased to 4.5 % and FAME transfer into the fresh oil filling was verified in the third endurance run.

Outlook

In conclusion, fuel-related differences, as known from previous applications, could not be verified for the tested EURO-VI engine which applies particularly to the typical increase of NO_x emissions due to FAME-containing fuels. Fuel-related restrictions of the engine operation could not be determined during both the short-term and endurance test runs.

It would be desirable to realise an adaptation of the engine control unit by programming selected fuel detection. Thus the improved EGR potential of fuels with high FAME content could be exploited. Additionally the AdBlue dosage could be adjusted to the current NO_x emissions in order to avoid misdosage.

10 Annex

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10.2 Index of Abbreviations

BHT	Butylated Hydroxytoluene
BMEP	Break mean effective pressure
Ca	Calcium
CCR	Conradson Carbon Residue
CFPP	Cold Filter Plugging Point
CO	Carbon Monoxide
CO_2	Carbon Dioxide
CR	Common Rail
CN	Cetane Number
DF	Diesel Fuel
DOC	Diesel Oxidation Catalyst
EGR	Exhaust Gas Recirculation
EGT	Exhaust Gas Turbocharger

DPF	Diesel Particulate Filter
FAME	Fatty Acid Methyl Ester
FSN	Filter Smoke Number
HFRR	High-Frequency Reciprocating Rig
HPSEC	High Performance Size-Exclusion Chromatography
HVO	Hydrogenated Vegetable Oil
ICP	Inductively Coupled Plasma
ID	Ignition Delay
Mg	Magnesium
NO	Nitrogen Monoxide
NO_2	Nitrogen Dioxide
TAN	Total Acid Number
O_2	Oxygen
OES	Optical Emission Spectroscopy
OS	Oxidation Stability
PI	Pilot Injection
PIBSI	Polyisobutylene Succinimide
PV	Peroxide Value
RME	Rapeseed Oil Methyl Ester
SCR	Selective Catalytic Reduction
SME	Soybean Oil Methyl Ester
TBN	Total Base Number
THC	Total Hydrocarbons
VI	Viscosity Index
VNT	Variable Nozzle Turbocharger

10.3 Index of Figures

10.4 Index of Tables

10.5 Wear Metals and Contamination in the Engine Lubrication Oil

Table 20: Wear Metals in the Engine Oil Dependent on the Operating Time of the First Endurance Run.

DF + 7 % FAME		Operating Time After Oil Change [h]								
Element	**Unit**	**0**	**100**	**200**	**250**	**300**	**350**	**400**	**450**	**500**
Iron	mg/kg	0.9	31.5	48.3	50.3	54.8	62.5	74.9	84.5	92.3
Chromium	mg/kg	0.1	1.1	1.7	1.8	1.9	2.2	2.6	2.9	3.3
Tin	mg/kg	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Aluminium	mg/kg	3.0	4.1	4.5	4.7	4.9	5.1	5.8	6.2	7.5
Nickel	mg/kg	0.1	0.5	0.6	0.5	0.6	0.6	0.7	0.8	0.6
Copper	mg/kg	<0.1	7.5	10.8	11.9	12.7	15.2	17.6	19.9	22.0
Lead	mg/kg	<0.1	0.1	0.1	0.2	0.2	0.2	0.2	0.2	0.3
Moldybdenum	mg/kg	0.4	0.3	0.3	0.3	0.3	0.3	0.4	0.4	0.4

Table 21: Wear Metals in the Engine Oil Dependent on the Operating Time of the Second Endurance Run.

DF + 30 % FAME		Operating Time After Oil Change [h]							
Element	**Unit**	**0**	**100**	**200**	**300**	**350**	**400**	**450**	**500**
Iron	mg/kg	0.9	27.8	41.2	54.4	63.2	71.1	79.7	88.9
Chromium	mg/kg	0.1	1.0	1.4	1.9	2.2	2.4	2.7	3.0
Tin	mg/kg	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Aluminium	mg/kg	3.0	3.2	3.9	4.0	4.4	4.6	4.9	5.2
Nickel	mg/kg	0.1	0.3	0.4	0.5	0.6	0.6	0.7	0.7
Copper	mg/kg	<0.1	8.7	12.7	14.1	15.7	17.0	18.0	20.6
Lead	mg/kg	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Moldybdenum	mg/kg	0.4	0.4	0.5	0.5	0.5	0.5	0.5	0.5

Table 22: Wear Metals in the Engine Oil Dependent on the Operating Time of the Third Endurance Run.

DF + 30 % HVO		Operating Time After Oil Change [h]								
Element	**Unit**	**0**	**100**	**200**	**250**	**300**	**350**	**400**	**450**	**500**
Iron	mg/kg	0.9	36.2	43.1	50.8	59.2	53.5	65.1	69.1	78.0
Chromium	mg/kg	0.1	1.2	1.5	1.8	2.1	1.8	2.2	2.3	2.6
Tin	mg/kg	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Aluminium	mg/kg	3.0	2.9	3.4	4.0	4.6	5.1	6.2	5.3	6.8
Nickel	mg/kg	0.1	<0.1	0.3	0.4	0.4	0.4	0.5	0.5	0.5
Copper	mg/kg	<0.1	7.2	9.2	10.4	12.5	7.2	9.2	10.4	12.5
Lead	mg/kg	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Moldybdenum	mg/kg	0.4	0.3	0.4	0.5	0.5	0.4	0.4	0.5	0.5

Table 23: Additives and Contamination Components in the Engine Oil Dependent on the Operating Time of the First Endurance Run.

DF + 7 % FAME		Operating Time After Oil Change [h]								
Element	**Unit**	**0**	**100**	**200**	**250**	**300**	**350**	**400**	**450**	**500**
Calcium	mg/kg	1520	1410	1480	1340	1370	1330	1420	1390	1410
Magnesium	mg/kg	4.0	4.5	4.9	4.5	4.5	4.5	4.7	4.8	4.8
Boron	mg/kg	1.8	1.9	1.9	0.8	0.8	0.9	1.0	0.8	0.8
Zinc	mg/kg	672	589	635	540	569	544	593	582	630
Barium	mg/kg	<0.1	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.3
Phosphorus	mg/kg	572	535	554	487	506	485	514	502	514
Sulphur	mg/kg	1930	1950	2050	1620	1700	1610	1730	1700	1720
Silicon	mg/kg	<0.1	4.9	7.2	6.3	6.9	6.9	7.9	9.3	14.5
Sodium	mg/kg	2.2	5.8	5.5	6.2	5.1	5.5	5.1	5.4	1.8

Table 24: Additives and Contamination Components in the Engine Oil Dependent on the Operating Time of the Second Endurance Run.

DF + 30 % FAME		Operating Time After Oil Change [h]							
Element	**Unit**	**0**	**100**	**200**	**300+**	**350**	**400**	**450**	**500**
Calcium	mg/kg	1520	1470	1410	1480	1470	1480	1470	1480
Magnesium	mg/kg	4.0	4.6	4.8	4.9	5.2	5.3	5.3	5.6
Boron	mg/kg	1.8	2.4	1.9	1.5	1.8	1.7	2.1	1.7
Zinc	mg/kg	672	647	602	645	646	649	644	650
Barium	mg/kg	<0.1	0.2	0.1	0.2	0.1	0.1	0.1	0.1
Phosphorus	mg/kg	572	566	534	552	553	551	542	545
Sulphur	mg/kg	1930	1770	1640	1700	1700	1690	1660	1670
Silicon	mg/kg	<0.1	7.9	9.2	7.6	8.6	8.4	9.2	10.5
Sodium	mg/kg	2.2	8.0	7.4	7.5	7.9	8.3	8.7	9.0

Table 25: Additives and Contamination Components in the Engine Oil Dependent on the Operating Time of the Third Endurance Run.

DF + 30 % HVO		Operating Time After Oil Change [h]								
Element	**Unit**	**0**	**100**	**200**	**250**	**300**	**350**	**400**	**450**	**500**
Calcium	mg/kg	1520	1470	1590	1660	1740	1630	1750	1700	1770
Magnesium	mg/kg	4.0	4.8	5.2	5.5	5.9	5.2	5.8	5.7	6.1
Boron	mg/kg	1.8	1.7	1.5	1.6	1.6	1.4	1.1	1.1	1.0
Zinc	mg/kg	672	662	679	724	740	709	779	762	788
Barium	mg/kg	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.2	0.2	0.2
Phosphorus	mg/kg	572	618	577	614	623	565	609	589	615
Sulphur	mg/kg	1930	2030	1850	1990	2010	1620	1890	1750	1930
Silicon	mg/kg	<0.1	8.8	8.4	8.8	9.7	7.1	8.8	9.0	10.4
Sodium	mg/kg	2.2	10.1	6.8	6.8	6.9	8.5	6.7	7.9	7.2

10.6 Post Mortem Analysis of the After-Treatment System

After completing the endurance runs, the after-treatment systems were analyzed by *Johnson Matthey* in England. The investigation was coordinated by Dr. Claus Gº rsmann.

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CHARACTERISATION REPORT C12674

19th January 2013

Johnson Matthey Catalysts

Post mortem analysis of three DOC/CSF/SCR systems from Rostock University

For circulation to FVV

M. Lawrence
Catalyst Characterisation Group

EMISSION CONTROL TECHNOLOGIES

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Introduction

INTRODUCTION (1)

Confidential

- Three DOC/CSF/SCR systems were submitted for analysis by Rostock University
- Each system comprised a DOC, a CSF and two SCR catalysts

System	Sample Label	Substrate	Dimensions (mm)
System 1	DOC	Metallic	134.8x72x63.5
	CSF	Silicon Carbide	198.33x102.2x170
	SCR A	Cordierite	140x75
	SCR B	Cordierite	140x150
System 2	DOC	Metallic	134.8x72x63.5
	CSF	Silicon Carbide	198.33x102.2x170
	SCR A	Cordierite	140x75
	SCR B	Cordierite	140x150
System 3	DOC	Metallic	134.8x72x63.5
	CSF	Silicon Carbide	198.33x102.2x170
	SCR A	Cordierite	140x75
	SCR B	Cordierite	140x150

INTRODUCTION (2)

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- The three DOC/CSF/SCR systems had been tested by Rostock University using different biofuel blends:
  - System (1): Diesel (B7)
  - System (2): Diesel + 30% FAME
  - System (3): Diesel + 30% HVO
- The FAME fraction was a blend of 70% RME (rape seed methyl ester) and 30% SME (soy bean methyl ester), stabilised with antioxidants
  - 100ppm of an anti-fouling detergent of the PIBSI class was also added to the FAME fraction

INTRODUCTION (3)

Confidential

- Three 500 hour tests were run to compare the exhaust after-treatment performance from standard fuel conditions vs. bio fuel blends
- All tests were carried out on a VW series EU-VI passenger car engine with 4cyl.-16V, engine number CBAC, 1968cm³ engine swept volume, 103kW at 4200rpm and max engine torque of 320Nm at 1750-2500rpm
- Post mortem analysis was carried out to investigate the level of poisoning present after ageing

EXPERIMENTAL & SAMPLE PREPARATION

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- X-ray fluorescence (XRF) was used to quantify the extent of poisoning present on all catalysts
- For the DOCs, the catalysts were drilled through and swarf collected
  - Swarf was ground and pelletized before XRF analysis
- For the CSFs cores were taken from each catalyst then divided into three sections: ‘Front’, ‘Middle’ and ‘Rear’
  - These sections were ground and pelletized before analysis
- For elemental analysis of the SCRs, a quarter of each catalyst was divided into three sections: ‘Front’, ‘Middle’ and ‘Rear’
  - These sections were ground and pelletized before analysis

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Results

CATALYST POISONING -DOC

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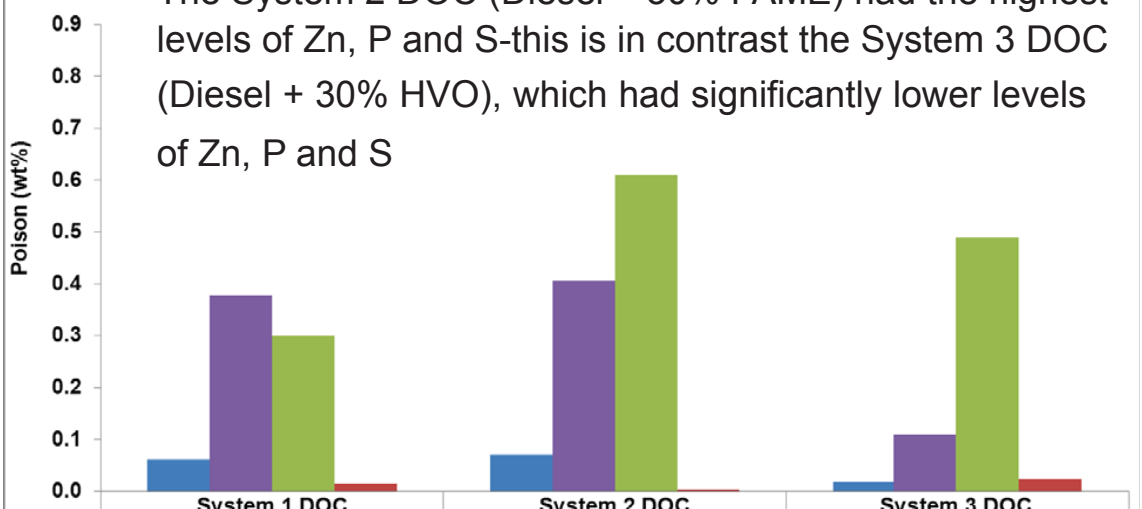
- The System 2 DOC (Diesel + 30% FAME) had the highest levels of Zn, P and S-this is in contrast the System 3 DOC (Diesel + 30% HVO), which had significantly lower levels of Zn, P and S



	System 1 DOC	System 2 DOC	System 3 DOC
Zn	0.06	0.07	0.02
P	0.38	0.41	0.11
S	0.30	0.61	0.49
Ca	0.01	0.00	0.02

CATALYST POISONING -CSF

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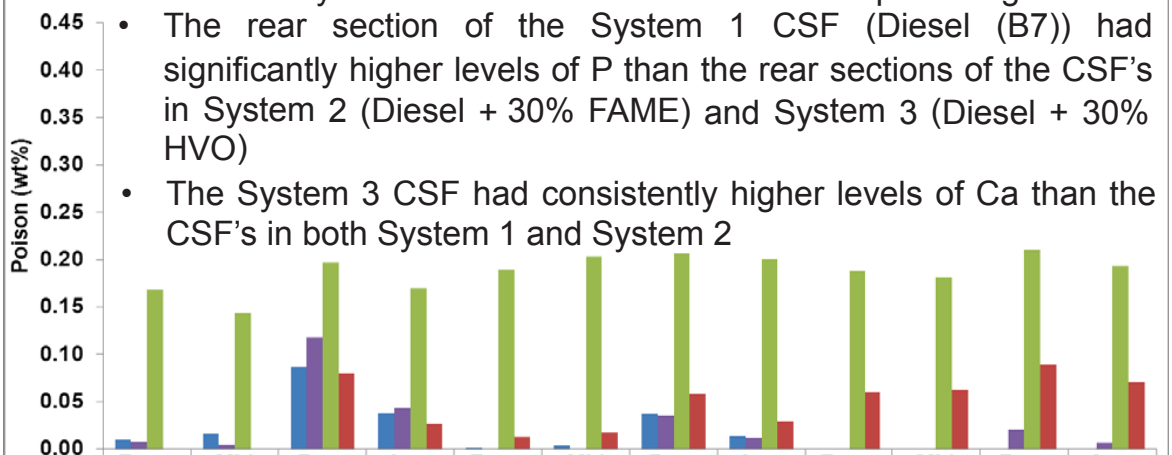
- All three system's CSF's had similar levels of S poisoning
- The rear section of the System 1 CSF (Diesel (B7)) had significantly higher levels of P than the rear sections of the CSF's in System 2 (Diesel + 30% FAME) and System 3 (Diesel + 30% HVO)
- The System 3 CSF had consistently higher levels of Ca than the CSF's in both System 1 and System 2



	Sytstem 1 CSF				System 2 CSF				System 3 CSF			
	Front	Mid	Rear	Avg.	Front	Mid	Rear	Avg.	Front	Mid	Rear	Avg.
Zn	0.01	0.02	0.09	0.04	0.00	0.00	0.04	0.01	0.00	0.00	0.00	0.00
P	0.01	0.00	0.12	0.04	0.00	0.00	0.04	0.01	0.00	0.00	0.02	0.01
S	0.17	0.14	0.20	0.17	0.19	0.20	0.21	0.20	0.19	0.18	0.21	0.19
Ca	0.00	0.00	0.08	0.03	0.01	0.02	0.06	0.03	0.06	0.06	0.09	0.07

CATALYST POISONING -SCR

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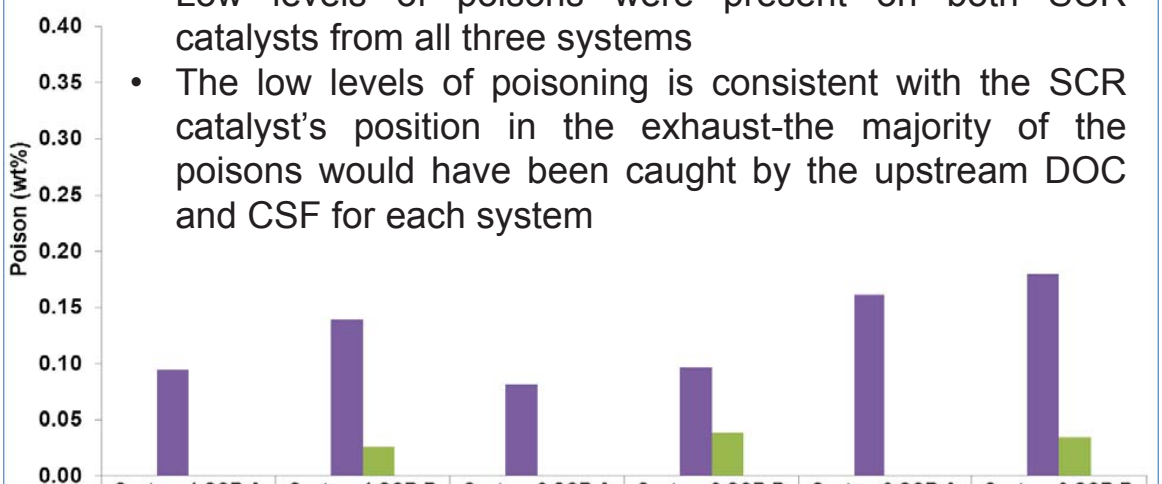
- Low levels of poisons were present on both SCR catalysts from all three systems
- The low levels of poisoning is consistent with the SCR catalyst's position in the exhaust-the majority of the poisons would have been caught by the upstream DOC and CSF for each system



	System 1 SCR A Average	System 1 SCR B Average	System 2 SCR A Average	System 2 SCR B Average	System 3 SCR A Average	System 3 SCR B Average
Zn	0.00	0.00	0.00	0.00	0.00	0.00
P	0.09	0.14	0.08	0.10	0.16	0.18
S	0.00	0.03	0.00	0.04	0.00	0.03
Ca	0.00	0.00	0.00	0.00	0.00	0.00

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Conclusions

CONCLUSIONS (1)

Confidential

- Three catalyst systems were submitted for analysis by Rostock University
  - Each system comprised a DOC, a CSF and two SCR catalysts
  - The three systems had been tested by Rostock University using different biofuel blends
- The System 2 DOC (Diesel + 30% FAME) had the highest levels of Zn, P and S-this is in contrast the System 3 DOC (Diesel + 30% HVO), which had significantly lower levels of Zn, P and S

CONCLUSIONS (2)

Confidential

- All three system's CSF's had similar levels of S poisoning
  - The rear section of the System 1 CSF (Diesel (B7)) had significantly higher levels of P than the rear sections of the CSF's in system 2 (Diesel + 30% FAME) and System 3 (Diesel + 30% HVO)
  - The System 3 CSF had consistently higher levels of Ca than the CSF's in both System 1 and System 2

- Low levels of poisons were present on both SCR catalysts from all three systems