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FINAL REPORT

Investigation into the interactions between fuels and fuel-carrying vehicle components in Plug-in Hybrid Electric Vehicles – Sub-project investigation of additionally stabilised diesel fuel blends

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Investigation into the interactions between fuels and fuel-carrying vehicle components in Plug-in Hybrid Electric Vehicles - Sub-project investigation of additionally stabilised diesel fuel blends

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Final report for the

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1. Summary

Within the scope of the FVV overall project "Fuels for PHEV Vehicles", the interactions between fuel-carrying vehicle components and fuels and their chemical components are to be determined during prolonged storage of different fuels in PHEV vehicles under near-application conditions. In terms of fuels, aged fuels and fuel blends primarily from diesel fuel and FAME and synthetic diesel fuel such as HVO and GTL were particularly to be investigated. Within the UFOP sub-project, the matrix was extended with four diesel fuel FAME blends, which were additionally stabilised (with additives) specifically for PHEV applications. The long-term storage carried out ensured a defined and reproducible ageing of the diesel-FAME blends used. These blends were analytically evaluated every month.

The stabilisation of the diesel-FAME blends showed a reduction of autoxidation reactions over the storage period, despite the fact that some of the FAME qualities were already prestressed. An increase in the measured value of the total contamination was shown by one of the diesel-FAME mixtures at the end of storage (as of the 7th month). The determination of water content, acid number and oxidation stability according to PetroOxy and the Rancimat method remained unremarkable. This suggests that the fuel blends used are sufficiently stabilised. This conclusion is additionally supported by the consideration of permittivity, which showed fluctuation of the measured values in the range of the systematic error of the measurement set-up over the storage period of nine months. Using the highly sensitive fluorescence measurement, only changes in the diesel RME/SME blend with the FAME mixtures which were two years older could be detected. During the storage period of nine months, an increase in fluorescence was detected, indicating that the chemical structure of the mixtures has changed.

Taking into account the application in PHEV vehicles, a significantly longer dwell time of the fuel in the vehicle tank is assumed. While the fuel in diesel vehicles has a maximum dwell time of 90 days, dwell times of several months (6-9 months) are expected in PHEV vehicles depending on driving behaviour. The results of this sub-project showed a stabilisation of the diesel-FAME mixtures over a correspondingly long storage time at 40 °C.

2. Introduction

By 2020, the average CO_2 emissions of a manufacturer's vehicle fleet must be reduced to 95 g/km [EU 2014]. By 2050, road traffic should be almost climate-neutral in order to limit average global warming to a maximum of two degrees Celsius by 2100 [FVV 2018]. Savings in the average fuel consumption of a vehicle fleet are therefore necessary and required by policy. In order to achieve these goals, in addition to improvements to the vehicle such as an increase in the efficiency of the combustion engine or a reduction in wind and frictional resistance, a significant and more rapid expansion of the hybrid vehicle market (especially the Plug-in Hybrid Electric Vehicle, abbreviated PHEV) is also being considered. With the introduction of PHEV vehicles, it can also be expected that the fuels in tank systems will have longer dwell times, as the electric motor can be used as the main drive unit.

For a detailed assessment of the ageing condition of the fuels during the operation of PHEVs, chemical and physical examinations and the findings of fuel-carrying vehicle components such as the tank system, the pre-feed pump, fuel filters, the fuel lines, the high-pressure pump, the rail and the injection system are required. With long dwell times in the fuel supply system especially, the interaction behaviour of the fuel cannot be reliably predicted.

Within the scope of the overall project, the interactions between fuel-carrying vehicle components and fuels and their chemical components are to be determined during prolonged storage of different fuels in PHEV vehicles under near-application conditions. In terms of fuels aged fuels and fuel blends primarily from diesel fuel and FAME and synthetic diesel fuel such as HVO and GTL are particularly to be investigated. Within the sub-project, the matrix is extended to four diesel-FAME blends, which were additionally stabilised especially for PHEV applications.

3. Task

The long-term stability of a diesel-FAME fuel matrix stabilised for PHEV applications is to be investigated in long-term storage as part of this sub-project.

A blend of fossil diesel fuel with up to 7% fatty acid methyl ester is currently available across the board in the diesel fuel sector. Particularly with increasing proportions of FAME, the probability of age-related reaction products occurring during long storage periods also increases, depending on the FAME degree of saturation. Oxidative processes are responsible for this, leading to the formation of higher molecular weight ageing products.

Within the sub-project, the diesel-side fuel ageing was therefore simulated by the incorporation of diesel-FAME mixtures with a stabilising additive specially designed for PHEV applications. In Figure 1, the sub-project of the incorporation tests is shown as part of the overall project.

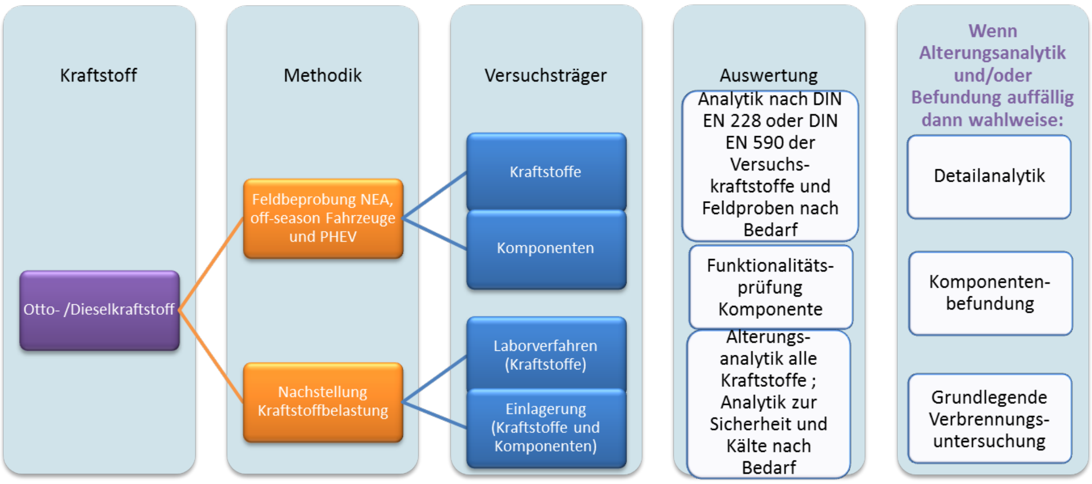

Figure 1: Schematic overview of the overall project

4. State of the art

To determine the quality of fuels, different laboratory procedures are required according to the standard for biodiesel (FAME according to DIN 14214) and diesel fuel (DIN EN 590). With regard to fuel ageing, the oxidation stability is particularly important, determined for diesel fuels, petrol and biodiesel using different methods.

In addition to oxidation stability, the fuel composition is also important for the operation of diesel and petrol engines. Here the standards provide key data, but fuels may vary within these standards. In non-European countries the fuel quality may also differ from European quality. For optimal operation even after a longer dwell time in the tank, especially when using advanced fuel metering and exhaust after-treatment systems, the interaction between aged fuels and fuel-carrying vehicle components must be reduced so that there are no restrictions on the operational behaviour and safety of the vehicle.

Due to the addition of alternative fuels such as FAME and HVO to diesel fuels, the chemical and physical properties of an otherwise purely fossil fuel matrix are sometimes greatly altered [Tenboh. 08; Richter 12; Zhang 04]. The lower energy density, the changed boiling point due to the high proportion of low or high boilers, as well as the hygroscopic behaviour of the biogenic component are mainly responsible for this. The additional component of reactive substance groups can lead to a decrease in oxidation stability and a greater thermo-oxidative degradation of the fuel blends. Autoxidation reactions in particular play a role, as well as different polymerisation and hydrolysis reactions for the ageing of fuels and combustibles, which can lead to the formation of sediments, among other effects. While autoxidation takes place slowly at low temperatures (<120 °C) in an oxygen atmosphere and can be catalysed by non-ferrous metals, the polymerisation reactions also take place when oxygen is excluded. A further distinction can be made between polycondesation reactions, polyaddition and polymerisation.

While condensation achieves chain growth by splitting off various by-products (often highly volatile components), polyaddition takes place without by-products. In both cases, no reactive radicals are formed and growth occurs gradually through the chemical reaction of monomers to oligomers. In contrast to polymerisation reactions, the reaction of two chains with each other does not terminate the polyreaction.

Polymerisation can be initiated either radically or ionically. The reaction is continuous and is interrupted by the coming together of two chains [Beyer 76]. Radical polymerisation is started by radical formers (primarily peroxides), which are formed at low temperatures by the decomposition of O-O bonds. The radical formed attacks a monomer and forms a new radical that can interact with other monomers. It is through this interaction that the chain growth is started. Elevated temperatures and exposure to light can also start the radical polymerisation [Mortim. 03]. Autoxidation is one of the main causes of ageing in the storage of diesel fuels. The degradation is also based on a radical chain reaction. The reaction of hydrocarbons with atmospheric oxygen produces peroxides, which decompose into radicals and subsequently form acids, alcohols and water. The reaction of two hydrocarbon radicals can produce substances with higher molecular weights that can sediment [Zhang 04]. Through the release of water, ester compounds can also saponify, react with metals and also sediment [Rheinb. 08].

In addition to the changes in the chemical and physical properties of the fuel blends, the different operating conditions also have an influence on the ageing mechanisms. The reaction behaviour is significantly influenced by the presence of foreign substances and additives. The basic theory of ageing of liquid hydrocarbons by thermo-oxidative degradation (autoxidation) has been studied by Cosgro. 87, Frankel 84, Fürst 80, Lundbe. 62, Belitz 00, Belitz 01, Zhang 04, Denisov 05, Zabel 05, Falk 04, Tenboh.

08, Edenho. 10, Liska 09 and Sarin 12. The effect of catalytic metals has been studied in detail by Denisov 05, Neulen 15, De Guz 09, Sarin 09 and 10. If the changes in the chemical-physical properties of the fuel blends become too large, individual components can sediment and lead to deposits within the technical system due to density gradients and viscosity changes (increasing polymerisation), but above all due to increasing polarity (oxygen incorporation). The tendency for sediment to build up and the coking tendency has been studied by Ullmann 08, Ullmann 09, Lacey 11, Quigley 11 and Willia. 09. The application properties have been described at OWI by Hoffmann 10, Neulen 15, Edenhofer 10, Hoffmann 11, Fischoeder 06, Liska 09, Neulen 15 and van Rheinberg 08.

At present, fatty acid methyl esters (FAME) are mainly used to replace diesel fuels of mineral oil origin, in which vegetable oils such as rapeseed oil, soybean oil, palm oil and used cooking oil are used as raw materials. However, the possible uses of these products, which can be obtained from vegetable oils via transesterification with methanol after prolonged storage, are limited due to their application-related disadvantages (including chemical or storage stability, corrosion, energy density, cold resistance) [Mengel 06; Rheinb. 09; Jaschi. 12; Ackerm. 15; Feldho.15; Neulen 15]. When FAME is mixed with diesel fuels and hydrogenated vegetable oils (HVO), some positive effects of FAME such as the improvement of lubricity (in HVO, lubricity additives are used) can be seen. According to DIN EN 590, for example, a mixture of FAME and diesel fuels of up to 7% is currently possible.

5. Material and methods

Two different diesel grades were selected from the FVV project for the study on the stabilisation of diesel-FAME blends (B0 EU 1 and B0 EU 2). Two FAME qualities from the stock were specified as mixing components. For this, a pure and non-additive RME with a storage time at the OWI of 6 months and an RME/SME blend (70/30) with unknown pre-additive and a storage time at the OWI of about 2 years were selected. The pre-additive could not be exactly determined, presumably a BHT was used. The FAME was stored at OWI in closed canisters in the dark at about 15-19 °C.

For the assessment of the ageing condition of the diesel/biodiesel blends with stabiliser used, the analysis procedures described below were carried out.

Oxidation stability using PetroOxy according to DIN EN 16091

The oxidation stability according to DIN EN 16091 is measured using PetroOxy and is specified in minutes. 5 ml of the fuel is placed in a pressure reactor and 7 bar of pure oxygen is added (oxygen 5.0). The sample is then heated to 140 °C and the pressure and temperature curves are recorded. Due to the autoxidation reactions, oxygen is incorporated into the liquid hydrocarbon matrix. As a result, the supernatant pressure is reduced. The pressure drop of 10 % is used as criteria to terminate. The time until this pressure drop occurs is defined as oxidation induction time (OIT) and is given in minutes.

Oxidation stability using Rancimat according to DIN EN 15751

The oxidation stability according to DIN EN 15751 is measured using Rancimat. 7.5 g of the fuel is placed in a glass cylinder and heated to 110.9 °C. During the measurement, compressed air is continuously passed through the fuel (10 l/h). The discharged and highly volatile components are transferred to a conductivity measuring cell. The conductivity is recorded over the test time. Autoxidation reactions lead to the formation of highly volatile components, which result in an increase in conductivity. Achieving a conductivity of 200 μS/cm or a test duration of 48 h serve as criteria to terminate. The time until the termination criteria is reached is defined as oxidation induction time (OIT) and is given in hours.

Water content using Karl Fischer titration according to DIN EN ISO 12937

The water content according to DIN EN ISO 12937 is determined coulometrically by Karl Fischer titration and expressed in mg/kg.

The samples are checked visually. If they are clear and bright and do not contain any water droplets or suspended particles when turned over, a weighed portion is added to the Karl Fischer titration vessel, where the iodine for the Karl Fischer reaction is produced coulometrically at the anode. When all water has been titrated, excess iodine is detected by an electrometric end-point detector and the titration is stopped. According to the stoichiometry of the reactions, 1 mole of iodine reacts with 1 mole of water, therefore the amount of water is proportional to the integrated current according to Faraday's Law.

Total contamination according to DIN EN 12662-98

The total contamination according to DIN EN 12662 is indicated in mg/kg. A sample of 250 g is weighed and heated to 40 °C. The fuel is then filtered under vacuum through a filter which has been previously weighed. The filter with the residue is washed, dried and weighed. The contamination is calculated as the difference between the mass of the filter and the sample mass, given in mg/kg.

Acid number according to DIN EN 14104

The acid number according to DIN EN 14104 is measured by potentiometric titration and given in mgKOH/g. 20 g of the fuel is dissolved in a mixture of ethanol and diethyl ether. The resulting single-phase solution is titrated at a temperature of 18 °C to 28 °C with 0.1 M alcoholic potassium hydroxide solution to the end point indicated by the colour change of the added phenolphthalein solution as indicator solution. The quantity of caustic potash consumed is used to calculate the content of acidic components.

Density using a Stabinger viscometer according to DIN EN ISO 12185

The density according to DIN EN 12185 is measured using a Stabinger viscometer and is given in g/l. 1 ml of the sample is injected into a sample cell at a controlled temperature. The vibration frequency is recorded and the density of the sample calculated using the cell constants previously determined by measuring the vibration frequency when the cell is filled with calibration liquid of known density.

Fluorescence spectroscopy

The fluorescence was determined with a Hitachi F-4500 fluorimeter with PMT detector (Tokyo, Japan). The instrument emits monochromatic light of different wavelength ranges into a sample. The intensity of the emitted fluorescence light, also wavelength-dependent, is measured with a photomultiplier perpendicular to the excitation radiation. The Hitachi fluorimeter has an excitation range from 250 to 600 nm and an emission range from 250 to 900 nm. This allows for a three-dimensional graphic of the measured sample to be generated with the intensity as Z axis and the excitation and emission wavelengths in the X-Y plane (3D-EEM). For better clarity, the results section shows the emission maxima at one emission wavelength and the emission spectra at three different excitation wavelengths. The measurements were performed at room temperature. Rectangular cells with PTFE plugs are used to hold the samples (type 23/Q/10 from Starna: internal width 10 mm, wall thickness 1.25 mm, volume 3.5 mL).

Permittivity

Permittivity describes the electrodynamic permeability of a medium for electric (alternating) fields, whereby the permeability is influenced by the properties of the medium. Permittivity sensors are generally based on electrical capacitors in which two electrically conductive surfaces are exposed to an alternating current. If a dielectric is inserted between the capacitor plates, the dielectric parameters change according to the incurred polarisation effects. Four different polarisation types are distinguished here (electron, interface, orientation and ion polarisation). Electron polarisation is based on an interaction between electric fields and the electron shell. Polar compounds possess a permanent dipole moment that causes the dipoles to be oriented in the alternating field according to the applied field. Nonpolar compounds do not exhibit any orientation polarisation, whereby nonpolar compounds exhibit small permittivity values, and polar compounds larger values. This allows polar and nonpolar compounds to be differentiated based on the magnitude of the relative permittivity. Ion polarisation refers to the displacement of negatively and positively charged particles in the electric field.

Relative permittivity is defined by the quotient of the capacitance of the medium C (ω,T) and the empty capacitance C0 (ω,T), whereby ω is the frequency of the alternating voltage and T is the temperature (equation 1).

$$\boldsymbol{\varepsilon_r' (\omega, T) = \frac{C(\omega, T)}{C_0(\omega, T)}}$$

Moreover, permittivity is a complex-valued function comprising the real part εr‘ (ω,T) and its imaginary part ε_r‘‘ (ω,T) (equation 2). The real part (relative permittivity) is influenced by the polarisation effects, whereas the imaginary part ε_r‘‘ (ω,T) reflects the resulting losses in polarisation and conductivity.

$$\varepsilon_r(\omega, T) = \varepsilon_r'(\omega, T) - j\varepsilon_r''(\omega, T)$$

An interdigital sensor is used for permittivity measurements. Measurements were made with an impedance analyser (Keysight E4990A), which determines the capacitance and dissipation factor. The frequency of the alternating voltage is modulated in a range between 200 Hz and 120 MHz, whereby the values of the relative permittivity between10 kHz and 10 MHz are displayed. Outside these limits, the sensor used shows too much noise. Using a temperature controller (Belektronig HAT control; temperature sensor PT100) and external cooling, all measurements were conducted at 25 °C.

6. Implementation of the long-term storage

Autoxidation is a self-accelerating process. At room temperature and without catalytic materials, ageing can in some cases occur very slowly. A temperature of 50 °C was therefore chosen for the storage implemented in this sub-project. This can accelerate the ageing process. Depending on the season, a peak temperature of up to 80 °C can be reached in vehicle tanks. The 50 °C chosen therefore also reflects possible temperatures in the real storage tank.

The storage was done in 1000 ml glass bottles to prevent a catalytic effect from the storage container. The bottles were secured with caps made of polyethylene (PE). This made a low exchange with the ambient air possible. One glass bottle was stored for each retrieval interval so that no movement of the bottle or change in storage conditions occurred until the time of retrieval.

The analysis was carried out monthly.

7. Results and discussion

In the following, the results of the analytical evaluation of the added fuels used are presented. The bar charts show the measured values (Y axis) of the four fuels (Black: Diesel 1 + 10 % (V/V) RME/SME + stabiliser; Red: Diesel 1 + 10 % (V/V) RME + stabiliser; Orange: Diesel 2 + 10 % (V/V) RME/SME + stabiliser; Green: Diesel 2 + 10 % (V/V) RME + stabiliser) depending on the storage time in months on the X axis.

Figure 2 shows the results of the determination of oxidation stability using PetroOxy according to DIN EN 16091. Experience shows that the measured values decrease continuously in the course of storage. Stabilisation by the additive used showed high measured values > 75 min in the blends with the addition of the RME/SME mixture (70/30). The blends with pure RME also showed measured values > 50 min at the beginning of storage.

Over the course of long-term storage over 9 months, the progressive autoxidation led to a decrease in the measured values using the PetroOxy method. In some cases, briefly stagnating measured values were observed (e.g. between 4 and 5 months and between 7 and 8 months), which can be attributed to the variability of the samples (a separate bottle for each ageing interval) and do not contradict the general ageing trend. In the investigations, the blends with pure RME showed a clearer drop in the measured values after 9 months of almost 20 min in the diesel 2 blend, and about 25 min in the diesel 1 blend. The blends with a mixture of RME and SME (70/30) as a FAME proportion showed a decrease of the measured values after 9 months to about 50 min in both diesel fuels.

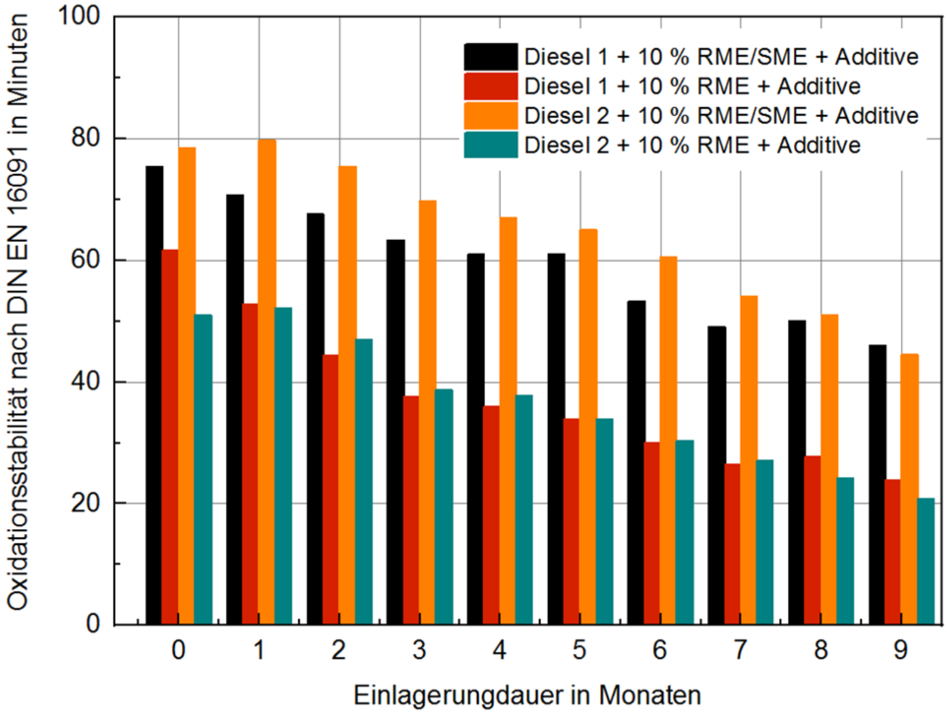

Figure 2: Oxidation stability according to DIN EN 16091 of the used diesel-biodiesel blends with stabiliser additive over the course of the storage time.

Similar to the results of the PetroOxy tests, the measurements according to DIN EN 15751 (Rancimat) showed a similar picture (see Figure 3). A determination of oxidation stability of the fuel blends according to the Rancimat method was metrologically possible even after 9 months of storage and still shows oxidation stability of more than 15 h for the blends with a mixture of RME and SME (70/30). Even the blends with pure RME content still had an oxidation stability of 4 and 7 h respectively. The stabilisation of the blends by the additional additives can therefore be considered successful.

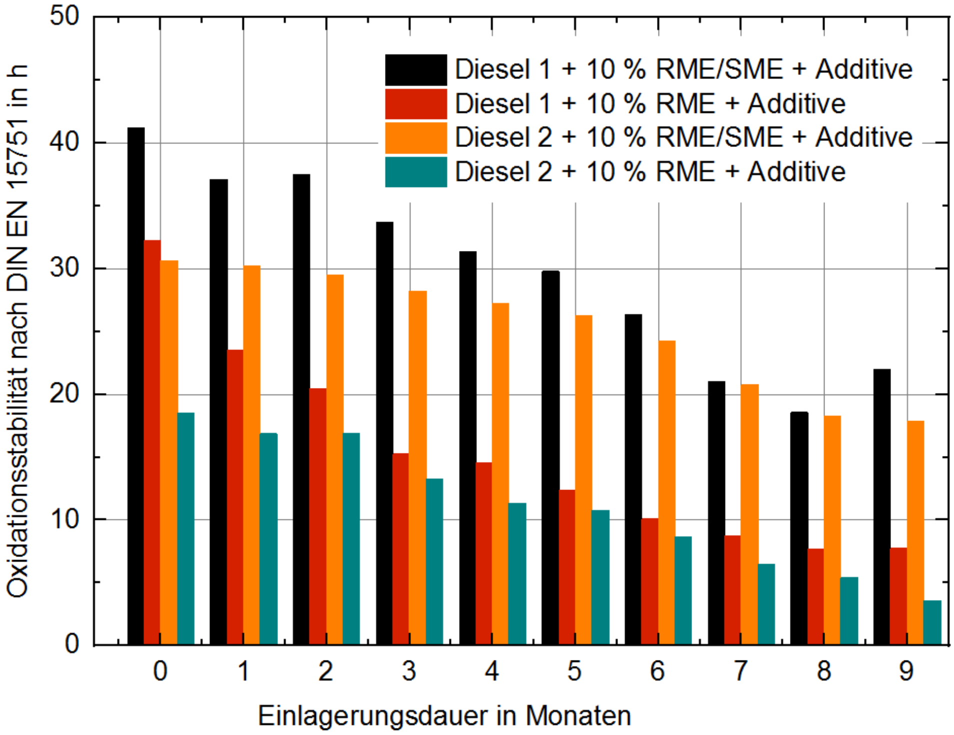

Figure 3: Oxidation stability according to DIN EN 15751 of the used diesel-biodiesel blends with stabiliser additive over the course of the storage time.

In Figure 4 the water content of the diesel-FAME blends used is plotted over the storage period. The water content remained at a very low level (below 65 mg/kg) over the running time, which indicates low ageing of the fuel blends. The observed increase up to month 5 or 6 and the subsequent decrease in water content is probably due to fluctuations in environmental conditions. Depending on the temperature and relative humidity, the water content in the fuel also changes due to hygroscopy according to Henry's Law. The four different fuels showed similar measured value curves. Only the diesel 2 + 10% (V/V) RME mixture showed an increase after 9 months that differed from that of the other fuels, although at just under 60 mg/kg it is low.

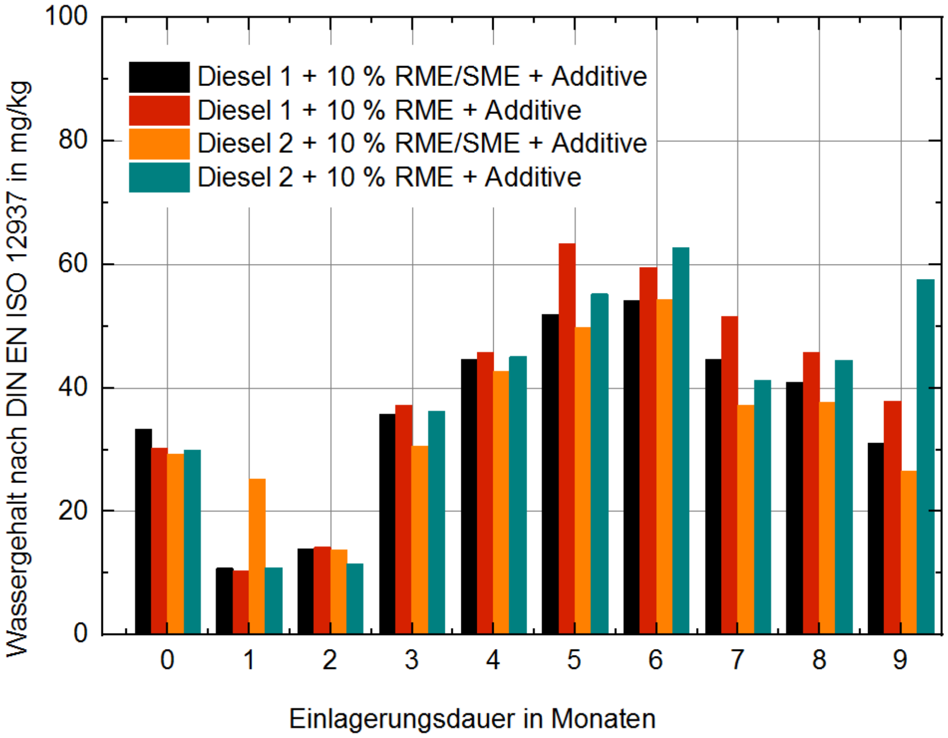

Figure 4: Water content according to DIN EN 12937 of the used diesel-biodiesel blends with stabiliser additive over the course of the storage time.

A further parameter to describe the ageing or storage stability is the determination of the acid number. In Figure 5 the acid number of the different fuel blends is shown as a function of storage time.

Due to the ageing condition of the FAME qualities used, acid numbers between 0.1 mgKOH/g and 0.22 mgKOH/g are determined before the beginning of storage. Particularly in diesel 1 with RME/SME mixture, the values fluctuate over the storage period but do not exceed 0.2 mgKOH/g. Increases in the acid number are determined in the remaining diesel-FAME blends. The limit value is partially exceeded. The observed increases in acidity are generally within the expected range. The stabilisation of the partly pre-aged FAME qualities within the respective diesel fuels showed an effective effect against the autoxidation reactions.

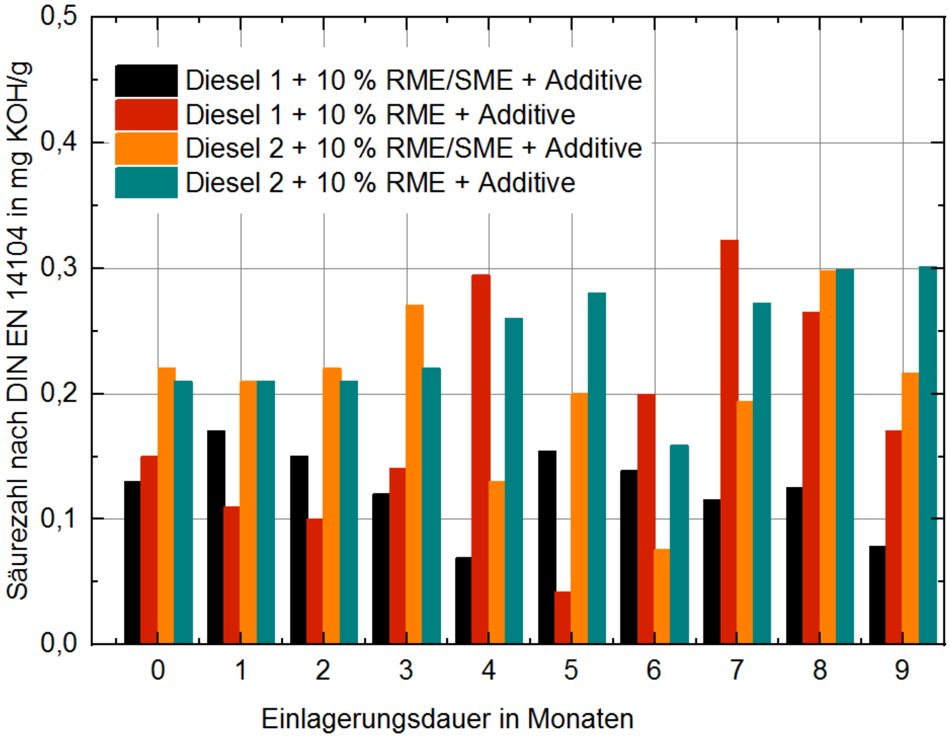

Figure 5: Acid number according to DIN EN 14104 of the used diesel-biodiesel blends with stabiliser additive over the course of the storage time.

The total contamination was used to determine ageing products precipitating from the liquid hydrocarbon matrix. The results of these investigations are shown in Figure 6. With the exception of the diesel 2 + 10% (V/V) RME blends, no blend used showed an increase in total contamination (< 10 mg/kg). Stabilisation by means of additives also proved to be a promising approach to ensure long storage times. After 7 months of storage, a commencing increase in total contamination above 10 mg/kg could be observed for blend diesel 2 + 10% (V/V) RME. After 8 months a total contamination level of about 20 mg/kg was determined; after 9 months the level increased to about 60 mg/kg.

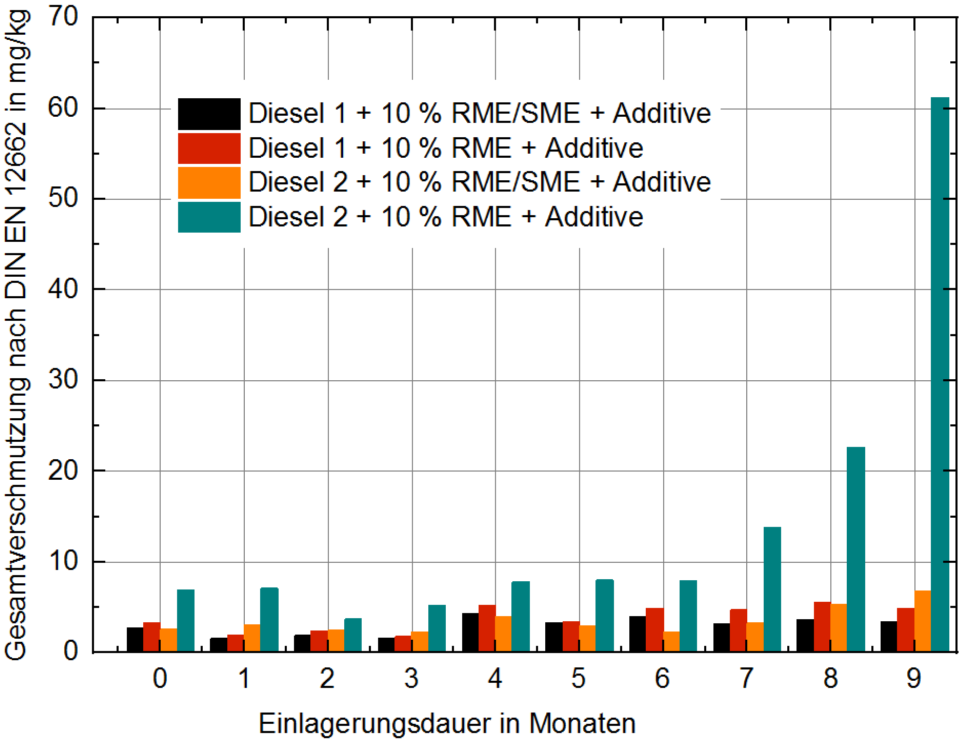

Figure 6: Total contamination according to DIN EN 12662 of the used diesel-biodiesel blends with stabiliser additive over the course of the storage time.

The observation indicates that a solubility limit has been reached for ageing products which can no longer be dissolved in the hydrocarbon matrix. By determining the total contamination, primarily higher-molecular ageing products such as long or highly branched polar polymers are shown. These cannot necessarily be detected by the other standard procedures, as neither water is incorporated nor is there a predominant acidic character. The decrease in oxidation stability, e.g. according to Rancimat, indicates a linear ageing process. However, since an oxidation stability of 4 h was still given after nine months, the ageing process determined here cannot be derived from these measurements.

In addition to the analysis methods in accordance with the standard, two measuring methods were used which are also used in fuel sensors to detect fuel ageing. For one, fluorescence spectroscopy at a constant excitation wavelength can produce specific spectrum shapes for individual fuels. The fuel change associated with the increased residence time can be detected using the fluorescence signal. Using fluorescence, both deposits and the fuel composition can be detected. In Figure 7 to Figure 10, the fluorescence signals of the diesel-FAME blends at various storage times up to nine months are shown.

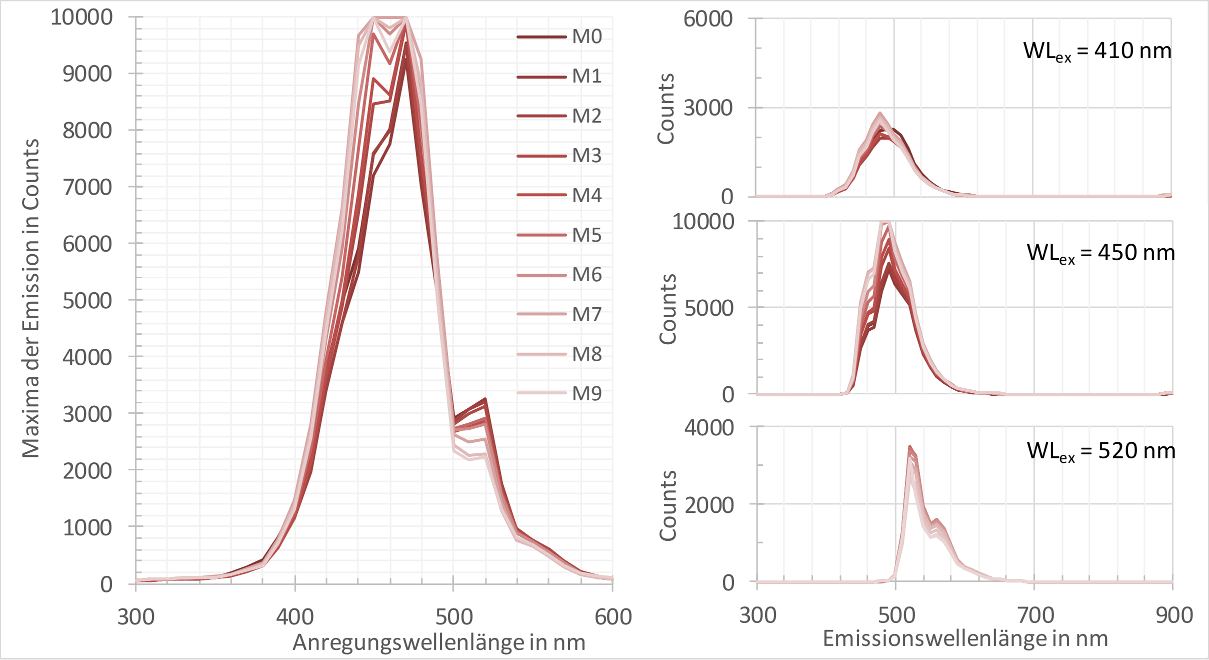

Figure 7: Fluorescence signal of the sample "Diesel 1 + 10% RME/SME + additive" over the storage period of nine months

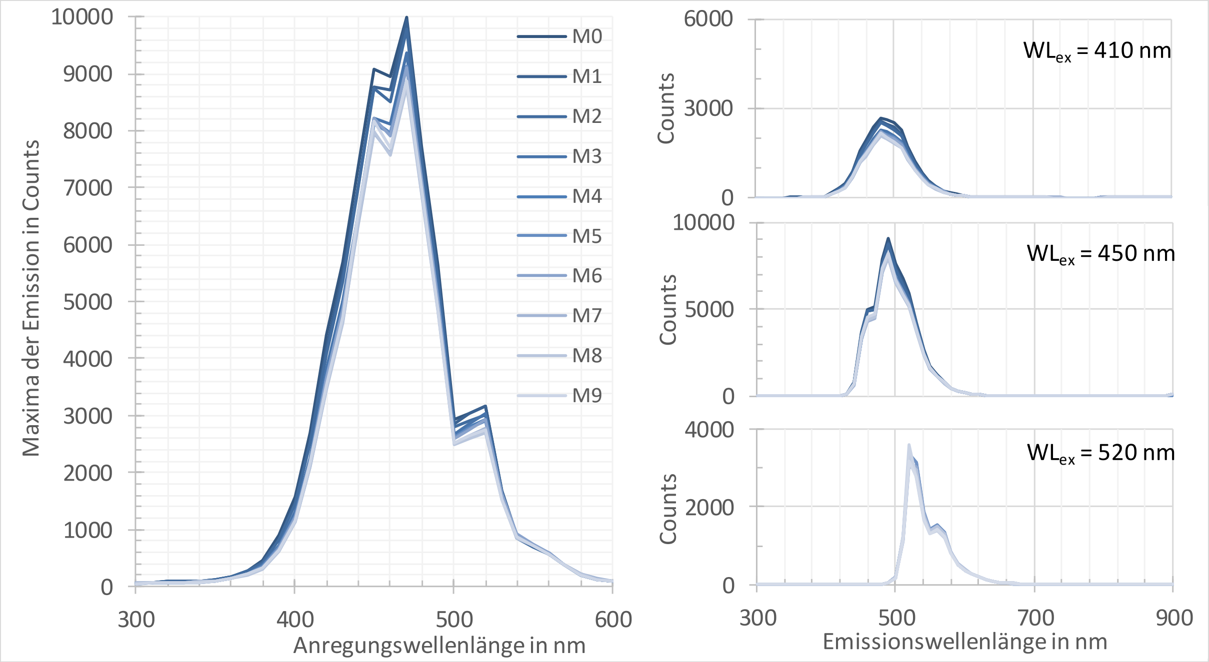

Figure 8: Fluorescence signal of the sample "Diesel 1 + 10% RME + additive" over the storage period of nine months

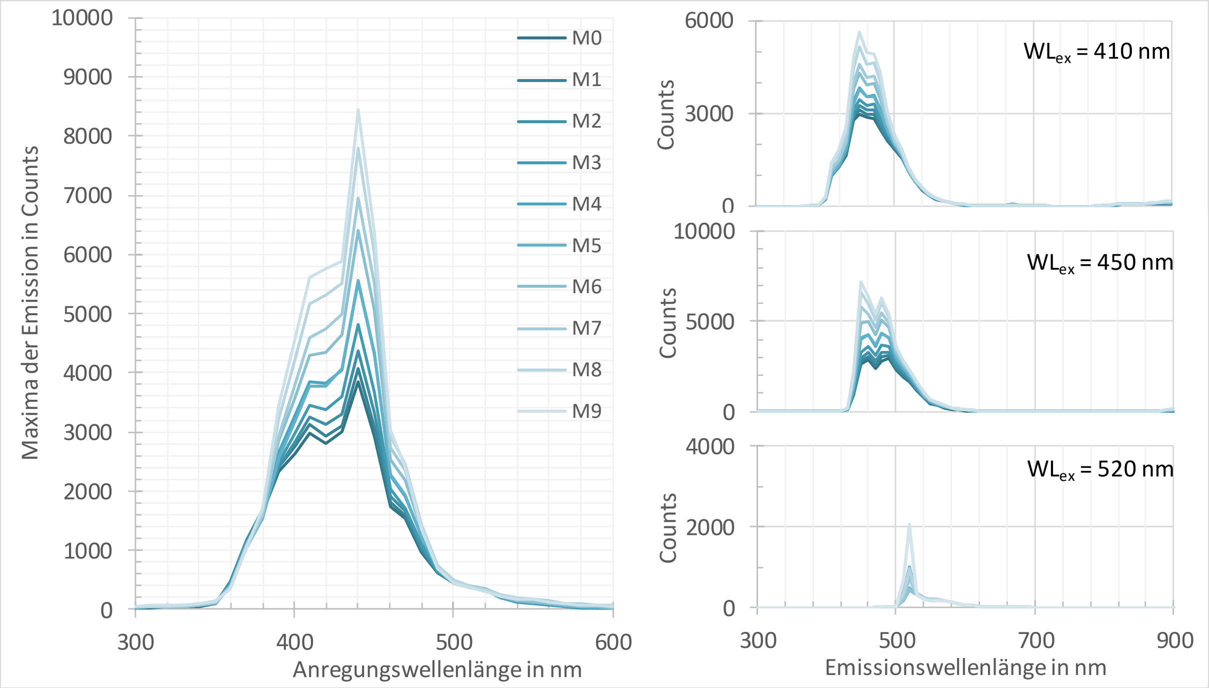

Figure 9: Fluorescence signal of the sample "Diesel 2 + 10% RME/SME + additive" over the storage period of nine months

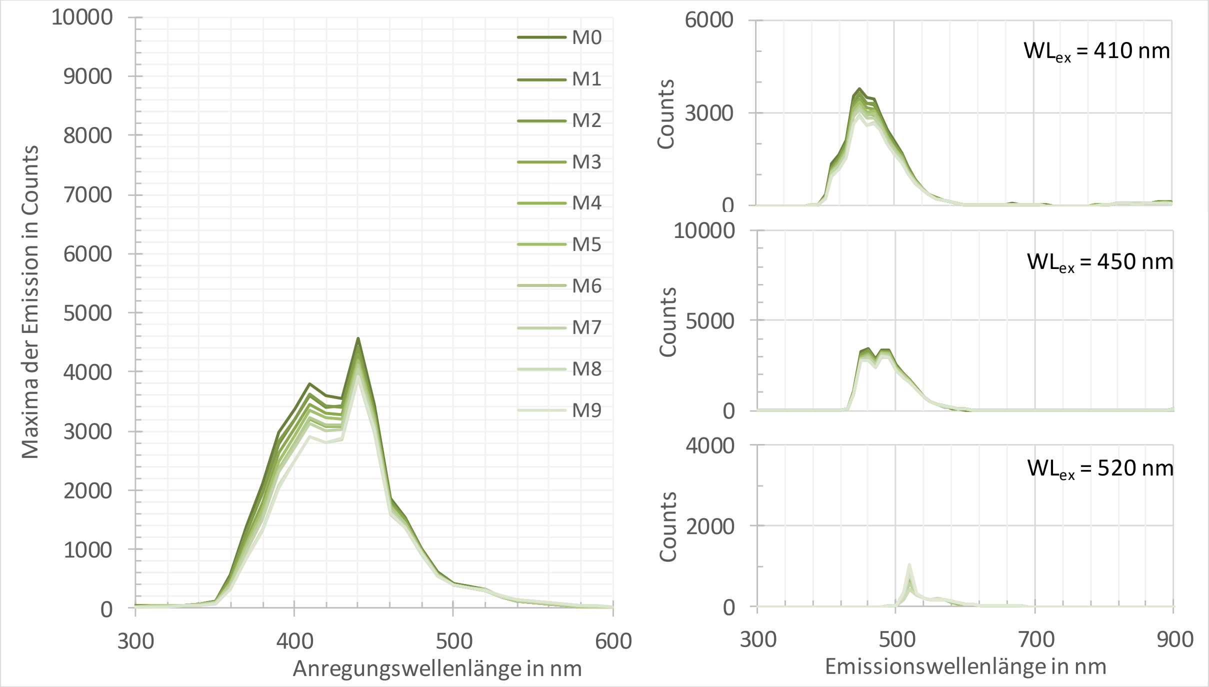

Figure 10: Fluorescence signal of the sample "Diesel 2 + 10% RME + additive" over the storage period of nine months

By observing the fluorescence signals, differences in the signals for the two diesel fuel and FAME qualities can be detected. The differences in the diesel fuel qualities are characterised on the one hand by the different forms of the signals, and on the other by different maxima of the emissions. Fossil diesel fuel 1 shows a double peak with an emission maximum at 10,000 and a pronounced shoulder at the excitation wavelength 520 nm with an emission maximum of 3,000. While the maximum for diesel 1 was 10,000, the maximum for diesel 2 was between 4,000 and 5,000.

The comparison of the two FAME qualities also showed a difference in the increase of the emission signal during the storage period of nine months of the RME/SME mixture. The diesel mixtures with pure RME showed no signal increase during the storage period. The increase in fluorescence in RME/SME blends can presumably be attributed to the consumption of natural antioxidants, which have a quenching effect when unused and lose this effect when they react with radicals. Pure RME does not contain these antioxidants. A fluorescence change indicating oligomer formation even during storage could not be observed, although the total contamination does indicate this.

In addition to measurements using fluorescence spectroscopy, the embedded samples were examined using dielectric relaxation spectroscopy. This method can be used to detect the oxidation products of higher molecular weights which are produced during the ageing process. For this purpose, the real and imaginary proportion of permittivity must be recorded over a wide frequency range. If higher molecular degradation products are formed in the fuel they can no longer directly follow the field above the relaxation frequency, meaning that the movement of the molecules is delayed.

In Figure 11 to Figure 14 the permittivity spectra of the four samples over a storage period of nine months are shown. The spectra are divided into real and imaginary parts. When comparing the individual samples over the storage period of nine months, it becomes clear that the signals change by about 0.005 to 0.01. Even if some samples show a clear trend over the storage time, the change is within the range of the systematic error of the instrument. It can also be seen here that no higher molecular degradation products were formed that would cause an increase in the real part.

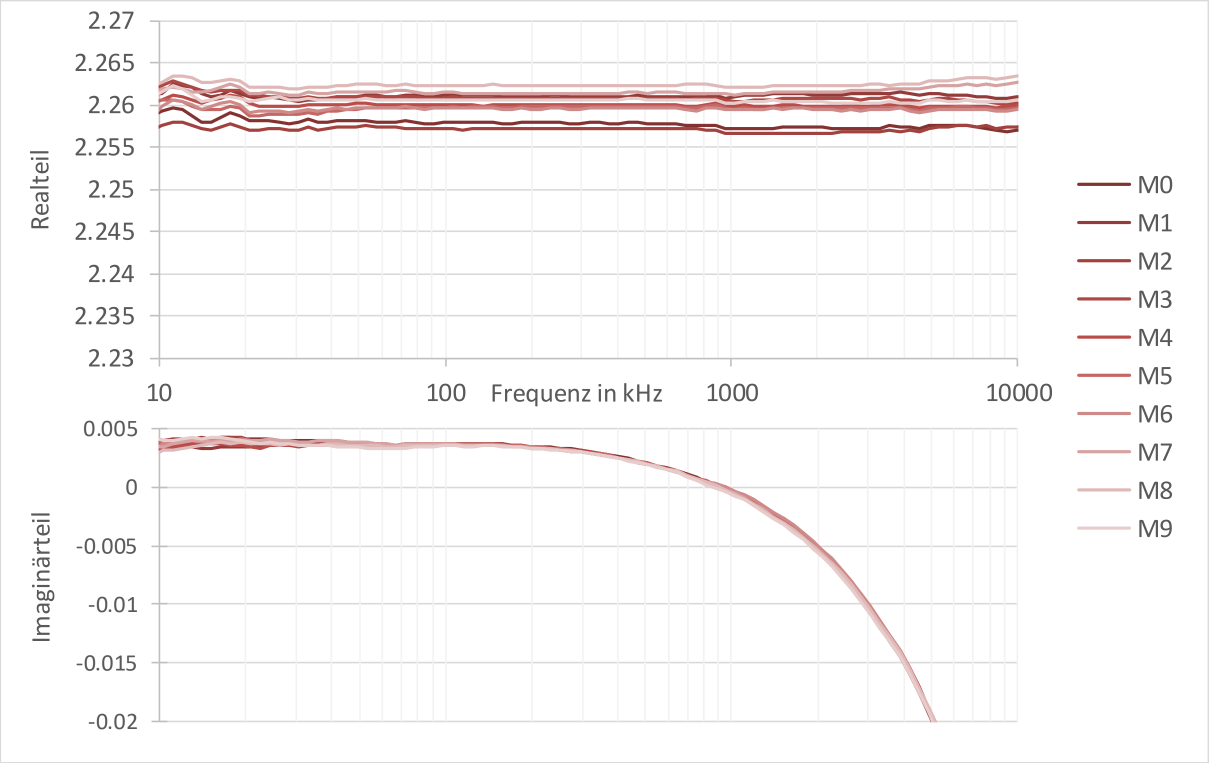

Figure 11: Permittivity of the sample "Diesel 1 + 10% RME/SME + additive" over the storage period of nine months

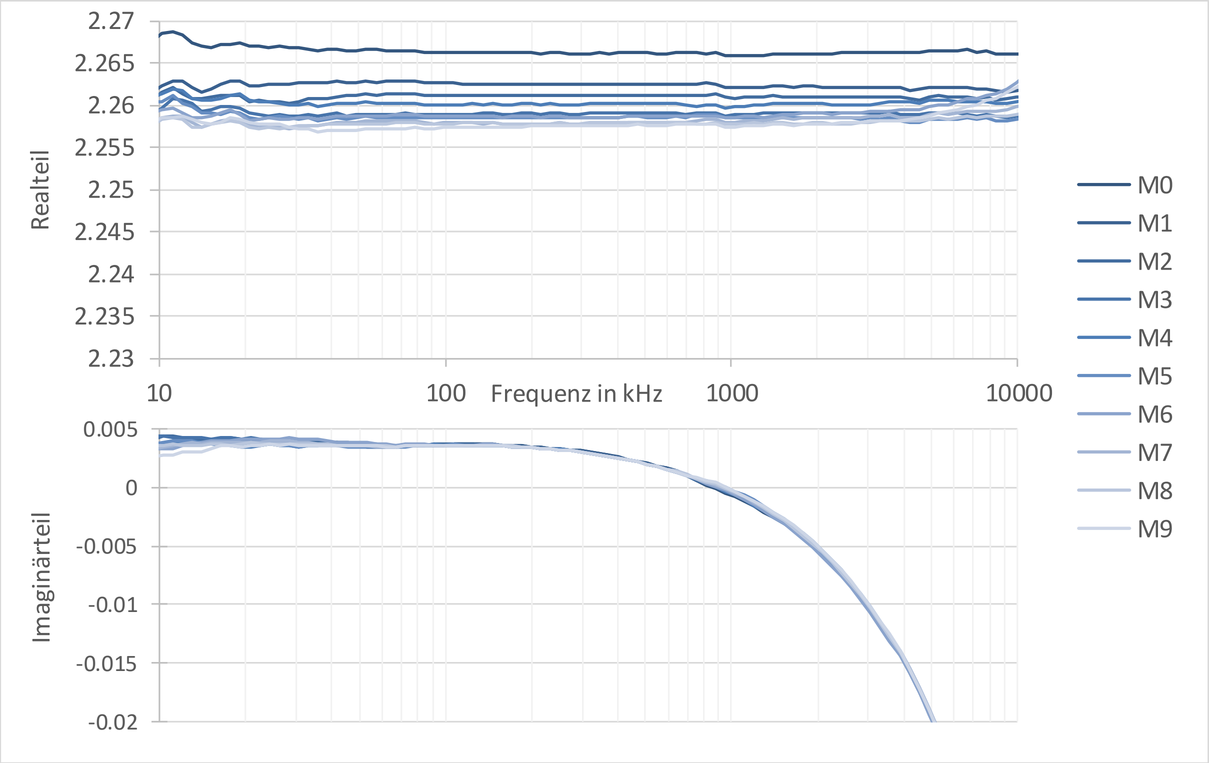

Figure 12: Permittivity of the sample "Diesel 1 + 10% RME + additive" over the storage period of nine months

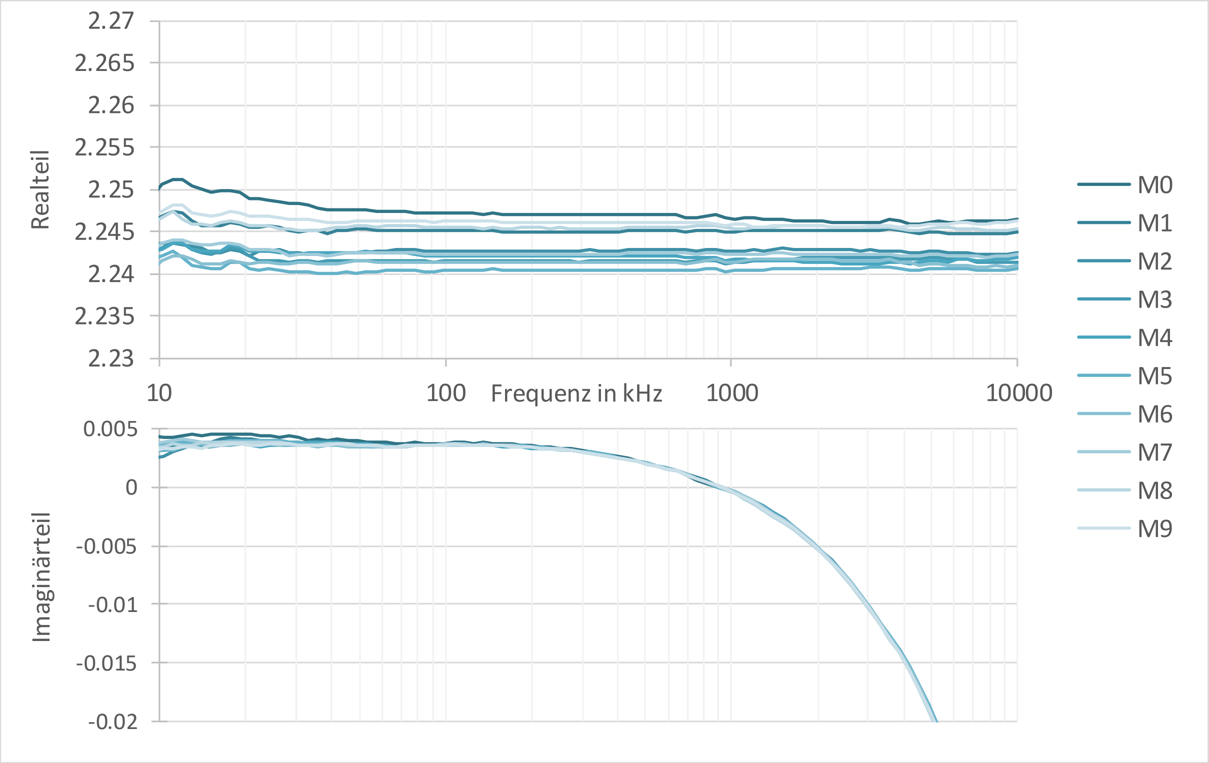

Figure 13: Permittivity of the sample "Diesel 2 + 10% RME/SME + additive" over the storage period of nine months

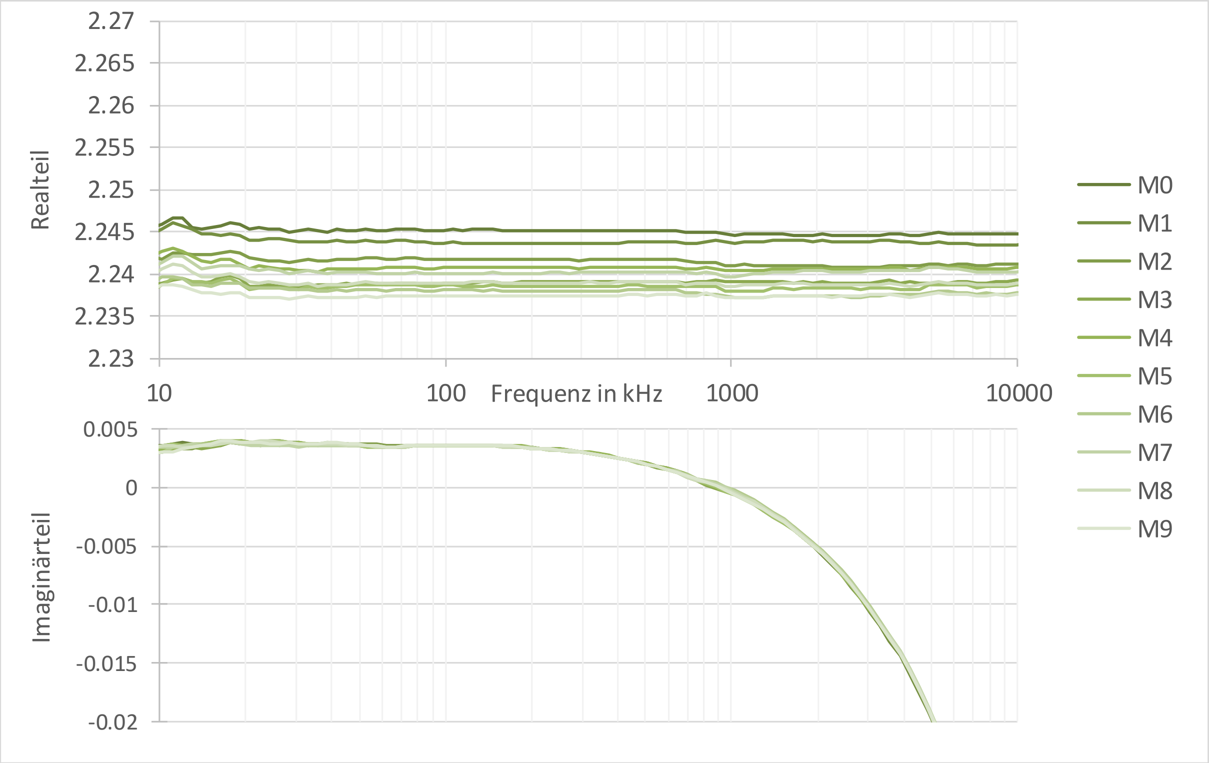

Figure 14: Permittivity of the sample "Diesel 2 + 10% RME + additive" over the storage period of nine months

The comparison of all four samples in Figure 15 over the storage period of nine months in one spectrum shows only a slight difference in the real part between the two diesel qualities. No changes in the imaginary part are detectable. To get a closer look at the differences of the real part, the real part was chosen at a frequency of 100 kHz and displayed in a bar chart in Figure 16.

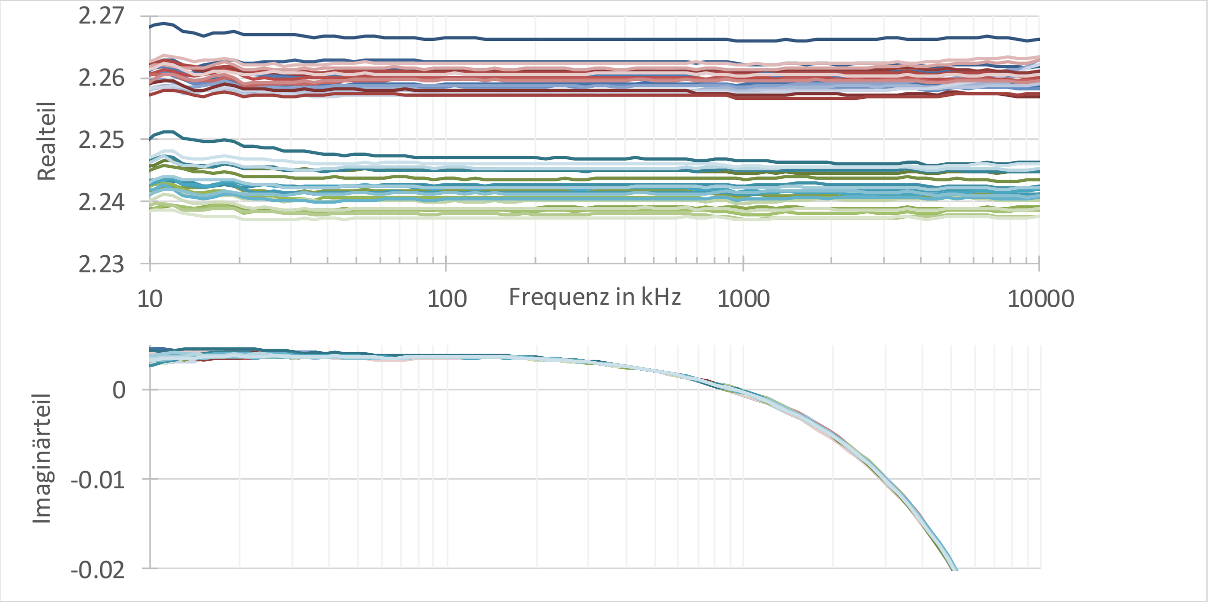

Figure 15: Comparison of the permittivity of all four samples after a storage period of nine months

From the bar chart in Figure 16, it is clear that there are no changes in the respective samples over the storage period of nine months. While diesel fuel 1 shows a permittivity between 2.256 and 2.266, the permittivity of diesel fuel 2 is between 2.237 and 2.247.

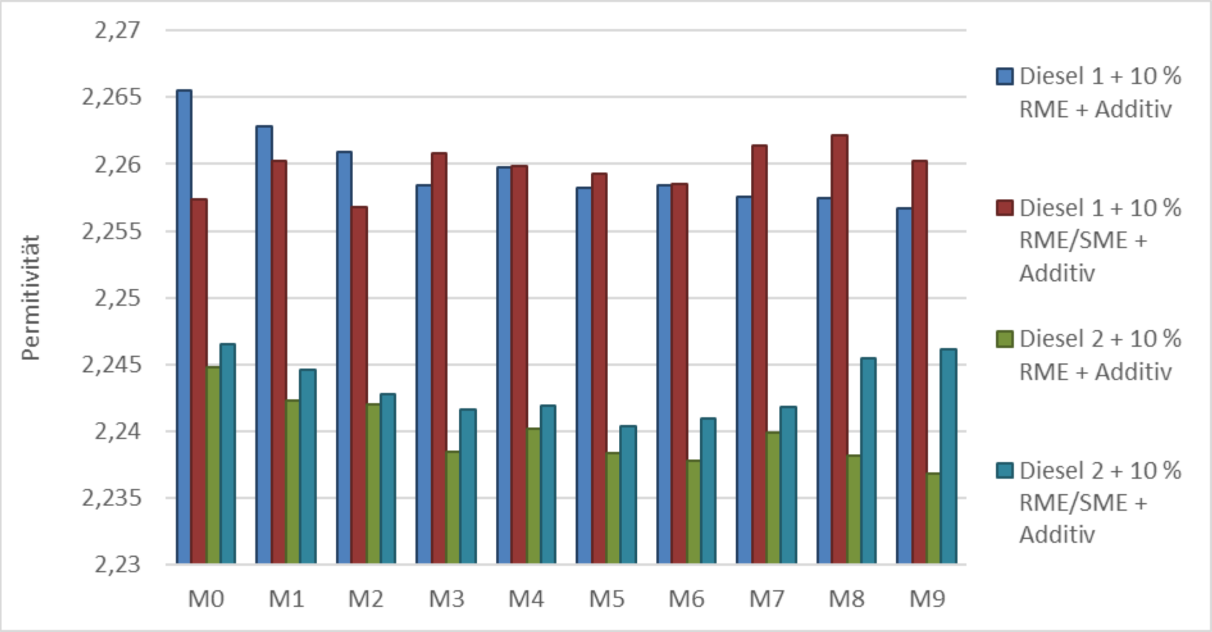

Figure 16: Real part of permittivity at 100 kHz and 25 °C

8. Summary

In addition to the FVV project "Fuels for PHEVs", four fuel blends with a biodiesel content of 10% (V/V) were investigated with regard to their storage stability over a period of 9 months. The investigations focused on the evaluation of an additive formulation that was added to fuel blends for stabilisation. The evaluation of additive effectiveness was based on regularly conducted fuel analysis. Common fuel analysis methods (oxidation stability, acid number, total pollution, etc.) were conducted, supplemented by innovative methods (fluorescence spectroscopy, permittivity spectroscopy).

In order to produce the fuel blends to be investigated, two basic diesel fuels without biodiesel content and two different biodiesel qualities were selected. These were a pure and non-additive RME with a storage time at the OWI of 6 months and an RME/SME blend (70/30) with unknown pre-additive and a storage time at the OWI of about 2 years. The four resulting fuel blends were stored at an elevated temperature of 50 °C for a period of 9 months to deliberately accelerate autoxidation. The ageing condition of the fuels was evaluated monthly by fuel analysis.

All four fuels exhibited typical ageing reactions that could be demonstrated using standard analytical methods. For example, the oxidation stability of all fuels decreases during storage. However, it is noticeable that the two blends with RME/SME addition have a significantly higher oxidation stability than the blends with pure RME. This is independent of the base diesel fuel and applies to both PetroOxy analysis and the Rancimat test. After a 9 month storage time, the oxidation stability, according to Rancimat, is 4 h in the lowest case (diesel 2 + RME) and approx. 20 h in the highest case (diesel 1 + RME/SME). The mixture of diesel 2 + RME is also conspicuous in the analysis of the total contamination and clearly exceeds the limit value according to EN 590 after the end of storage (approx. 60 mg/kg).

The fuel mixtures with pure RME showed no increase in fluorescence during the storage period. The increase in fluorescence in RME/SME blends can presumably be attributed to the consumption of natural antioxidants, whose degradation in this fuel mix can be easily tracked over time using this method. Permittivity measurements can be used to detect higher molecular weight oxidation products formed during the ageing process. The changes observed in the measured values over the course of the storage period are, however, not noticeable here; the changes are within the range of the systematic error of the instrument. The high analytical value of the total contamination of the fuel mixture diesel 2 + RME could not be confirmed by the permittivity measurements.

In summary, based on the available results, it can be said that the blending of RME and RME/SME with fossil diesel fuel in the order of 10% (v/v) is technically possible, and the fuel blend can be stabilised over a longer period of time with suitable additives. If necessary, the additives must be matched to the FAME used. Furthermore it should be noted that the ageing behaviour of fuel blends is based on interactions between the fossil matrix and the FAME, and is not solely due to the ageing properties of the FAME quality.

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