

# BMW project “Solare Kraftstoffe” – Technical Fuel Assessment

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## Summary

Sustainably produced drop-in fuels offer great potential for reducing greenhouse gases in the transport sector, and the possibility of using existing infrastructures facilitates a quick implementation into the transportation system. Hence, drop-in fuels are the only option that can address the existing vehicle fleet. Nevertheless, renewable fuels have to be economically competitive and comply with technical specifications.

An intriguing concept are solar-thermal produced renewable drop-in fuel components for gasoline engine with time horizon up to 2030. The techno-economic consideration and the studies of technical fuel assessment for selected solar fuels are activities embedded in the BMWi funded project “Solare Kraftstoffe”.

The goal is the identification of optimized, low-pollutant, synthetic fuel components as well as the evaluation of the engine performance including pollutant behavior. Therefore, chemical analytic experiments, engine tests and the development of a digital platform for the model-based assessment and optimization of fuels are carried out and presented here.

## 1. Introduction

Since the transport sector accounts for a large proportion of the global greenhouse gas emissions, it is important to implement new technologies with the potential to reduce greenhouse gas emissions. Besides of battery electric vehicles and vehicles powered by renewable hydrogen, sustainably produced synthetic fuels offer great potential for reducing greenhouse gases in the transportation system. The introduction of renewable synthetic fuels enables a quick reduction of emissions and offers striking benefits: use of existing vehicle fleet, reduction of emissions and compatibility with existing infrastructure. Other notable benefits are the high energy density as well as the fast refueling.

Synthetic fuels open up the chance to not only mimic existing fossil-based fuels, but make them even better in terms of performance. The optimization of the fuel's composition via fuel design allows the enhancement of the performance and the pollutant behavior can be reduced compared to non-synthetic fuels e.g. by reduction of heavy aromatic components (Wiese et al. [1]). For a successful implementation, renewable fuels have to be economically competitive and comply with technical specifications.

Within the project "Solare Kraftstoffe" funded by the Bundesministerium für Wirtschaft und Energie (BMWi), the entire process, starting from CO<sub>2</sub> and H<sub>2</sub>O as the feedstock and ending with the combustion in the engine, is investigated and schematically illustrated in Figure 1.

For the production of the synthesis gas, the use of concentrated solar power (CSP) in a two-stage thermochemical cycle is being investigated. This technology is

particularly attractive for regions with high solar irradiation. Monnerie et al. [2] studies the application of the thermochemical cycle for the production of methanol as an alternative fuel, also considering techno-economic aspects. The actual principle of operation of the two-stage thermochemical cycle for splitting CO<sub>2</sub> and water using metal oxides to produce syngas is discussed in detail by Lu et al [3]. For improved efficiency, Rosenstiel et al [4] describes CSP power plants with the possibility of thermal energy storage (TES) in combination with photovoltaics (PV). In the following we will focus on the downstream challenge, i.e. application and optimization of a gasoline product suitable to be produced in a solar process.

For the application in gasoline engines, fuels need to fulfil the current valid fuel standard, which is EN 228 [5] for Europe. This standard restricts certain fuel properties (e.g. density, boiling behavior) and fuel components especially the maximum concentration of oxygenated components (e.g. ethanol, ethers). Within the EN 228 standard, the admixture of renewable synthetic components is possible, as long as the final blend has standard-compliant properties. These fuel mixtures can be denoted as drop-in renewable fuels.

The fuel candidates selected in this study use different renewable blending components and compositions for exploring the EN 228 limits. All selected fuels (listed in Table 1) are liquid gasolines for spark-ignition engines which comply with the standard EN 228 with the exception of E30, containing 30 vol.% of ethanol, where the volumetric ethanol content was increased above the allowed 10% according to EN 228.

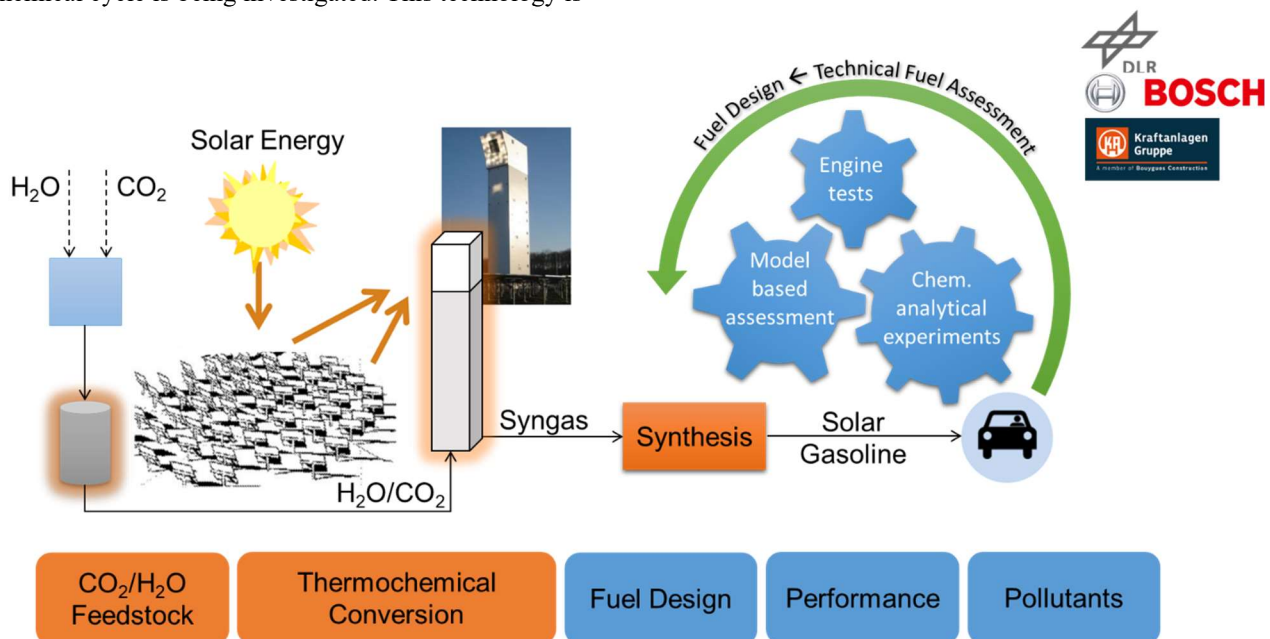


Figure 1: Illustration of the complete solar fuel process. The present work is focused on the marked downstream processes.

Table 1: Fuel list with blend shares, their abbreviation and their compatibility to EN 228 standard

Specification (EN 228 limit)	abbreviation	EN 228
Fuel blend with max. ETBE-concentration (22%v/v)	ETBEmax	✓
Fuel blend with max MTBE-concentration (20%v/v)	MTBEmax	✓
Fuel blend with max. isobutanol-concentration (14.5%v/v)	iBuOHmax	✓
Fuel blend with max. „Renewable“-concentration: FT_Surrogat (18%v/v) and ETBE (22%v/v), enriched additionally with iso-oktane (23%v/v)	ReMax	✓
Fuel blend with ETBE (22%v/v) and FT_Surrogat (20%v/v)	FT20-ETBE	✓
Fuel blend with MTBE (20%v/v) and FT_Surrogat (18%v/v)	FT18-MTBE	✓
Fuel blend with EtOH (30%v/v), exceed the standard	E30	✗

The focus of this work is the technical evaluation of the fuel list above. The work is experimental as numerical likewise. The physical-chemical properties of the liquid fuels are to be analyzed and fundamental combustion properties will be determined. Investigations of the combustion chemistry from a molecular point of view were performed in an atmospheric laminar flow reactor (ALFR) system, which allows tracing the formation and destruction of most of the important combustion intermediates in great detail. In addition, engine tests are carried out, where fuel effects were evaluated on combustion behavior, criteria pollutant emissions and calibration neutrality. In this paper an overview of the engine measurement procedure is given. Furthermore, an exemplary result of injector coking endurance run is presented and discussed.

A digital platform for the model-based assessment and optimization of fuels is also to be developed as part of this work. This platform includes the training and application of machine-learning models for the prediction of certain fuel properties. An important part of this project is also to gain an understanding of the relationship between the chemical composition and the resulting ignition delay time and the octane number. Therefore, a quasi-dimensional model approach was developed to predict the octane number through the simulation of ignition delay times by using chemical kinetic mechanisms.

## 2. Fuels

The study focuses on liquid drop-in fuels which are compliant to the current EN 228 standard and may be produced from a solar route. This approach ensures the usage of the fuels in new and stock vehicles as well as the fuel supply infrastructure, which can lead to prompt CO<sub>2</sub> reduction in the current vehicle fleet. The renewable components were chosen according to potential near time availability with the target by 2030. The

matrix of the chosen drop-in fuel candidates is listed in Table 1.

The fuels were designed in order to maximize the renewable content with renewable drop-in blend components. The fossil base fuel quality was adjusted for each fuel candidate in order to meet the EN 228 limits. For the gasoline blends ETBEmax and MTBEmax the maximum content of ethyl tert-butyl ether (ETBE), and methyl tert-butyl ether (MTBE), respectively, was achieved. For iBuOHmax the maximum possible Isobutanol content was chosen. FT18-MTBE and FT20-ETBE include maximum MTBE and ETBE amounts and furthermore a Fischer-Tropsch surrogate was added to maximum possible amount, which could be achieved within EN 228. ReMax contains 63% of possible renewable components which compose of isooctane, FT-surrogate and ETBE. In addition, a near drop-in fuel candidate E30 was chosen. This candidate does not meet the EN 228, but should be tested in order to see effects of a potential higher ethanol content on series calibrated engine combustion and emission behavior. The renewable test fuels were blended by the supplier Coryton and do not contain any additives. As reference fuel a EU5 certification fuel (Bosch EU5 Cert) was used. The fuel list and the blend shares can be found in Table 1 and the key properties of the fuels are listed in Table 2

## 3. Technical Fuel Assessment Approach

### 3.1. Assessment of the fuels using the SimFuel platform

The SimFuel platform connects distributed models and combines them with datasets and knowledge to gain additional insight. The two main application areas are the holistic assessment and optimization of fuels in an interdisciplinary and complex context. The platform also supports the development of models by providing massive data for the validation of models and the training of Machine Learning (ML) models [6]. .

Table 2: Relevant key fuel properties

Fuel	Bosch EU5 Cert	ETBE max	MTBE max	iBuOH max	ReMax	FT20- ETBE	FT18- MTBE	E30
RON [-] <sup>a</sup>	96.8	97.4	98.3	98.8	98	97.4	97.5	103.3
MON [-] <sup>a</sup>	87.0	86.0	87.5	87.1	88.9	86.8	86.1	88.6
Density @15°C [kg/m <sup>3</sup> ] <sup>a</sup>	748.2	754.9	755.8	757.1	730.7	765.2	764.7	741.5
Vol. lower heating value [MJ/l] <sup>a</sup>	31.43	30.97	31.1	31.01	30.62	31.37	31.27	28.41
DVPE @37.8 °C [kPa] <sup>a</sup>	58.8	58.8	58.5	58.1	57.6	55.3	59.0	101.9
E70 [%v/v] <sup>a</sup>	32.2	29.7	39.2	29.8	22.5	20.0	32.4	41.7
E150 [%v/v] <sup>a</sup>	82.7	79.9	82.3	78.2	88.4	81.9	82.3	92.8
FBP [°C] <sup>a</sup>	201.5	197.3	197.9	195.1	197.4	196.2	196.2	199.6
C9/C9+aromatic [%v/v] <sup>a</sup>	17.5	16.5	16.2	16.1	11.1	17.2	16.8	1.7
Ethanol [%v/v] <sup>a</sup>	4.8	0.4	0.1	0.1	0.3	0.4	0.1	29.2
Aromatic [%v/v] <sup>a</sup>	32.8	30.8	31.8	31.4	11.3	30.3	33.2	19.2
Olefins [%v/v] <sup>a</sup>	8.2	7.8	6.9	7.7	4.0	6.9	7.2	14.9
C [%-m/m] <sup>a</sup>	84.81	83.20	83.21	83.12	81.88	83.37	83.55	75.54
H [%-m/m] <sup>a</sup>	13.43	13.17	13.13	13.27	14.45	13.02	12.85	13.59
O [%-m/m] <sup>a</sup>	1.76	3.63	3.66	3.61	3.68	3.61	3.60	10.87

<sup>a</sup> Measurement resource: Coryton, England

The platform was originally developed for aviation fuels, but is currently extended to other sectors including road transport. It consists of four main components: databases, models, a distributed model environment and the human-in-the-loop concept.

The databases consist of composition, property and performance values of conventional fuels, synthetic fuels and blends as well as of over 5300 single compounds and their properties. A visualization of the pure compounds in the database is given in Figure 2, as scatter plot of quantitative structural components of the molecules, reduced to two dimensions with a dimension reduction algorithm. The datasets are systematically used to assess new fuels as well as to create new ML models or validate physical based models.

Those models are used to predict unknown properties or performance metrics of the fuels. Model types include correlations as well as physical based and ML based property and performance models. If the models have a quantified predictive capability [7] they can play an important role for the pre-screening of fuels [8].

The distributed model environment allows the connection of distributed models from partners to perform a completely digital multidisciplinary assessment and optimization across institutions, operating system and other boundaries. The Remote Component Environment (RCE) software [9] is used, which handles the secure

data transfer from and to the models including a rights management.

The human-in-the-loop concept finally captures the implicit knowledge of experts by providing interactive visualization of the relevant data and model predictions enriched with reference data as well as e.g. the appropriate specification limits. Hence, the human-in-the-loop concept integrates the platform into real world decision making.

## Results

Fuels for road transport significantly differ from aviation fuels, e.g. in terms of hydrocarbon families present in the composition, where oxygen containing compounds are not allowed in aviation. Hence, the models as well as the single compound database had to be extended to include those additional families and molecules. Also, the fuel database had to be extended to contain enough diesel and especially gasoline fuels not only for use as a reference (range of experience) when assessing new synthetic fuels, but also for training and validation of the property models.

First machine learning models for density and motor octane number (MON) were trained directly on the composition data as input and show good predictive capability with an accuracy of 0.1% for the density at 15°C and 0.5% for MON, respectively.

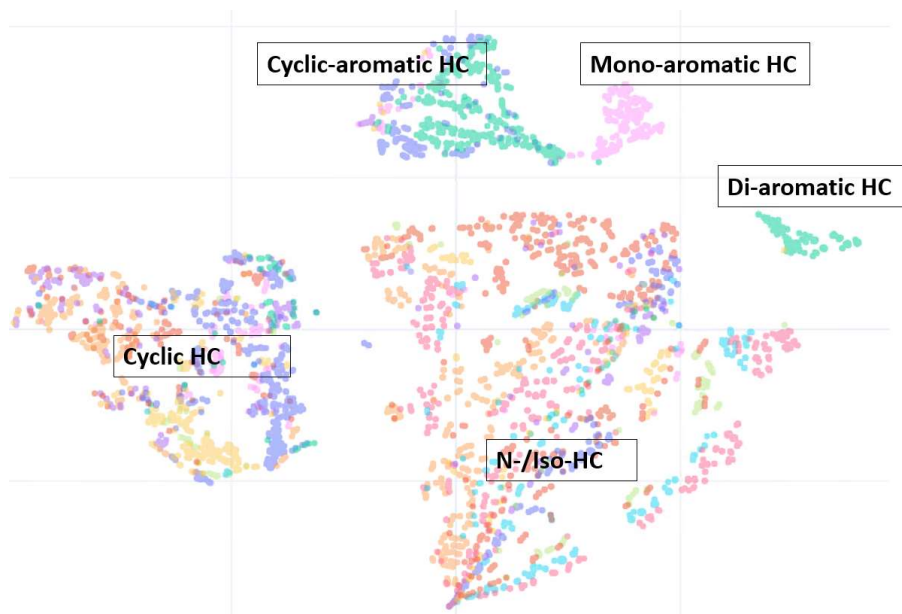


Figure 2: Visualization of single compound database (dimensionality reduction). Colors indicate the 60 different hydrocarbon families.

However, since the training data was limited to conventional crude oil based gasoline, the applicability to synthetic fuels is not directly given. Hence, new machine learning models are under development, which are not trained on the fuels composition, but on all single components from the single component database, which may sum up to a fuel.

When the composition of the synthetic fuels from Table 1 is available, the models will predict relevant properties. These properties will then be visualized together with measured data in the context of relevant specification limits and real fuel data of conventional fuels as an indicator for the range of experience to support the technical fuel assessment of the fuels.

### 3.2. 2-Zone-Cylinder-Model

Sustainably produced synthetic fuels offer a great possibility for decarbonizing the public transport. In addition, a further option for reducing CO<sub>2</sub> emissions through an increase of the compression ratio, which results in a better thermodynamic efficiency. However, the limiting factor hereby is the fuel itself, which tends to uncontrolled self-ignition, also called engine knock, since increasing the compression ratio leads to higher temperatures and pressures in the cylinder.

The resistance of the fuel against uncontrolled self-ignition is given by the octane number (ON), which can be basically derived through a comparison between the knocking behavior of the fuel and the knocking behavior of a primary reference fuel (PRF). A PRF is a blend of *iso*-octane and *n*-heptane, where its composition, the volume fraction of *iso*-octane, respectively, determines the octane number.

Experimental measurement of the ON. The experimental determination of the octane number is carried out in a

single cylinder Cooperative Fuel Research (CFR) engine. This purpose build engine features a variable compression ratio which allows to adjust the in-cylinder conditions to the point, where the fuel starts to self-ignite. If the fuel has the same knocking behavior as the PRF, the fuel's octane number corresponds to the composition of the PRF. The exact boundary conditions for the experiment are set in the ASTM D2699 [10] for the research octane number (RON) and in the ASTM D2700 [11] for the motor octane number (MON).

Motivation for modelling the ON. The fuel quantities required for the experimental tests make preliminary parameter studies very cost-intensive, which is why numerical methods are being developed. In literature there are various approaches specified. There are empirical models, like the one introduced by Morgan et al. [12], as well as machine learning models based on experimental data.

A different approach is to use chemical kinetic models to determine the octane number through the well-known correlation to ignition delay times. With this method, there are different options for the spatial resolution of the combustion chamber or the cylinder, respectively. The easiest modelling-approach is to assume the cylinder as a zero-dimensional reactor with fixed motor related boundary conditions [13]. This simple approach supports the applications of detailed chemical kinetic mechanisms and a correlation between the simulated ignition delay times and the octane number can be evolved. Studies carried out by Badra et al. [13] show promising results.

Nevertheless, the zero-dimensional approach comes with some simplifications. One quite significant drawback is the absence of the burned gas, which takes a

significant role during the compression of the unburned fuel-air mixture.

Computational fluid dynamics (CFD) simulations provide a very good spatial resolutions of the cylinder and offer separate consideration of different gas states. The better physical modeling leads to higher computational costs and make the application of detailed chemical mechanisms unfeasible.

To overcome this, within the project "Solare Kraftstoffe" a quasi-dimensional approach is chosen, in which the cylinder is divided into two different zones, a burned and an unburned one. This separate reflection of the burned and unburned gas enables the model to replicate the impact of the burned gas on the compression with a moderate increase in computational cost compared to the zero-dimensional approach.

### Modelling approach

The idea behind the 2-zone-cylinder model, is to reproduce the experimental procedure for deriving the octane number and provide engine related boundary conditions for chemical kinetic simulations. For the modelling of the combustion, the gasoline surrogate mechanism from the Lawrence Livermore National Laboratory [14] is used.

In the first step, the model searches in an iterative process for the compression ratio leading to self-ignition of the unburned fuel air mixture. Subsequently, the obtained critical compression ratio can be related to the octane number. Applying these two steps on a set of PRFs results in a clear correlation between the critical compression ratio and the octane number. During the simulation, an engine cycle is simulated from the time when the inlet valve closes on to the opening of the outlet valve.

Figure 3 visualize the structure of the model. The burned and the unburned zone in the cylinder are each represented by homogeneous zero-dimensional reactor. The

volumes are time depended functions and are defined by the CFR-engine's piston stroke under RON conditions. Both reactors are linked through a pressure conditions which ensures the same pressures in both zones.

The flame front is modeled through mass transfer from the unburned to the burned zone. The actual mass flow, the burning rate, respectively, is calculated via Vibe's Burning Law [15]. The heat flux into the reservoir with the burned gas, shown in Figure 3, equals the compression work of the piston into the system and is necessary to fulfill the energy conservation.

Lacking a real radial spatial resolution of the combustion chamber, no direct possibility is given to model a temperature profile with dropping temperatures near the wall. To overcome this issue, the adiabatic core hypothesis is applied and the wall heat losses are modeled through an isentropic expansion. This method is commonly used for the simulation of rapid compression machines [16].

### Validation and first results

With the implemented model, the critical compression ratio of fuels can be derived, provided that all included species occur in the chemical-kinetic mechanism and are validated.

Table 3 lists already simulated fuel blends with known octane numbers from the literature. The octane number of the PRFs can be determined from their composition. If the simulated critical compression ratios of the fuels are linked to their octane numbers, a clear correlation of both quantities becomes visible as illustrated Figure 4-left. The PRFs data set is used to derive a correlation visualized by the black line in Figure 4-left.

The derived correlation between the critical compression ratio of the PRF blends and the octane number can now be used to calculate octane numbers for the other datasets.

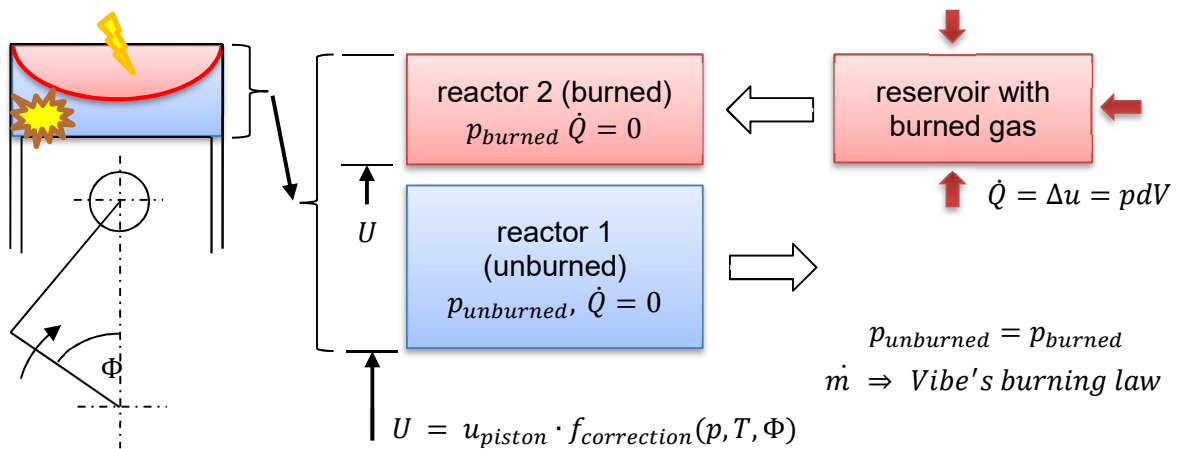


Figure 3: Schematic view of a cylinder during the compression cycle with spreading flame front and the 2-Zone-Cylinder-Model visualizing the two homogeneous reactors for the burned and the unburned zone plus the reservoir for the unburned gas.

Table 3: Collection of relevant fuel-blends with known octane number from literature.

Fuel	Composition	Source ON
PRF (primary reference fuel)	iso-octane, n-heptane	blending ratio
TRF (toluene reference fuel)	iso-octane, n-heptane and toluene	[12]
PRF + ethanol	PRF91 + ethanol	[17]
TRF91-15 + ethanol	TRF mit 15 vol.% toluene + ethanol	[17]
TRF91-30 + ethanol	TRF mit 30 vol.% toluene + ethanol	[17]
TRF91-45 + ethanol	TRF mit 45 vol.% toluene + ethanol	[17]

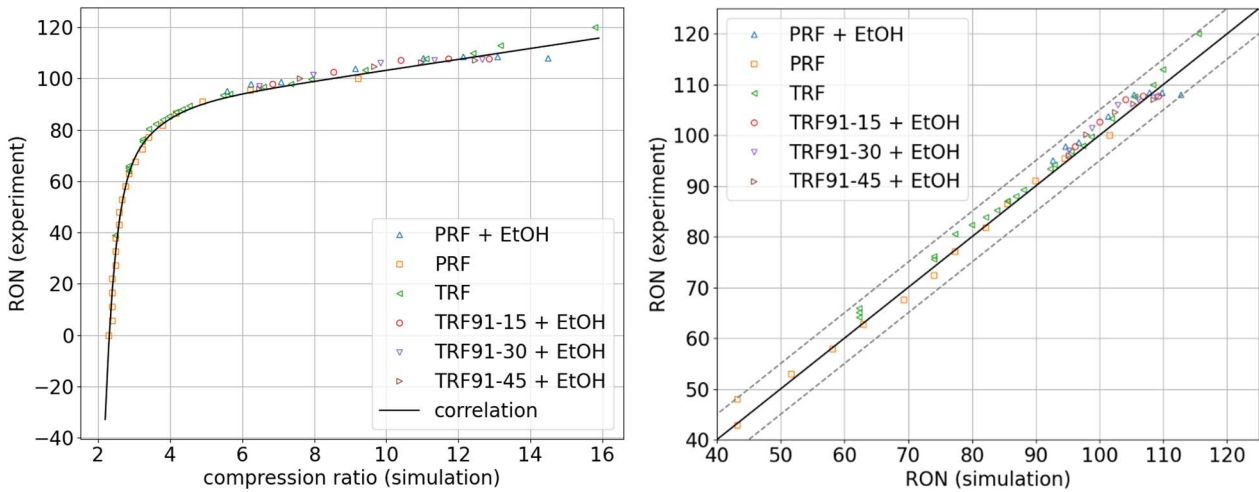


Figure 4: Modelling results of the 2-Zone-Cylinder-model. Left: comparison between the experimental derived octane number and the simulated critical compression ratio, the black line visualizes the derived correlation. Right: experimental derived octane number vs. the octane number calculated using the correlation.

Figure 4-right shows the comparison between the experimental derived octane numbers from the literature and the calculated ones. The results are found to deviate less than  $\pm 5$  octane numbers compared to the actual values. The current results confirm the promising approach for deriving the octane number. For the application of the method to all relevant fuels listed in Table 1 within the project "Solare Kraftstoffe", the chemical kinetic mechanism has to be extended to include the species ETBE, MTBE and isobutanol. Further, an optimization of the implementation of the combustion rate is considered. This will enable a better representation of the fuel-specific influence on the combustion process.

### 3.3. Flow reactor experiments

#### Approach

To study technical fuels' combustion chemistry reactor-experiments were performed at DLR's atmospheric high-temperature laminar flow reactor (ALFR) coupled with molecular-beam mass spectrometry (MBMS) detection. Instrumentation and design as well as experimental methodology are described in high detail in

Oßwald et al. [18]. Thus, the experimental approach is only briefly summarized below.

In DLR's ALFR fuel oxidation, from fuel consumption over intermediate species pool, to final combustion products can be examined in the homogeneous gas phase. The pre-evaporated and premixed fuel is fed to the reactor in high argon dilution ( $\text{Ar} > 99\%$ ) including oxygen as oxidizer. Examinations were performed from intermediate to high temperature regime (800-1200 K) for lean and slightly-rich equivalence ratios ( $\phi = 0.8$  and  $1.2$ ) and air-fuel ratios ( $\lambda = 1.25$  and  $0.83$ ), respectively. Depending on the temperature, residence times are about 2 s. Flow rates are controlled by precise Coriolis mass flow controllers (MFC). *In-situ* sampling is performed by means of a quartz nozzle/skimmer differential pumping system, where the gas probe is transferred to a molecular-beam and further reactions are prevented. Finally, soft electron ionization (EI; actual energy 11.5 eV) is applied and the individual combustion species are detected in a time-of-flight mass spectrometer (TOF-MS). Note that there is no isomer-specific differentiation here. Data evaluation and quantification is processed according to [18, 19].

## Results

Figure 5 shows a general mass spectrum for mass to charge ratios ( $m/z$ ) up to 200 u of the oxidation of the reference gasoline Bosch EU5 Cert under lean conditions ( $\lambda = 1.25$ ) for highly reactive temperature ( $T = 1057$  K). The temperature has been chosen in a way to ensure that most of the fuel molecules have already been consumed and a large number of important combustion intermediates have relatively high concentrations. Each mass peak corresponds to one or more partially oxygenated hydrocarbons. We observed intermediate species within a broad mass range from low molecular-weight aliphatic species up to high molecular-weight species such as polycyclic aromatic hydrocarbons (PAHs). Based on the high mass resolution ( $R = 3000$  [18]) separation of species with the same nominal mass is possible, which is shown in Figure 5-insert for  $m/z = 42$  u. Here, ketene ( $C_2H_2O$ ) is properly separated from propene ( $C_3H_6$ ).

Selected detailed speciation data of some major species, key intermediates, and aromatic soot precursors are presented and discussed below of fuel oxidation under lean conditions ( $\lambda = 1.25$ ).

**Major species.** Oxidative reactivity of the fuels can be examined by following the species profiles of major species shown in Figure 6 where the mole fractions of  $O_2$  and  $H_2O$  under lean air-fuel ratios ( $\lambda = 1.25$ ) are plotted as a function of the gas temperature. Overall, the comparison of the gasoline blends compliant with standard EN 228 shows very similar species profiles in quality and quantity and thus, similar combustion behavior within experimental uncertainty can be stated. Only the non-standard-compliant fuel candidate E30 shows a deviating behavior. With regard to the water profile (Figure 6-bottom),  $H_2O$  is already formed at lower temperature in higher amounts than for oxidation of the other blends. The higher reactivity of E30 can be attributed to a high volume fraction  $\phi_i$  of ethanol

( $\phi_{EtOH} = 30$  %-v/v) and the associated higher oxygen content  $w_O$  ( $w_O = 10.9$  %-m/m) [20]. Thus, most small carbonyl compounds are also formed earlier and a broader species profile emerges, as shown in Figure 7-top/left for formaldehyde ( $CH_2O$ ).

**Key intermediate.** We chose species with maximum mole fractions  $> 10$  ppm as key intermediates. This includes small paraffins like methane ( $CH_4$ ), and ethane ( $C_2H_6$ ), as well as small olefins like ethylene ( $C_2H_4$ ), propene ( $C_3H_6$ ), butadiene ( $C_4H_6$ ), and butene ( $C_4H_8$ ), and small alkynes such as propyne/allene ( $C_3H_4$ ), which are known to be part of the PAH building block. Furthermore, we observed oxygenated key intermediates like formaldehyde ( $CH_2O$ ) and ketene ( $C_2H_2O$ ). Exemplary we discuss formaldehyde as a representative for oxygenated key intermediates in the following.

In Figure 7-top the species profiles of formaldehyde and maximum mole fractions for fuel oxidation under lean conditions ( $\lambda = 1.25$ ) are presented and compared to the fuel's oxygen content. It is known that a higher oxygen content in the system favors the formation of oxygenated combustion intermediates [20, 21]. The reference gasoline Bosch EU5 Cert with the lowest oxygen content ( $w_O = 1.8$  %-m/m) exhibits one of the lowest  $CH_2O$ -concentrations and the gasoline blend E30 with the highest oxygen content ( $w_O = 10.9$  %-m/m) has one of the highest concentrations in  $CH_2O$ . Looking at the group of standard-compliant gasoline blends, with approximately the same oxygen content ( $w_O \approx 3.6$  %-m/m) it becomes clear, that not only the fuels' oxygen content can be decisive for the formaldehyde formation. For example, MTBEmax ( $w_O = 3.7$  %-m/m), in which the fuel oxygen is bound in methyl tert-butyl ether (MTBE;  $C_5H_{12}O$ ) yields a higher formaldehyde concentration than the ETBEmax ( $w_O = 3.6$  %-m/m), in which ethyl tert-butyl ether (ETBE;  $C_6H_{14}O$ ) is the oxygenated fuel additive.

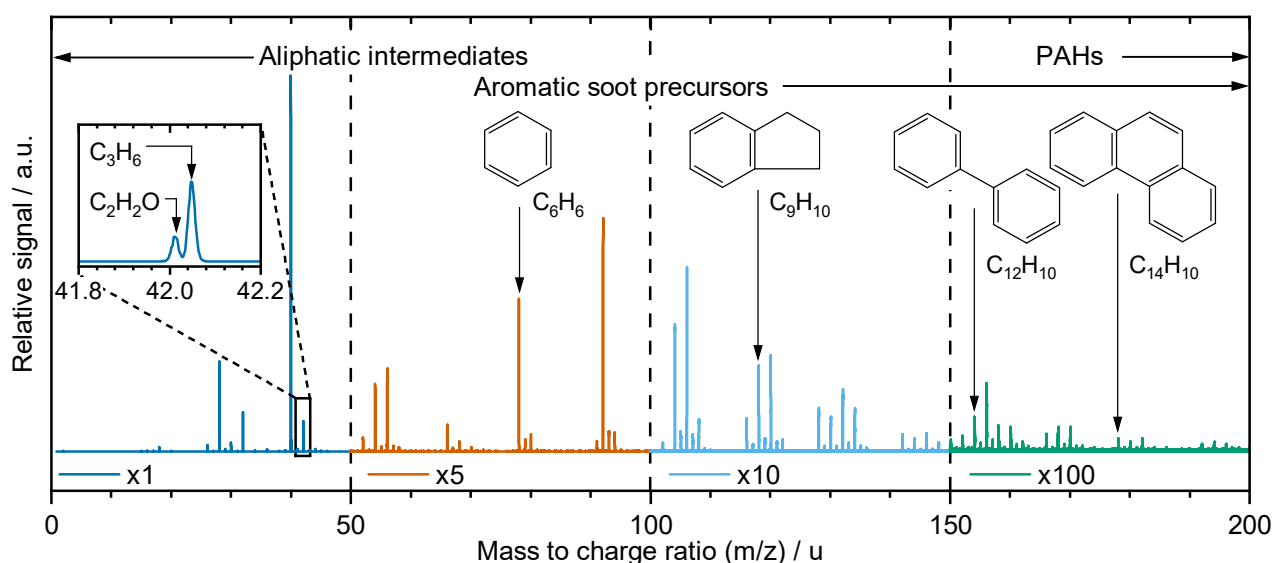


Figure 5: Mass spectrum of Bosch EU5 Cert oxidation under lean condition ( $\lambda = 1.25$ ) at highly reactive temperature ( $T = 1057$  K), selected aromatic soot precursors are marked. Insert: Separation on nominal mass  $m/z = 42$ .



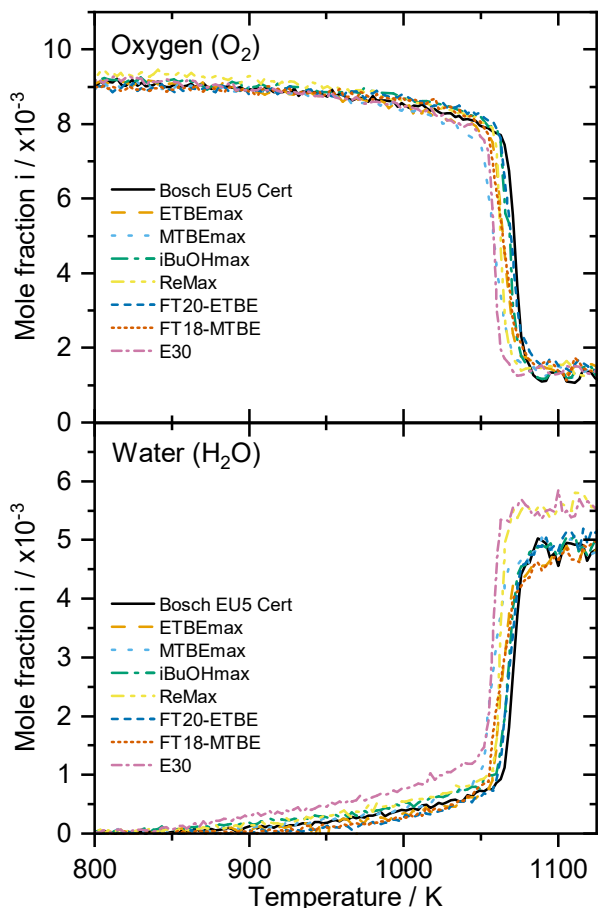


Figure 6: Mole fractions of selected major species ( $O_2$  and  $H_2O$ ) of fuel oxidation under lean condition ( $\lambda = 1.25$ ) plotted as function of the gas temperature.

The highest  $CH_2O$  amount within this fuel group is reached by the gasoline blend ReMax ( $w_O = 3.7\%$ -m/m), although also ETBE is the primary oxygen carrier as for the blend ETBEmax. This is where the different composition of each base gasoline used for fuel blending comes into play. In contrast to the other standard-compliant blends, ReMax has a relatively low aromatic volume fraction ( $\varphi_{Arom.} = 11.3\%$ -v/v) and also a decreased volumetric content of olefins ( $\varphi_{Olefin} = 4.0\%$ -v/v). Overall, the maximum  $CH_2O$  concentration increases as follows: Bosch EU5 Cert  $\approx$  FT20-ETBE  $<$  ETBEmax  $<$  iBuOHmax  $<$  FT18-MTBE  $<$  MTBEmax  $<$  ReMax  $\approx$  E30. It could be stated, that not only the fuels oxygen content but also the molecular structure of the oxygenated blending component and the fuel itself play an important role in formation processes of oxygenated combustion intermediates.

**Aromatic soot precursors.** Benzene is considered a flagship aromatic soot precursor. The formation reaction of the first aromatic ring structure is strongly dependent on the fuel-specific intermediate pool, which result from fuel degradation [22]. In addition to mono-aromatics, PAHs play a crucial precursor role in soot formation [23–25]. Generally, aromatics are used as octane boosters and are therefore present in high proportions in standard-compliant gasolines, with up to 35 %-v/v

permitted according to EN 228 [5]. Peak position of selected aromatic soot precursors and PAHs are marked in the mass spectrum of reference gasoline Bosch EU5 Cert oxidation in Figure 7, namely benzene ( $C_6H_6$ ), indane ( $C_9H_{10}$ ), biphenyl/acenaphthene ( $C_{12}H_{10}$ ), and phenanthrene/anthracene ( $C_{14}H_{10}$ ). These species occur almost exclusively as intermediates in the oxidation of the fuels under consideration and are therefore particularly suitable for investigating the combustion reaction process. This does not apply to toluene and naphthalene, for example, as these are already contained in high percentages in the fuels themselves. In the following we discuss the experimental data of benzene as typical representative of the aromatic soot precursors.

The benzene species profiles and maximum mole fractions for fuel oxidation under lean conditions ( $\lambda = 1.25$ ) are shown in Figure 7-bottom in comparison to the hydrogen content of the fuels. For non-oxygenated technical fuels, like kerosene or diesel, the benzene concentration formed during fuel oxidation correlates well with fuels hydrogen content  $w_H$  [26–28]. In H/C-fuel systems, a low hydrogen content promotes benzene formation. In addition, it is known that the aromatic content of the fuel has a major impact on the aromatic intermediate species pool, as fuel’s aromatics can skip decomposition and act directly as soot precursors [24, 25].

As expected, the standard-compliant gasoline blend ReMax with the highest hydrogen content ( $w_H = 14.4\%$ -m/m) and the lowest aromatics volume fraction ( $\varphi_{Arom.} = 11.3\%$ -v/v) shows the lowest benzene concentration within the fuel series studied. The second lowest  $C_6H_6$  maximum mole fraction is reached by the non-standard-compliant blend E30 with reduced volume fraction of aromatics ( $\varphi_{Arom.} = 19.2\%$ -v/v). The hydrogen content of E30 ( $w_H = 13.5\%$ -m/m), on the other hand, is nearly as high as that of the reference gasoline Bosch EU5 Cert ( $w_H = 13.4\%$ -m/m), which has one of the highest benzene concentrations. Consequently, the correlation between fuels hydrogen content and benzene formation seems to fail for C/H/O-fuel-systems. Moreover, it seems to be not sufficient to consider only the aromatic concentration in the fuel. Thus, the gasoline blend FT18-MTBE with the highest aromatics content ( $\varphi_{Arom.} = 33.2\%$ -v/v) and the lowest hydrogen content ( $w_H = 12.9\%$ -m/m) is only in the middle range of the high-aromatic fuel blends in terms of maximum mole fraction of benzene. Therefore, the fuels molecular structure also be considered for the soot precursor chemistry, including the oxygen in the fuel.

Overall, based on the flow reactor study, it can be assumed that the standard-compliant fuel candidate ReMax and the near drop-in gasoline blend E30 have a lower tendency to form soot in the engine operation, than the other investigated fuels. Note, that the observed benzene reduction for these fuels cannot be transferred directly into real engine emissions, thus other fuel properties like vaporization behavior matter too. However, a relative soot reduction should be visible.

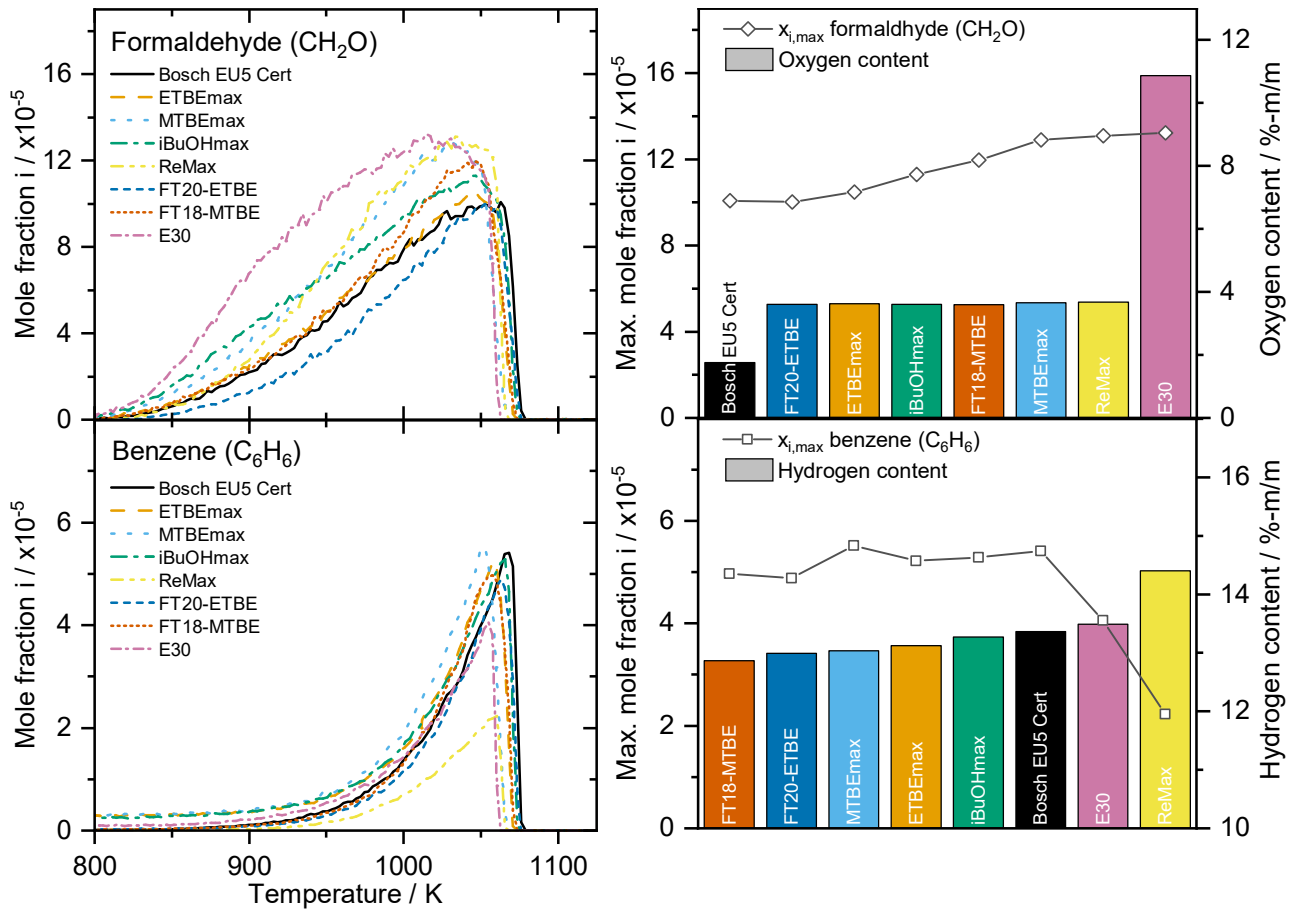


Figure 7: Left: Mole fractions of formaldehyde ( $\text{CH}_2\text{O}$ ) as representative for oxygenated key intermediates and benzene ( $\text{C}_6\text{H}_6$ ) as representative for aromatic soot precursors of fuel oxidation under lean condition ( $\lambda = 1.25$ ) plotted as function of the gas temperature. Right: Measured peak mole fraction of the respective combustion intermediate (lines, left axis) compared to the fuel's oxygen content or hydrogen content (bars, right axis).

### 3.4. Engine test

The renewable fuel candidates were evaluated using a production calibrated turbo charged gasoline direct injection engine with 4 cylinders (in-line), a displacement volume of 2 liters and a central mounted Bosch high-pressure-injector (Bosch Hochdruckeinspritzventil, HDEV 6). The system fuel pressure is 350 bar. Fuel effects were evaluated on calibration robustness, combustion characteristics and criteria pollutant emissions.

Engine test bench includes an engine dynamometer with external controllable coolant, fuel, air and intercooler temperatures. Engine oil temperature is not controlled. This temperature results from constant coolant temperature and specific load. In-cylinder pressures were measured by piezoelectric pressure transducers (Kistler 6041B). Gaseous and particulate emissions were measured using a Horiba Mexxa 7100 and a Horiba SPSC 2100 respectively.

### Measurement program

The Bosch renewable fuel evaluation program includes mixture formation measurements in a spray test chamber as well engine measurements. For the engine fuel investigation, a special test approach was developed containing engine map evaluation at cold and warm conditions, an injector coking drift run, fuel knocking behavior at full load conditions, transient operation as well as special engine operation modes e.g. catalyst heating and EGR variation. In order to evaluate the calibration neutrality of the fuel candidates, for all operating points mainly the series calibration data was used. However, in some program points, the calibration robustness was tested e.g. by SOI sweeps at different engine loads. Also, an engine oil dilution test is assessed at cold start conditions. In Table 4 the fuel evaluation program is listed including engine operating points and measurement conditions.

Table 4: Spray and engine evaluation program

Program	Details and Conditions
Spray measurements	Evaluation of mixture formation behavior @ spray chamber test bench under engine relevant conditions
Endurance run: PN drift of injector / engine	2000 rpm / medium load for 14h at 200 bar and 4h at 350 bar @warm engine
Engine out emissions, fuel consumption, combustion parameters	Engine map at 1000/2000/4000/6000 rpm, idle → full load @warm engine Engine map at 1000/2000/4000/6000 rpm, Idle → full load @cold engine
Calibration robustness	Start of injection (SOI) sweeps, 1500 rpm, low medium and full load @warm engine
Engine knocking	1500/2000/3000/4000/5000/6000 rpm, full load, ignition angle sweep @warm engine
Transient operation	Load step at 1500 rpm, low load → full load @cold engine
Catalyst heating	Catalyst heating operating point incl. ignition angle sweep @cold engine
Internal EGR variation	1500 rpm, low load, variation of exhaust valve timing @cold engine
Oil dilution	1500rpm medium load, medium engine coolant temperature

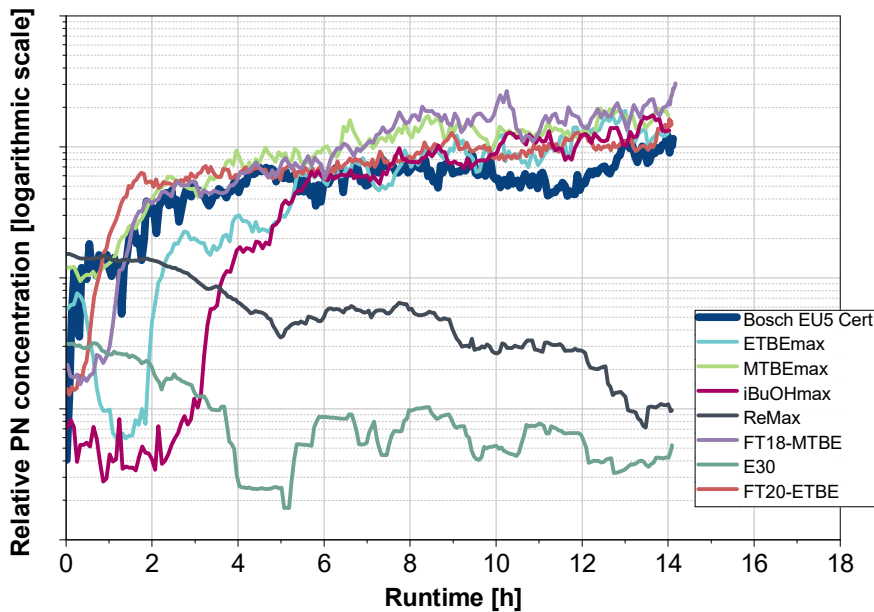


Figure 8: 14 hours PN endurance run results for 200 bar rail pressure and all tested renewable fuel candidates.

### Results engine measurement program

For this paper, only the results of the particle number (PN) drift run at 2000 rpm and warm engine are exemplary presented and discussed. The main operating parameters of the engine map are listed in Table 5. The aim of the drift endurance run is, to see if a fuel candidate tends to injector coking and subsequent temporal PN drift. In order to provoke this behavior, the system pressure is reduced from 350 bar to 200 bar. Before start of the drift run, the injector tips were cleaned. Thereafter, the engine was stationary operated at 2000 rpm and 10

bar Break mean effective pressure (BMEP) for 14 h. If a fuel tends to injector drift the PN concentration will increase and stabilize at high PN emission level during the drift run time. In Figure 8 the results of the 14 h drift run are shown for all tested fuel candidates.

It can be seen that all fuels except of ReMax and E30 show significant PN drift after minimum of 6 hours. At this point in time a similar high steady level of PN concentration is reached. After the drift run the injectors were removed and the injector tips were imaged. The results are shown in Figure 9.

Table 5: Endurance run operating conditions

Parameter	Unit	Value
Speed	rpm	2000
Load BMEP (Break mean effective pressure)	bar	10
Rail pressure	bar	200 / 350
Runtime	h	14 / 4
Temperature Coolant	°C	90
Temperature engine oil	°C	95
SOI	°CA	Fuel specific optimization for low PN emission: Bosch EU5 Cert: 320 / 320 ETBEmax: 320 / 310 MTBEmax: 320 / 310 iBuOHmax: 300 / 310 ReMax: 310 / 300 FT20-ETBE: 300 / 300 FT18-MTBE: 320 / 310 E30: 300 / 290
Ignition angle	°CA	Optimized for MFB50 (50% mass fraction burned) at 8°CA

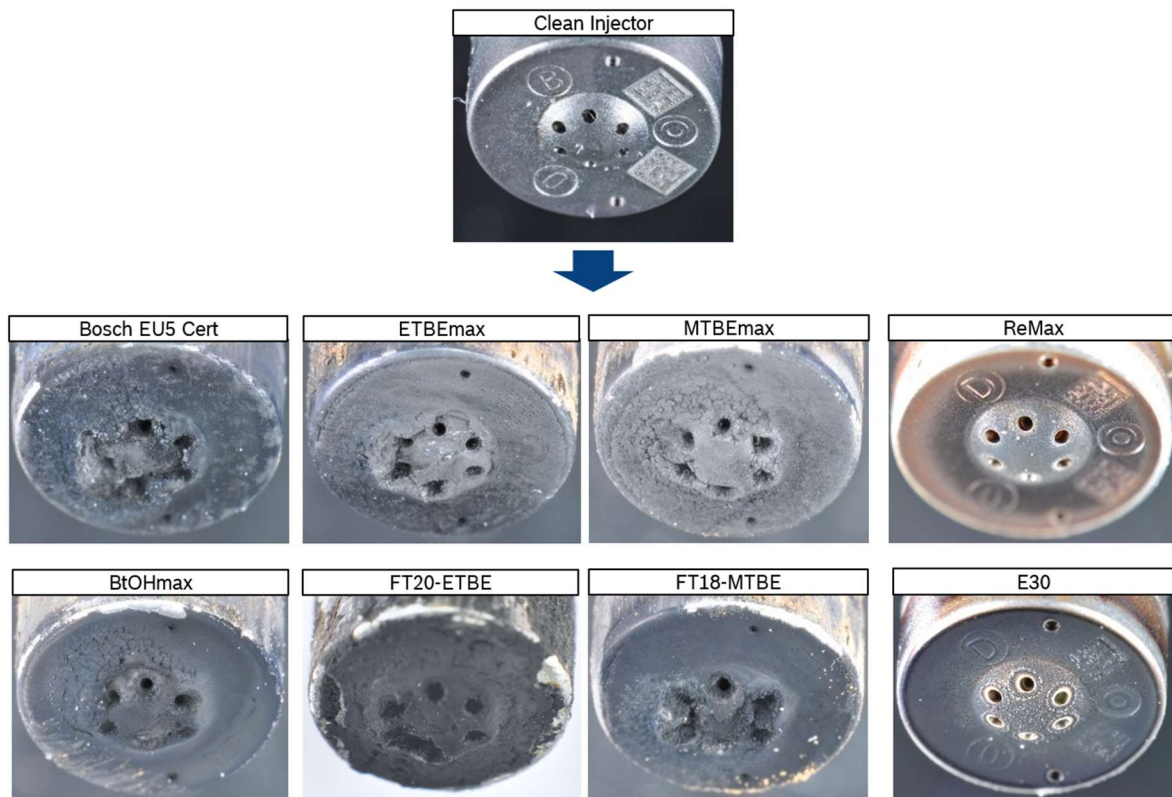


Figure 9: Images of injector tip after 14 h endurance run for all tested fuels including an example image of a clean injector tip at the top row before the endurance run.

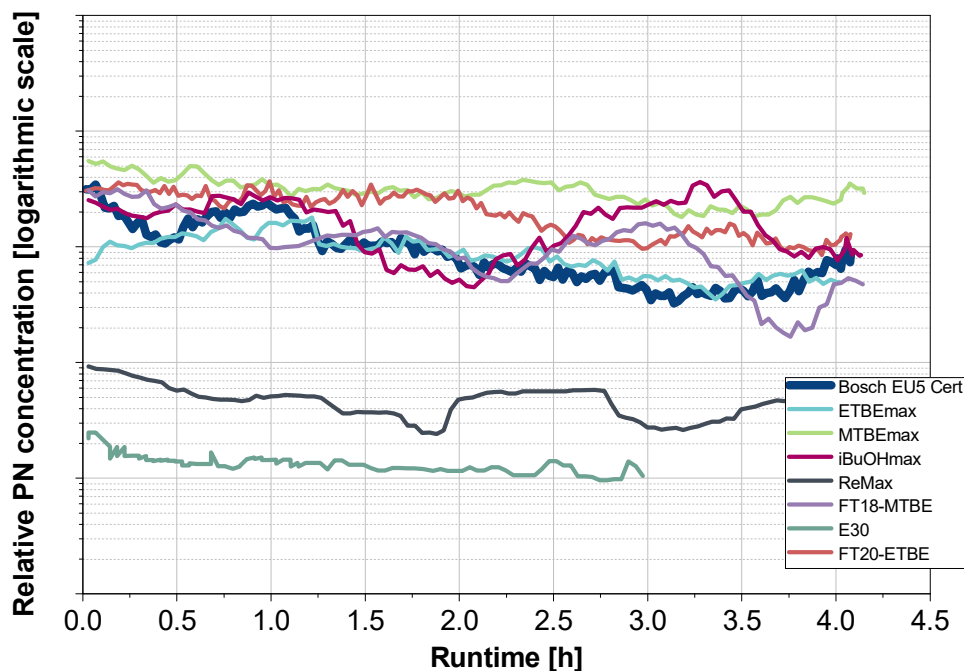


Figure 10: 2 hours PN stabilization run results for 350 bar rail pressure and all tested renewable fuel candidates

The reason for this fuel drift behavior may be ascribed to the volumetric concentration of heavy aromatics with carbon chain lengths equal and greater than 9 atoms (C9/C9+ aromatics). E30 and ReMax exhibit lowest C9/C9+ aromatic content in comparison to the other fuel candidates. The mechanisms and the effect of gasoline fuel properties on emission behavior for the injector drift run were investigated in Wiese et al. [1] and Fatouraie et al. [29].

All fuel candidates except of ReMax and E30 show significant injector deposits at the injector tip (see Figure 9). ReMax and E30 are free of deposits. The images prove the emission test results of the PN concentration drift in Figure 8.

After the 14 hours drift run the injectors were rebuilt and a stabilization run for 2 hours at system pressure (350 bar) followed. The purpose of this measurement was to see how the fuels behave at series calibration and if the fuels may show a cleaning behavior by decreasing PN concentration.

For the coked and drifted injectors, a slight decrease in PN concentration can be measured. After 1 h the PN emission level slightly decreases. The injectors which did not show coking (E30 and ReMax) have a lower stable PN concentration level.

It can be concluded that, although the fuel candidates ETBEmax, MTBEmax, IBuOHmax, FT18-MTBE and FT20-ETBE show significant injector drift, the PN emission behavior is in the same order of magnitude as for the reference fuel Bosch EU5 Cert, which can be seen as a bad case market fuel. Moreover, the content of heavy aromatics of the fuel is connected to the fossil base fuel and not to the renewable fuel component. So,

the behavior of PN drift is not directly influenced by the renewable blend component. As seen in the homogeneous gas phase experiments (Chapter 3.3) the ReMax fuel exhibits the lowest amount of soot precursor intermediates. For ReMax with high renewable share (e.g. iso-octane, ETBE and FT surrogate) the fossil fuel components are diluted enough to reduce C9/C9+ aromatics. A similar reason could be quoted for E30 where Ethanol states the dilution blend component.

Moreover, from the study of Wiese et al. [1], it is known, that by additives of detergents, the PN drift of the fuel can be reduced. This could be a possible measure for such fuel candidates, which show high coking tendency.

#### 4. Conclusions

This paper provides an overview of the status of the work being done as part of the BMWi-funded project “Solare Kraftstoffe” to evaluate synthetic fuels that can be produced sustainably via a solar powered, thermal conversion route. All the fuels considered, with the exception of the E30 blend, are compatible with the EN 228 standard and can be quickly established on the market with the existing fleet of vehicles.

In order to evaluate the synthetic fuels and to identify particularly suitable fuel components for improving the fuel properties in terms of combustion and emission behavior, model-based methods were used as well as analytical tests and experiments on the engine were carried out.

DLR’s SimFuel platform, originally developed for aviation fuels, was extended to the application of transportation fuels. Based on the detailed fuel’s composition further properties of the fuel could be predicted. New

machine learning models are currently being developed, which are trained on single components and fuels. These models then can also predict unknown complex fuels (e.g. renewable gasoline), for which not yet enough training data exists.

Provided that the detailed composition of the fuel candidates in “Solare Kraftstoffe” is available, as it can be analysed e.g. by two-dimensional gas chromatography (GCxGC), properties of these real fuels can be predicted and then visualized and assessed in context to the range of experience using the SimFuel platform.

To evaluate the octane number of the fuels as well as to identify especially suitable fuel compositions the 2-Zone-Cylinder-Model was developed. The model provides engine related boundary conditions combined with reaction models for the numerical estimation of octane numbers. First numerical predictions of the research octane numbers by the model are in good agreement with experimental data. In the next step, the chemical kinetic mechanism has to be extended and validated, in order to be able to simulate all fuel components, which are important within the project.

The analytical research in the flow reactor shows that the standard-compliant fuel candidate ReMax and the close drop-in gasoline blend E30 have a lower tendency to form soot during engine operation than the other fuels.

It must be noted, however, that the observed benzene reduction for these fuels cannot be directly extrapolated to real engine emissions, as other physical fuel properties such as evaporation behavior also influence emissions.

Despite the highly idealized boundary conditions of the analytical study, they confirm the particle number tests carried out on a turbo charged gasoline direct injection engine. The evaluations of the PN concentration in an endurance run where injector drift was provoked at medium load condition show that both the E30 and the ReMax exhibit significantly reduced particulate number emissions and no injector coking in comparison to the other fuel candidates. Both results can mainly be attributed to the reduced amount of heavy aromatic components in the fossil base fuel because of the high share of renewable components with low sooting tendency.

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