

# Assessment of the Full Thermodynamic Potential of C8-Oxygenates for Clean Diesel Combustion

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## ABSTRACT

Within the Cluster of Excellence “Tailor-Made Fuels from Biomass” (TMFB) at the RWTH Aachen University, two novel biogenic fuels, namely 1-octanol and its isomer dibutyl ether (DBE), were identified and extensively analyzed in respect of their suitability for combustion in a Diesel engine. Both biofuels feature very different properties, especially regarding their ignitability.

In previous works of the research cluster, promising synthesis routes with excellent yields for both fuels were found, using lignocellulosic biomass as source material. Both fuels were investigated as pure components in optical and thermodynamic single cylinder engines (SCE). For 1-octanol at lower part load, almost no soot emission could be measured, while with DBE the soot emissions were only about a quarter of that with conventional Diesel fuel. At high part load (2400 min<sup>-1</sup>, 14.8 bar IMEP), the soot reduction of 1-octanol was more than 50% and for DBE more than 80 % respectively.

Based on these promising initial results, this paper will report about additional experimental investigations that were initiated to exploit the complete potential of both advanced biofuels in terms of emissions and efficiency. A single cylinder research engine was utilized and the engine calibration was optimized using design of experiments at lower and higher part load. At high part load, it was possible to increase the efficiency by more than one percent point compared to the Diesel reference in the same load point. Furthermore, the already low soot emissions of both biofuels, compared to Diesel fuel, could also be further halved compared to the base calibration. In a last step, a sensitivity analysis was performed in order to validate the previously built models and to get further insight into the influence of the single calibration parameters on engine performance.

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## INTRODUCTION

Currently the transport sector is dominated by internal combustion engines which run on fossil fuels. However, due to climate change and increasingly stringent emissions legislation alternative solutions have to be found. Electro-mobility and fuel cells might be a long term solution for this dilemma, but in order to achieve a sustainable transition until these technologies have matured, biofuels possess a huge potential. Besides the CO<sub>2</sub> benefits of biofuels it was found that especially oxygenated fuels have big advantages in terms of engine- and emissions performance. These benefits can even further be increased by tailoring the fuel for the needs of the combustion engine. Therefore the Cluster “Tailor-Made Fuels from Biomass” was established in 2007 at the RWTH Aachen University as part of the Excellence Initiative to promote fundamental research at German universities. It is the long term goal of the cluster to establish a model

based design process to identify and assess possible future fuel candidates, derived from lignocellulosic feedstock materials [1, 2, 3, 4, 5]. For that purpose, not only the combustion of the fuels is included in the research work, but also the energy efficient and sustainable production of these possible fuels is being addressed, using process reaction network flux analysis [6]. Over the course of the last decade, many fuel candidates, e.g. 2-methylfuran, 2-butanone and many different alcohols were identified for the spark ignition engine [7, 8]. For the compression ignition engine, 2-methyltetrahydrofuran, 1-decanol, 1-octanol and dibutyl ether (DBE) were extensively investigated [9, 10].

The presented paper will focus on the combustion and optimization of the TMFB fuels 1-octanol and DBE for the compression ignition engine. These two fuels have ther

2013 and very promising features were observed. In first studies, Heuser et al. [11], compared 1-octanol and 1-decanol to fossil Diesel fuel and found greatly reduced soot emissions for both alcohols, with 1-octanol showing the biggest soot reduction potential. Fundamental reasons for this effect are the shorter carbon chain length of 1-octanol, the absence of aromatics, higher oxygen content and the lower reactivity, which leads to an improved mixture homogenization. In subsequent investigations by Heuser et al. [12], 1-octanol and DBE were compared to Diesel fuel in a single-cylinder engine, a high pressure chamber and by means of computational fluid dynamics (CFD). Here, it was found that surprisingly both fuels showed a similar soot reduction potential, despite the higher reactivity of DBE. The investigations in the high pressure chamber and the results of the CFD simulation determined that two completely different mechanisms are causing the soot reduction. While, on the one hand, the oxygen content in both fuels results in lower soot emissions, the low reactivity of 1-octanol gives sufficient time for mixture formation and therefore a good homogenization. For DBE on the other hand, its high volatility is favorable for the mixture formation, despite the short ignition delay, and the shorter carbon chain length is less prone to form soot precursors. Nonetheless, the low cetane number of 1-octanol leads to higher HC and CO emissions under low load and cold start conditions. It also causes a higher combustion noise excitation. Therefore, an increased compression ratio was investigated for 1-octanol [13]. With the higher compression ratio, it was possible to limit the HC and CO emissions and to raise the indicated efficiency. Furthermore, the combustion noise excitation of 1-octanol could be reduced with the higher compression ratio for the higher part load points. Additionally, the particle size distribution was investigated using the engine exhaust particle sizer from TSI. Here, it was found that the particle number of 1-octanol and DBE combustion was greatly reduced compared to Diesel fuel. However, the soot emissions of 1-octanol in combination with the higher compression ratio increased, compared to the lower compression ratio. Additionally, the composition of the HC emissions of 1-octanol and DBE were analyzed by gas chromatography and mass spectroscopy. A more in depth analysis of the soot emissions has been published by Heuser et al. [14] and Mühlbauer et al. [15]. In order to get further insight into the mixture- and emission formation phenomena under engine relevant conditions, investigations with an optical single cylinder engine, which features the same geometry as the thermodynamic engine, were conducted by Hülser et al. [16]. Additional optical investigations for DBE were conducted by Mühlbauer et al. [15]. The authors observed that for 1-octanol a near stoichiometric mixture is present close to the periphery of the piston bowl at low loads. This can be attributed to the low reactivity of 1-octanol, which results in fuel droplet impingement on the piston wall and increased HC and CO emissions of 1-octanol compared to DBE at low loads. For DBE with its high volatility and therefore short liquid penetration length, this behavior was not observed. In the recent past, both biofuels were blended with conventional Diesel fuel in order to assess their potential for more application focused purposes [17]. During these investigations, a strongly non-linear behavior between the amount of biofuel within the mixture and the emission reduction potential was found. In the case of 1-octanol, already 20 % v/v in Diesel fuel lead to a reduction of the specific soot mass by more than 60 % at higher part load compared to pure Diesel fuel. For DBE, the addition to Diesel fuel resulted in an increase in

soot emissions at low loads due to the increased cetane number of the blend. At higher loads however, the lower aromatic content of the blend and higher oxygen content lead to reduced soot emissions, compared to neat Diesel fuel. Furthermore, the cetane number impact at higher loads diminishes. Besides blends with Diesel fuel, 1-octanol was also blended with hydrogenated vegetable oil (HVO) [18], in order to assess the potential of aromatic free blends and to increase the cetane number of the 1-octanol blend. Here it was found that the beneficial properties of HVO and 1-octanol could be combined and the result was a fuel which features very low HC, CO and soot emissions as well as low combustion noise emissions. 1-Octanol blends of up to 30 % in Diesel were also investigated by Zhang et al. [20] and Kumar et al. [22] and similar trends in soot reduction were observed. Additionally, Kumar et al. [23] compared a 30 % 1-octanol / Diesel blend to iso-butanol, n-pentanol, and n-hexanol blends and found that the 1-octanol blend has the lowest soot reduction potential. The reason for this behavior is however that the 1-octanol blend is showing the highest cetane number of the blends and the lowest oxygen content. To take steps even further towards practical application, 1-octanol / Diesel fuel blends were also investigated in a series production vehicle. Three New European Driving Cycle (NEDC) tests were conducted on a chassis dynamometer [19]. Here, the same trends, as previously determined during the single cylinder engine testing, were observed with a reduction of engine out soot mass per kilometer by more than 85 %, compared to Diesel fuel and a reduction of the tail-pipe particle number by more than 90 %.

Nevertheless, all the previous investigations were carried out using a fixed engine calibration, which was optimized for Diesel fuel, considering limits for soot emissions, pressure gradients, exhaust gas temperatures and peak pressures. Although, efficiency increases were observed in the previous studies, which were mainly due to shorter burn durations, lower exhaust gas temperatures and lower emissions, the full potential of the new biofuels was not fully exploited so far. Therefore, further investigations were initiated to optimize the engine calibration for 1-octanol and DBE, using Design of Experiments (DoE) in order to maximize engine efficiency.

Hereinafter, the properties of the investigated fuels and the SCE setup are presented and the DoE methodology is explained in the research approach section. Afterwards the results from the single cylinder engine tests of both biofuels with and without the optimized engine calibration are shown and compared to a Diesel fuel reference. Finally, a sensitivity analysis is presented in order to assess the effect of the single calibration parameters on engine performance.

## RESEARCH APPROACH

### Investigated Fuels

The isomers 1-octanol and DBE can both be produced from lignocellulosic biomass and feature the same sum formula ( $C_8H_{18}O$ ). While 1-octanol is a straight chain C8 alcohol, DBE is an ether with two C4 chains linked together by an oxygen molecule. Within the TMFB, a promising production route for 1-octanol was developed starting from the lignocellulose-based platform chemicals furfural and acetone. Through an aldol condensation, furfural and acetone are converted into furfuralacetone, which subsequent hydrogenation

forms 4-(2-tetrahydrofuryl)-2-butanol (THFA) [21]. Key to the process has been the design of bi-functional catalyst systems that can selectively transform THFA into C8-oxygenates including butyltetrahydrofuran, 1-octanol and dioctylether with excellent yields [24, 25]. DBE can easily be obtained via etherification of n-butanol, which can then again be produced from lignocellulosic biomass by e.g. fermentation.

**Table 1. Properties of the investigated fuels. The derived cetane number (DCN) was measured using the Advanced Fuel Ignition Delay Analyzer (AFIDA [26]) [27, 28, 29, 30]**

|                             | Unit  | EN590 Diesel | 1-Octanol  | DBE       |
|-----------------------------|-------|--------------|------------|-----------|
| Boiling range               | °C    | 180-350      | 195        | 141       |
| Cetane number               | -     | 56.5         | 33.8 (DCN) | 115 (DCN) |
| Density (15°C)              | kg/m³ | 832.9        | 837        | 770       |
| Vapor pressure              | mbar  | <1           | 0.125      | 6.4       |
| Surface tension             | mN/m  | 20.5         | 27.5       | 22.2      |
| Oxygen content              | % w/w | 0.14         | 12.3       | 12.3      |
| Enthalpy of vaporization    | kJ/kg | 358          | 562        | 346       |
| Kinematic viscosity (40 °C) | mm²/s | 3            | 5.4        | 0.68      |
| Lower heating value         | MJ/kg | 43           | 37.6       | 38.0      |
| Flash point                 | °C    | 89           | 81         | 25        |

Due to their different functional groups, very different combustion relevant physical properties arise which are summarized in [Table 1](#). For example, the reactivity of 1-octanol is relatively low with a derived cetane number (DCN) of 33.8, while the reactivity of DBE is very high with a DCN of 115. This is on the one hand due to the chemical properties and on the other hand due to the physical ones. A comparison of kinetic modeling studies of shock tube simulations for 1-octanol [31] and DBE [32] suggests that the chemical ignition delay times for both fuels are relatively similar for the high temperature regime well above 1500 K. Although one has to note that the simulations for DBE have not been validated for the high temperature regime yet. Moving towards lower temperatures and therefore engine relevant regimes, the ignition delay times begin to diverge but due to the stronger negative temperature coefficient (NTC) of 1-octanol, the ignition delay times of both fuels are in the same order of magnitude around 800 K, which is roughly the in-cylinder temperature during injection. Therefore, the physical properties of the fuels are playing a major role in the combustion behavior as well. The low viscosity and high vapor pressure of DBE indicates a fast mixture formation and hence a short physical ignition delay. Due to the high viscosity and surface tension, a worse mixture formation of 1-octanol can be expected, increasing the already longer chemical ignition delay even further. This was confirmed during the investigations in the high pressure chamber, where DBE was showing much shorter liquid penetration lengths compared to Diesel fuel and 1-octanol was showing a longer liquid penetration length in comparison to Diesel fuel [12].

## Experimental Setup

All the investigations shown in this paper were conducted on a SCE and its key specifications are given in [Table 2](#). The combustion chamber as well as intake and exhaust ports were derived from the PSA DV6 engine and the displacement of the SCE is 0.39 liter. The piston bowl is having a conventional  $\omega$ -shape which was optimized together with the injector spray target to achieve low engine out soot and  $\text{NO}_x$  emissions. This, in combination with high amounts of cooled high-pressure exhaust gas recirculation (EGR) results in EU6 compliant engine-out emissions without  $\text{NO}_x$ -aftertreatment. The engine is capable of peak firing pressures up to 220 bar and it features a state of the art common rail fuel injection system with a piezo injector, capable of injection pressures up to 2200 bar. A turbocharger is simulated by an external, electrically driven boosting device and a backpressure valve in the exhaust. With this system boost pressures up to 3.6 bar are possible and the charge air temperature can be controlled by a series of intercoolers.

**Table 2. Specifications of the used single cylinder research engine**

| Parameters                 | Units   | Specifications |
|----------------------------|---------|----------------|
| Displacement               | cm³     | 390            |
| Stroke                     | mm      | 88.3           |
| Bore diameter              | mm      | 75             |
| Compression ratio          | -       | 15             |
| Valves per cylinder        | -       | 4              |
| Maximum peak pressure      | bar     | 220            |
| Maximum injection pressure | bar     | 2200           |
| Hydraulic flow rate (HFR)  | cm³/30s | 310            |
| Nozzle hole diameter       | µm      | 109            |
| Number of spray holes      | -       | 8              |
| Spray cone angle           | °       | 153            |
| Charging                   | bar     | 3.6 abs.       |

The cylinder pressure trace as well as the intake and exhaust pressure traces are measured using Kistler pressure transducers with a resolution of 0.1° CA and 0.5° CA respectively and are recorded using FEV's "Combustion Analyzing System". Indicated values are averaged over 50 cycles and the indicated mean effective pressure (IMEP) is calculated by a ring integral over the high- and low pressure cycle and then averaged over the 50 cycles. Other engine related values like air and fuel mass flow are averaged over 60 seconds. The indicated efficiency is calculated using the indicated power, which is determined from the IMEP, and the fuel energy which is determined from the fuel mass measurement, using a Coriolis type mass flow sensor with high accuracy.

In order to analyze emissions, exhaust gas is extracted with heated lines to avoid condensation and the following emissions are measured with the corresponding equipment:

- $\text{NO}_x$ : Chemiluminescence Detector (CLD): EcoPhysics CLD 700 EL
- THC: Flame Ionization Detector: Rosemount - NGA Platform 2000 Series (as C3H8 equivalent)



- CO and CO<sub>2</sub>: Non Dispersive Infrared Absorption Analyzer: Rosemount - NGA Platform 2000 Series
- O<sub>2</sub>: Paramagnetic detector: Rosemount - NGA Platform 2000 Series
- Filter Smoke Number (FSN): AVL 415 Smoke Meter

The sample lines for the Smoke Meter are heated up to 75 °C and the extraction site is in the exhaust manifold at low loads and downstream of the backpressure valve for higher load points due to the high exhaust gas temperatures.

### Design of Experiments (DoE) Methodology

In order to optimize the engine calibration for the biofuels, design of experiments was chosen. Opposed to a conventional approach, where the engine calibration is optimized at a test bench and usually only one parameter is varied, the DoE approach is capable of significantly reducing the experimental effort. Furthermore, by only varying one parameter, the interaction of multiple factors cannot be captured, while with DoE several parameters are changed at the same time.

Before the DoE optimization can start, the parameter space for the setup of the test plan has to be defined. As calibration parameters for the optimization of 1-octanol, the boost pressure, injection pressure, the pilot injection duration and its offset to the main injection as well as the center of combustion (CA50; point of 50 % fuel conversion) were chosen. Since DBE is having a very high cetane number, its combustion is mainly mixing controlled and therefore the combustion noise emissions are low. Hence, the pilot injection was omitted and only the boost pressure, injection pressure and CA50 were varied for the tests with DBE. Furthermore, the engine-out NO<sub>x</sub> emissions were kept constant for every load point by an adjustment of the EGR-rate and the exhaust back pressure was kept at a constant offset to the boost pressure, depending on the load point. The varied ranges of the chosen parameters, including the base calibration are listed in Table 3. Besides the training points for the DoE modeling, the test plan also contains repetition points in order to compensate drifts as well as validation points to validate the generated models.

After the generation and execution of the test plan, models for engine efficiency, soot, HC and CO emissions as well as combustion noise emission have to be generated. Here, a Gaussian process is utilized where Bayesian inference is used in order to increase the likelihood of the model to represent the experimental data. The goal of the base calibration was to achieve engine-out EU6 NO<sub>x</sub> emissions at the highest possible efficiency and since the emissions performance of the biofuels is superior to Diesel, the goal of the subsequent optimization was to increase engine efficiency, while the exhaust emissions were not allowed to exceed the ones of Diesel fuel. Solely the noise emissions of 1-octanol were allowed to surpass the ones of Diesel fuel, since the utilized single pilot strategy is not capable of reducing the noise emissions below the Diesel fuel reference without major drawbacks in efficiency and emissions. This is due to the low cetane number of 1-octanol which leads to a high homogenization of the pilot injection and therefore increased combustion noise. Hence, a multiple pilot injection strategy would be necessary to efficiently decrease the noise emissions. A retardation of the center of combustion in order to reduce the noise emission would also be possible but counteract the goal of an efficiency increase.

Table 3. Parameter space of the DoE for both load points and the base calibration [7]. \*) Pilot injection is only utilized for 1-octanol

|                                    |                   | Lower part load |          | Higher part load |           |
|------------------------------------|-------------------|-----------------|----------|------------------|-----------|
|                                    |                   | Base            | Range    | Base             | Range     |
| Engine speed                       | min <sup>-1</sup> | 1500            |          | 2400             |           |
| IMEP                               | bar               | 6.8             |          | 14.8             |           |
| Boost pressure                     | bar               | 1.5             | 1.2-1.7  | 2.6              | 2.1-3.1   |
| Back pressure offset               | bar               | 0.1             |          | 0.2              |           |
| Injection pressure                 | bar               | 900             | 500-1500 | 1800             | 1200-2000 |
| CA50                               | ° CA aTDC         | 5.8             | 2-10     | 10.8             | 6-14      |
| Pilot offset*                      | ° CA              | 11              | 7-20     | 28               | 15-38     |
| Pilot duration*                    | µs                | 140             | 100-250  | 120              | 100-200   |
| Charge air temperature             | °C                | 30              |          | 45               |           |
| Indicated specific NO <sub>x</sub> | g/kWh             | 0.2             |          | 0.6              |           |

Table 4. For both biofuels optimized engine calibration at lower and higher part load in comparison to the reference calibration

|                                    |                   | Lower part load |           |       | Higher part load |           |      |
|------------------------------------|-------------------|-----------------|-----------|-------|------------------|-----------|------|
|                                    |                   | Base            | 1-Octanol | DBE   | Base             | 1-Octanol | DBE  |
| Engine speed                       | min <sup>-1</sup> | 1500            |           |       | 2400             |           |      |
| IMEP                               | bar               | 6.8             |           |       | 14.8             |           |      |
| Boost pressure                     | bar               | 1.5             | 1.37      | 1.6   | 2.6              | 2.84      | 2.9  |
| Back pressure offset               | bar               | 0.1             |           |       | 0.2              |           |      |
| Injection pressure                 | bar               | 900             | 505       | 889   | 1800             | 1990      | 2000 |
| CA50                               | ° CA aTDC         | 5.8             | 5.3       | 2.6   | 10.8             | 8         | 6    |
| Pilot offset*                      | ° CA              | 11              | 16.2      | -     | 28               | 15        | -    |
| Pilot duration*                    | µs                | 140             | 100       | -     | 120              | 134       | -    |
| Total injected fuel mass per cycle | mg                | 15.19           | 16.84     | 16.24 | 31.11            | 34        | 33.5 |
| Charge air temperature             | °C                | 30              |           |       | 45               |           |      |
| Indicated specific NO <sub>x</sub> | g/kWh             | 0.2             |           |       | 0.6              |           |      |