

Advanced Fuel Formulation Approach using Blends of Paraffinic and Oxygenated Biofuels: Analysis of Emission Reduction Potential in a High Efficiency Diesel Combustion System

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ABSTRACT

This work is a continuation of earlier results presented by the authors. In the current investigations the biofuels hydrogenated vegetable oil (HVO) and 1-octanol are investigated as pure components and compared to EN 590 Diesel. In a final step both biofuels are blended together in an appropriate ratio to tailor the fuels properties in order to obtain an optimal fuel for a clean combustion.

The results of pure HVO indicate a significant reduction in CO-, HC- and combustion noise emissions at constant NO_x levels. With regard to soot emissions, at higher part loads, the aromatic free, paraffinic composition of HVO showed a significant reduction compared to EN 590 petroleum Diesel fuel. But at lower loads the high cetane number leads to shorter ignition delays and therefore, ignition under richer conditions. These circumstances cause slightly increased soot emissions due to the current engine calibration and could easily be compensated by an optimized engine calibration.

1-octanol was identified by the cluster of excellence "Tailor-Made Fuels from Biomass (TMFB)" as a promising alternative biofuel which is virtually showing no soot emission. At low loads the HC- and CO emissions are lower compared to Diesel as well but at higher loads the CO emissions surpass the ones of Diesel fuel. However, due to the relatively low cetane number of 1-octanol, the sound emissions are the highest of the investigated fuels.

By blending of HVO and 1-octanol the beneficial features of both fuels could be combined, while their individual drawbacks could be reduced. With the addition of 1-octanol, the higher soot emissions of HVO at low loads without an optimized calibration were reduced by more than 50 %. The soot emissions decreased due to the oxygen content of 1-octanol and the lower cetane number of the blend compared to neat HVO. In addition, much lower HC- and CO emissions were achieved, which are nearly half of petroleum based Diesel fuel. Also, the advantages of HVO in terms of combustion noise emissions are still maintained in the range of 3 dB less than baseline Diesel operation at lower part loads.

The blending of a novel biofuel candidate (1-octanol) with an advanced commercially available biofuel (HVO) is a potential key step towards a soot- and NO_x-free Diesel combustion.

CITATION: Zubel, M., Bhardwaj, O., Heuser, B., Holderbaum, B. et al., "Advanced Fuel Formulation Approach using Blends of Paraffinic and Oxygenated Biofuels: Analysis of Emission Reduction Potential in a High Efficiency Diesel Combustion System," *SAE Int. J. Fuels Lubr.* 9(3):2016, doi:10.4271/2016-01-2179.

INTRODUCTION

The fuel design process carried out at cluster of excellence TMFB, an extensive investigation program, was conducted to understand the effect of molecular structure and physico-chemical properties on the combustion and emission behavior of modern Diesel engines. Starting with pure component alkanes and alcohols such as n-dodecane, n-heptane and 1-decanol, the effect of ignitability and oxygen content especially on soot emissions was identified. It was proven that the integration of oxygen in the fuel molecule leads to a significant reduction in soot emissions. Also, soot emissions decrease with decreasing cetane number [1] due to more homogeneous mixture formation as a result of increased pre-mixed combustion. However, this approach leads to drawbacks with regard to CO, unburnt HCs, CSL (Combustion Sound Level) and could also lead to a deterioration in the cold start behavior [2].

Kremer et al. [2] have proven that even highly reactive fuels such as di-n-butyl ether (DnBE) with a derived cetane number in the range of 115, despite of its dominant diffusion controlled combustion, could lead to a drastic reduction in engine out soot emissions in a wide range of engine operation points. This research concluded that the positive effect of the oxygen and the low boiling characteristics on particulate emissions overcomes the influence of the long mixing time of low-CN fuels.

Previous studies have demonstrated that use of 1-octanol as a pure component or as a blend with Diesel leads to a significant reduction in engine out soot emissions. However, some drawbacks with regards to HC, CO and engine noise were noticed [3].

The impact of the increase in individual fuel properties on engine emissions are summarized in Figure 1.

	Cetane number ↑	Evaporation temp. ↑	Aromatic content ↑	O ₂ content ↑
Soot	⊖	⊖ ⊖	⊖ ⊖	⊕ ⊕
CO	⊕ ⊕	⊖	⊖	*
HC	⊕ ⊕	⊖	⊖	*
CSL	⊕ ⊕	⊖	●	*

⊕ ⊕ : Significant positive impact, ⊕ : Positive impact, ● : No direct impact

⊖ ⊖ : Significant negative impact, ⊖ : Negative impact

* The impact depends on the oxygen functional group and its chain

Figure 1. Impact of individual fuel property on the engine out emissions at identical engine out NO_x emission level: summary of literature review [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14]

In the recent years, tremendous R&D efforts have been put to investigate the impacts of paraffinic liquid fuels with a focus on their large scale implementation. These paraffinic fuels have typically higher cetane numbers and are virtually free from poly-aromatic hydrocarbons (PAH) and sulfur, which cause harmful particulate matter (PM) emissions and faster deterioration of the aftertreatment catalysts respectively [15, 16, 17]. One mainstream example of a high quality paraffinic Diesel fuel investigated in several previous studies is Hydrogenated Vegetable Oil (HVO). These studies [4, 5, 6, 11, 12, 15, 16, 17, 18, 19, 20, 21] reveal a significant benefit in HC-, CO- and engine noise emissions in existing and next generation Diesel engines. With regards to soot emissions, depending on the injection strategy, a slight increase could be observed at lower part loads mainly due to a reduction in premixed combustion phase due to its high cetane number in the range of 80. While at higher part loads, a significant reduction in soot emissions has been widely reported [4, 5, 6]. In order to improve the emission benefits of paraffinic fuel component over an extended engine operation map, Murtonen et al. [22] have investigated blends of HVO with oxygenated additives.

While the previous investigations were mainly focused on pure biofuel applications in combustion engines the objective of the present investigations was to formulate an advanced biofuel blend. Therefore, for the first time, a paraffinic and aromatic free biofuel, HVO, was blended with the oxygenated fuel 1-octanol, identified by the fuel design process of the cluster TMFB. This approach enables low emission combustion without any sacrifice in efficiency. In order to achieve this goal, in a first step (phase 1) the characteristics of the pure biofuels, HVO and 1-octanol, are compared to petroleum based Diesel. This will provide a deeper understanding of the influence of cetane number, ignition delay behavior and oxygen content of the fuels on the combustion and emissions. The second step (phase 2) is concerned with the blending of both fuels, since each individual fuel is showing its own advantages and drawbacks. The two biofuels were blended in an appropriate ratio (phase 2) to achieve an advanced paraffinic oxygenate for realizing maximum emission advantages and at the same time overcoming their individual disadvantages.

BIOFUEL PRODUCTION PATHWAYS

The production of bio-based Diesel fuels from vegetable oils is commonly accomplished using a process known as Trans-esterification. The product of Trans-esterification is Fatty Acid Methyl Ester (FAME), commonly known as biodiesel [23, 24, 25]. The utilization of biodiesel (FAME) in higher proportions / blends may cause some operational and durability issues in modern engines. Owing to this reason, the Fuel Injection Equipment (FIE) manufacturers have recommended to restrict the use of FAME blending by 7 % v/v [26]. Additionally, the EU commission has proposed to limit the use of edible oil based biofuels up to 5 %. In order to fulfil the existing EU bio-quota targets of 10 % by the year

2020, the remaining biofuel for transportation use is intended to be derived from nonfood cellulosic materials such as waste biomass sources and algae [27].

To help realizing these aims, one of the possible short term viable solutions is the use of HVO fuel produced from non-food based raw materials. The hydrotreating of vegetable oils and animal fats is a process based on oil refining know-how and is used for the production of biofuels for Diesel engines. In the process, hydrogen is used to remove oxygen from the triglyceride vegetable oil molecules and to split the triglyceride into three separate chains, thus creating hydrocarbons which are similar to existing high cetane Diesel fuel components. The process of isomerization is done to improve the cold properties. This allows the blending in any desired ratio to meet relevant Diesel fuel standards without any concerns regarding quality [4, 17, 28].

An alternative process, where complete plant material can be utilized is the so called Biomass to Liquid (BtL) approach, also known as Fischer Tropsch (FT) synthesis. In FT synthesis, the highly complex structures of the plant material are decomposed into a mixture of carbon monoxide (CO) and hydrogen (H_2) i.e. syngas, at high temperatures. The syngas is catalyzed into hydrocarbons with longer chains, which can be directly used as fuels or further processed in refinery processes. However, this process poses challenges due to its high input energy intensity [25].

The vision of TMFB fuel design is the joint model-based description and optimization of liquid fuel production in bio-refineries and energy conversion in internal combustion engines. Selective bio- and chemo-catalytic process steps aim for an energy- and carbon-efficient conversion of lignocellulosic biomass into molecularly well-defined fuel compounds. Generally, preservation of nature's synthetic power to the extent possible is envisaged to minimise the number of process steps in the transformation process (refer to Figure 2) [29, 30]. Since the biomass feedstock is generally rich in oxygen, the focus lies on medium-sized oxygenated hydrocarbons constituting promising fuel compounds. Oxygenates have been found to significantly reduce engine-out soot emissions in Diesel engines [30] and are nowadays routinely blended into gasoline to increase its octane rating [31].

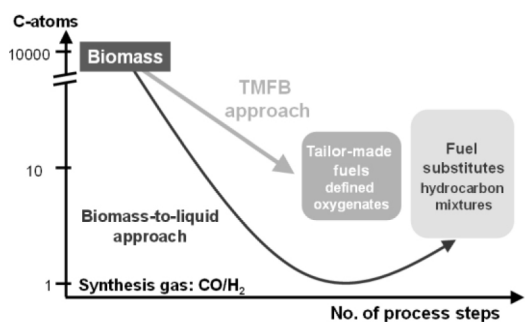


Figure 2. Direct refunctionalisation of biomass monomers to preserve the synthesis power of nature in contrast to the Biomass-to-Liquid (BtL) approach [13, 25]

Examples for the selective catalytic transformation of bio-derived platform molecules into fuel candidates have been reported by TMFB researchers in earlier publications [2, 3, 13, 30].

One of the potential future biofuel candidates identified in TMFB research is 1-octanol. Currently 1-octanol is mainly used in perfumery, as flavors and it is also important for the synthesis of 1-octene. Usually it is obtained by a petrochemical process but Julius and Leitner [32] developed a new synthesis route from biomass-derived platform chemicals within the TMFB with high yields of 1-octanol. The starting point for this new synthesis is furfural and acetone, which can also be derived from biomass [33]. Furfural and acetone can be converted into furfuralacetone by an aldol condensation [34] which is then hydrogenated into 4-(2-tetrahydrofuryl)-2-butanol (THFA). A multifunctional catalyst system developed within the TMFB is then capable of converting THFA into 1-octanol with an excellent yield of 93 % to obtain a linear C8 alcohol product. This catalyst system uses an acid additive, including functional ionic liquids together with a Ruthenium hydrogenation catalyst [32].

METHODOLOGY AND APPROACH

The present work focuses on the utilization of advanced paraffinic and oxygenated fuel properties in high performance passenger car Diesel engines for achieving lowest possible exhaust emissions. In the first phase of the research (Phase-1) pure oxygenated and paraffinic biofuel components are investigated to analyze their potential with regards to emissions and performance. In a subsequent phase, an advanced blend was formulated to maximize the benefits of the individual pure components. Figure 3 illustrates an overview of the systematic approach used in the present work.

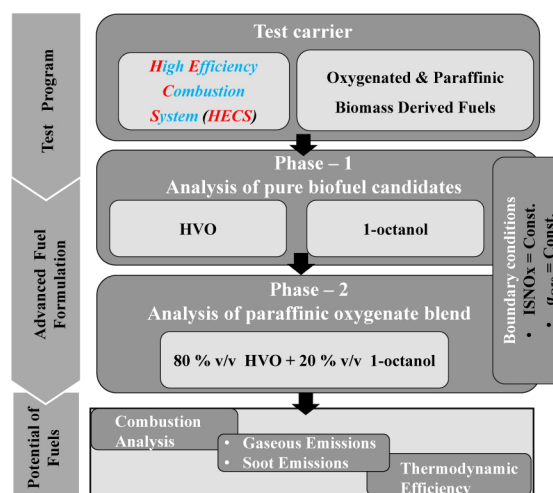


Figure 3. An overview of methodology and approach used in the test program

Test Fuels

In the first phase of the project two pure biofuel candidates were investigated to analyze their fundamental impact on the emissions and combustion behavior. One of the biofuel candidates (1-octanol) has oxygen content in the fuel molecular structure and the other biofuel candidate (HVO) is composed of normal and iso-paraffinic structures with a c-atom distribution which mainly lies in the range of $C_{15} - C_{18}$. A detailed c-atom distribution of a HVO sample was published by Authors previously [6]. The petroleum based EN590 Diesel fuel with (5-7 % FAME as available at filling stations in Germany) was used as a reference. In order to enhance the fuel property effects of the pure biofuel components, an advanced biofuel blend was formulated with 80 % v/v HVO and 20 % v/v 1-octanol. This blending ratio was chosen in order to maintain a lower heating value similar to Diesel and to reflect possible future availabilities of these fuels. The simple molecular composition of a paraffinic fuel candidate and 1-octanol can be seen in Figure 4.

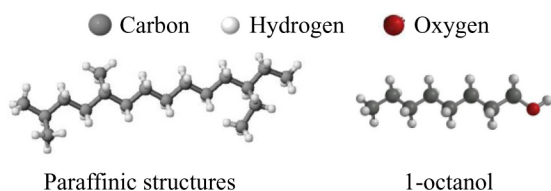


Figure 4. Molecular structures of the investigated fuels. The paraffinic fuels composed of a mixture of different carbon chain length consisting of normal and iso-paraffins. The paraffinic molecular structure shown in the picture is a representative example.

Normal paraffins are characterized by linear-chain hydrocarbons with a saturated single bond only. The lack of double bonds and cyclical structures leads to a uniform reaction during the combustion, and therefore, leads to positive impact on the soot emissions. The physico-chemical properties depend to a significant extent on the molecular structure. Hence, it is difficult to isolate the effects of fuel composition on individual fuel property.

The test fuels used in this study are designated as shown in Table 1.

Table 1. Designation of investigated fuels used in the present test program

S.No.	Designation of Fuel	Details of Fuel Compounds
1	Diesel	pure EN590 Diesel with 5 to 7 % FAME
2	HVO	pure Hydrogenated Vegetable Oil
3	1-OL	pure 1-octanol
4	HVO / 1-OL	Advanced Oxygenated-Paraffinic Fuel Blend (20 % v/v 1-OL + 80 % v/v HVO)

The detailed physico-chemical characterization of test fuels is presented in Table 2.

Table 2. Physico-chemical characterization of test fuels. All values were obtained from measurements with the exception of c/h/o content, molecular weight and lower heating value, which were obtained from a linear blending rule. The Derived cetane Number (DCN) was determined using the advanced fuel ignition delay analyser [35].

	Unit	EN590 Diesel	HVO	1-OL	HVO / 1-OL
Boiling Range	°C	180-350	220-300	195	190-304
Cetane Number	-	56.5	77 (DCN)	33.8 (DCN)	70 (DCN)
Density (15°C)	kg/m³	832.9	780	837	789.5
Carbon Content	w %	86.4	85.3	73.8	83.0
Hydrogen Content	w %	13.6	14.7	13.9	14.5
H/C Ratio		0.157	0.172	0.186	0.175
Oxygen Content	w %	0.14	0	12.3	2.5
Aromatic Content	w %	27	~ 0	0	0
Molecular Weight	g/mol	~ 199	~ 234	130	213
Kinematic Viscosity	mm²/s	3	3	5.7	3.13
Lower Heating Value	MJ/kg	43	43.8	38.2	42.7
Flash Point	°C	89	76	81	79

Description of the Experimental Setup

The measurement program for the present study was conducted on a single cylinder engine (SCE) with a displacement of 0.39 l. The fuel injection equipment (FIE) is close to series production and capable of rail pressures up to 2200 bar using a piezo fuel injector. The injection pattern as well as the rail pressure can be adjusted freely as desired in order to compensate for fuel effects. The combustion system is rated at 80 kW/l and is capable of withstanding peak firing pressures up to 220 bar. Due to charge air cooling and high pressure exhaust gas recirculation (EGR) the engine is capable of meeting the EU-6b (NEDC cycle) NOx emission limits without the application of any DeNOx aftertreatment system, however, the application of a DPF is necessary for meeting the particle mass and number limit. The combustion chamber features a re-entrant ω -bowl. Detailed information on this engine can be found in various publications [8, 7] and the key engine specifications are summarized in Table 3. Furthermore, a detailed layout of the used single cylinder engine can be found in the appendix.