

Utilization of HVO Fuel Properties in a High Efficiency Combustion System: Part 2: Relationship of Soot Characteristics with its Oxidation Behavior in DPF

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ABSTRACT

The present work is a continuation of the earlier published results by authors on the investigation of Hydrogenated Vegetable Oil (HVO) on a High Efficiency Diesel Combustion System (SAE Int. J. Fuels Lubr. Paper No. 2013-01-1677 and JSAE Paper No. 283-20145128). In order to further validate and interpret the previously published results of soot microstructure and its consequences on oxidation behavior, the test program was extended to analyze the impact of soot composition, optical properties, and physical properties such as size, concentration etc. on the oxidation behavior. The experiments were performed with pure HVO as well as with petroleum based diesel and today's biofuel (i.e. FAME) as baseline fuels. The soot samples for the different analyses were collected under constant engine operating conditions at indicated raw NO_x emissions of Euro 6 level using closed loop combustion control methodology.

The oxidation behavior results of optimized Thermogravimetric Analysis (TGA) correspond well with the previously published (part-1) results of the kinetics of soot oxidation (i.e. activation energy, reaction rate constant and regen. temperature) conducted on a Laboratory Gas Test Bench using a Temperature Programmed Oxidation (TPO). The results suggest that the soot oxidation temperatures of the HVO decreased by ~43 °C and 37 °C with O₂ and NO₂ respectively, as compared to petroleum based diesel. Finally, the relationship of the PM physico-chemical properties (i.e. O₂ content, C/O ratio, C/H ratio and microstructure parameters) is compared with the trends of the oxidation behavior. The overall results from the present work suggest that the oxidative behavior of a specific type of soot cannot be estimated based on a singular characteristic but is more dependent on a set of soot properties.

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INTRODUCTION

The stringent PM emission limits necessitate a particulate trap in most present day diesel engines. However, the trapped particulate matter (PM) needs to be oxidized from the DPF to reduce the back pressure on the engine. In the majority of DPF applications the "Filter Regeneration" is accomplished with the help of active regeneration measures, which involves an additional fuel penalty. To bring down the regeneration dependent fuel consumption, one critical requirement is to reduce the thermal soot oxidation temperatures. For instance, the use of fuel additives can lower the ignition temperatures of

diesel soot, but it suffers with the disadvantages of higher ash generation and the need for additional onboard components such as metering units and tanks [1].

In addition, to the engine operating parameters [2, 3, 4], the fuel formulation can also lead to the variation in the properties of the particulate matter, and thus, its combustion in the DPF. Recently, some studies using different types of petroleum diesel and biodiesel, have demonstrated that PM from different fuels have different physico-chemical characteristics and activation energy of oxidation [5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15]. Therefore, the properties of particulate matter like size,

number, concentration, composition, volatility, reactivity, etc. are of increasing interest with respect to the assessment of regeneration frequency and regeneration efficiency of a particulate trap.

Boehman et al. and other previous researchers have investigated the impact of crystallographic parameters on the oxidative reactivity of the soot. The oxidative reactivity should correlate to the amount of differences from an ideal crystallographic structure as well as to the number of edge atoms and therefore to the size of the crystallites [3, 4, 13, 15]. Strzelec and co-workers [16] in their study of petroleum diesel, B100 (FAME), and its blends, using a differential fixed-bed reactor, have recently demonstrated that a change in the engine fuelling can affect both the initial as well as highly oxidized particulate morphologies.

In the present study, an additional focus was set on the chemical structure of the soot particles as it is assumed, that the non-graphitized, amorphous aliphatic part of the soot has an important role in oxidative reactivity, due to their lower ignition temperature.

With regard to engine fuels, the focus of research is shifting towards the development of biogenic renewable fuels from non-food raw materials employing low temperature processes [17]. 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". The utilization of biodiesel (FAME) in higher proportions / blends may cause some operational and durability issues in modern engines. Owing to this reason, the FIE (Fuel Injection Equipment) manufacturers have recommended to restrict the use of FAME blending up to 7% v/v. [18].

The hydro-treating of vegetable oils (HVO) and animal fats is a process based on oil refining know-how (but not part of the standard production process) and is used for the production of biofuels for diesel engines. In this 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. This allows the blending in any desired ratio to meet relevant diesel fuel standards without any concerns regarding quality.

Also, commercial use as 100 % biofuel is demonstrated in several markets including USA, Austria, and Nordic countries [19]. One of the novelties of HVO technology is its ability to produce the same high quality product from a wide variety of raw materials. It is possible to use not only vegetable oils but different waste and residue streams like waste animal fat, waste fish fat, technical corn oil, used cooking oil and some side products of vegetable oil production. To further increase the feedstock base of HVO production, the research is

concentrating on algae and microbiological routes to produce feed for the HVO process besides the more conventional waste and residue routes of oils and fats. It is already demonstrated that both microbial and algae oils are suitable feed for HVO process, and the key for commercialization is the production of the oils.

The composition of this potential biofuel candidate is significantly different from today's commercially available biofuel i.e. FAME and petroleum based diesel. Figure 1 depicts the C-atom distribution of the petroleum based diesel fuel [20, 21] and HVO. Diesel fuel consists of ~ 300 different types of hydrocarbons with main contribution from:

- iso-Paraffins and n-Paraffins: ca. 25- 50 % v/v
- Naphtene (cyclic paraffins): ca.20-40 % v/v
- Aromatics: ca. 15-40 % v/v
- Olefins and others: ca. 4 % v/v

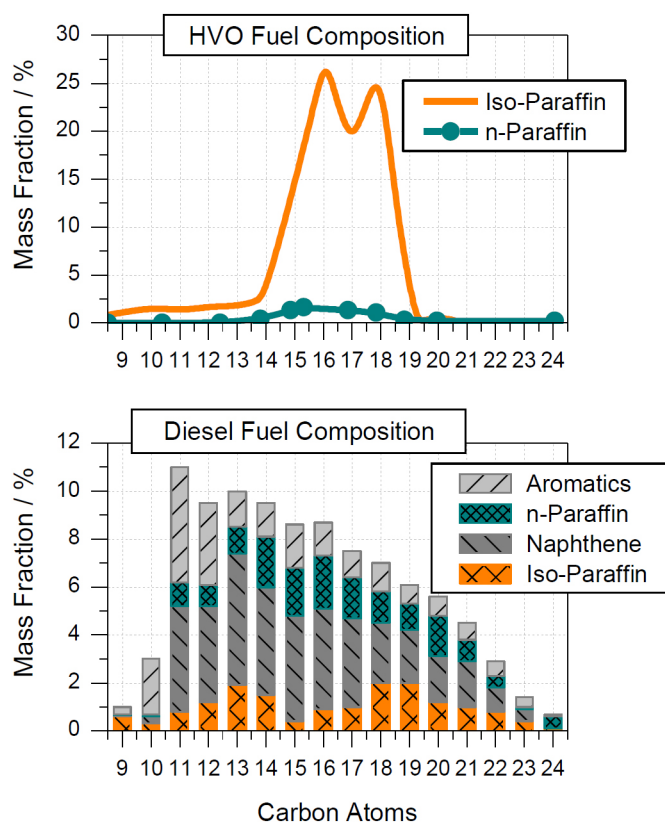


Figure 1. Carbon atom distribution of petroleum diesel and HVO [20, 21, 22]. Petroleum diesel consists of nearly 300 different types of hydrocarbons, while HVO contains mainly iso-paraffins.

With regards to HVO composition, it is mainly a mixture of n-paraffins and iso-paraffins, with iso-paraffins as the major component in the mixture [22]. On the other hand, as per Westbrook et al. the composition of biodiesel in RME is contributed mainly from C18:1 (~ 60%), C18:2 (~ 20%), C18:3 (~ 15%) and small fractions of C18:0 and C16:0 [23]. Hence,

each compound in the fuel hydrocarbon mixture has a unique impact on the engine combustion characteristics and emission formation.

In the first phase of this research [24, 25], the authors published the impact of the HVO on combustion characteristics, ignition behavior, engine noise emissions, gaseous emissions (CO , HC , NO_x), and PM reduction potential with respect to petroleum based diesel [24]. Furthermore, the structure of the soot was analyzed using X-Ray Diffraction (XRD) and the impact of structural parameters on the oxidation kinetic mechanism was studied in detail with Temperature Programmed Oxidation (TPO) on an innovative Laboratory Gas test Bench-LGB [25].

In order to further validate and interpret the previously published results of part-1, the test program was extended to analyze the soot elemental composition (oxygen content, H/C ratio), microstructure using HRTEM, physical properties such as packing density, particle size etc. The oxidation behavior was analyzed using an improved thermo-gravimetric analysis (TGA) with real soot loaded DPF samples. Finally, the analyzed physico-chemical properties of particulate matter are compared with the oxidation behavior from TPO as well as TGA to analyze the relationship of soot characteristics with DPF regeneration behavior.

SOOT CHARACTERISTICS AND ITS IMPACT ON THE DPF BEHAVIOR - A BRIEF REVIEW OF THE PRIOR WORK

The enhanced DPF regeneration interval and reduced regeneration temperatures with biodiesel fuelling have been reported in several previous studies. Boehman and co-workers, have reported that favorable NO_x/PM ratio with B20 (20% FAME blend with ULSD), leads to lower balance point temperature (BPT) and hence enhanced regeneration intervals [14]. Similarly, Williams et al. [11] has suggested that the Balance Point Temperature (BPT) is 45°C lower for B20 & 112°C lower for B100 than petroleum diesel fuel. Here, the decrease of BPT was not attributed to the increased NO_x , rather higher degree of disorder in the soot structure and higher oxygen content were reported as the main factors responsible for the observed effects. In another study, the increase in soluble organic fractions (SOF) and volatile fractions were observed with biodiesel. It was reported that these additional SOF provide reactive hydrocarbons to oxidize catalytically in the DPF [6]. This behavior was also studied by Strzelec et. al. where 40 % of the total PM sample was oxidized before the oxidation analysis, to avoid the influence of SOF and volatiles on the activation energy. As a result, it was observed that the activation energy of B100 soot was higher than B0 soot [26].

Concerning the impact of HVO fuelling on soot characteristics and DPF behavior, a little work has been done so far. Mikkonen et. al. have demonstrated that due to the reduced engine out soot emissions, HVO fuelling resulted in a slower increase of

exhaust gas back pressure in DPF, which will eventually lead to enhanced regeneration intervals and a reduction of regeneration related fuel penalty [27]. Happonen and co-workers analyzed the soot surface structure of HVO and petroleum based diesel soot using HRTEM. Both soot samples showed strongly bent graphene layers with an "onion" like shell-core structure. The HVO soot structure appeared to be slightly more curved and also more susceptible to oxidation reaction but the results from oxidation of the samples proved inconclusive [28].

Base Engine Parameters	Soot Emissions	+ + Reduced soot formation, however the benefit depends on the duty cycle
	Oil Dilution	- - FAME :Higher evaporation temperature (T_{90} high) + + Paraffinic fuels : No oil dilution (T_{90} low)
	DPF Soot Loading Rate	+ + As a result of lower engine soot emissions, favorable NO_x/PM ratio improves the CRT [®] effect
	T_{exh} (normal operation)	- + FAME :Lower heating value leads to low T_{exh} + + Paraffinic fuels :No change in T_{exh} reported
Soot Characteristics	Soot Oxidative Reactivity	+ Improved reactivity of Biodiesel soot was reported due to various factors (although these characteristics are not always consistent in the previous studies) • Higher share of organic / volatile carbon • Metal traces / ash content • Higher disorder in microstructure • Lower light absorption coefficient i.e. blackness • Higher edge C-atoms (smaller crystallite width) • Formation of surface oxygen groups • Internal burning (FAME soot) and Shrinking core oxidation (FT diesel soot)
DPF Regen Parameters	Passive Regen. η	+ Lower balance point temperature (BPT) due to improved engine out NO_x/PM ratio
	Active Regen. η	+ Low thermal Regeneration temperature
	Regeneration Interval	+ Increased regeneration interval due to reduced raw soot emissions & lower BPT

Figure 2. Summary: Impact of Biodiesel (FAME) and Paraffinic fuels on the particulate characteristics and DPF behavior [5, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 19, 24, 25, 26, 27, 28, 29, 30, 31, 32]

In another study using paraffinic fuel (Fischer Tropsch Diesel), J. Song and Boehman et al. proposed that FT diesel soot follows the shrinking core type oxidation. In shrinking core type oxidation the particles continue to burn from outside to inside with no inside burning. Because of the lack of internal burning, the abrupt mass loss is not seen, leading to low oxidation rate. In contrast to it, B100 (FAME) soot showed internal burning after 40% conversion, leading to faster oxidation rates than FT Diesel [31].

J. Song [13] has reported that the higher reactivity of the B100 soot as compared to FT Diesel soot is due to the formation of the surface oxygen groups. However, in contrast, Yehliu et al. [15] have reported that the enhanced reactivity of the B100 soot than FT diesel is not due to surface oxygen groups, rather it is attributed to the disorder in the nanostructure and smaller crystallite width (higher edge carbon atoms). The main findings of the discussed literature review on impact of biodiesel and paraffinic fuels have been summarized in Figure 2.

METHODOLOGY AND APPROACH

The primary aim of the research is to evaluate the impact of different generations of biomass derived fuels on the physico-chemical characteristics of diesel particulate matter emissions and its relationship with oxidation behavior in DPF.

Figure 3 illustrates a detailed outline of the methodology used during the test program. The experiments for particulate measurements and sampling were conducted with petroleum based diesel (EN 590 diesel without FAME) and two different biomass derived fuels. PM emissions were measured in terms of Filter Smoke Number (FSN), gravimetric mass, and number concentrations. Different physical and chemical methods were applied to analyze the various aspects of PM composition e.g. Soluble / Non-Soluble Organic Fractions (SOF/NSOF), Volatile fractionation, and elemental composition (C:H:O). Other physical measurements such as primary particle size, size based mass distribution, packing density, and specific surface areas were carried out to characterize the geometrical properties of soot emissions.

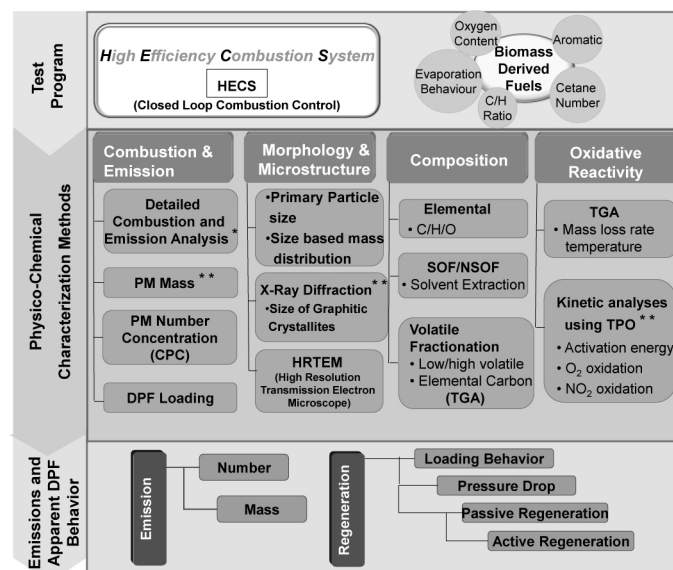


Figure 3. An overview of methodology and approach used in the test program (* Results published in [24], * Results published in [25])

For all of the investigated fuels, the rate of recirculated exhaust gas was chosen in a way that an identical indicated specific raw NO_x -emission level of 0.75 g/kWh was achieved. This level represents a modern Euro 6 conforming combustion [33, 24]. The center of combustion (α_{x50}) was maintained constant for all fuels. Both the equal " α_{x50} " as well as the identical NO_x -level, guarantee, from an emission standpoint of view, constant boundary conditions, allowing a basic analysis of the different behavior of all of the fuels.

Test Fuels

Three different diesel fuels were used for the present investigations. Petroleum based diesel fuel was used as a reference for baseline tests and the other two fuels were derived from biogenic sources, out of which one fuel has oxygen content in the fuel molecular structure.

EN 590 Diesel available in Germany at fuelling stations contains approximately 5-7 % FAME. For the present studies, a diesel fuel (without FAME) i.e. B0 was used as baseline reference instead of EN 590 diesel to avoid any influence of FAME content (in particular oxygen content) on soot emissions. One of today's commercially available 1st Generation biofuel candidates investigated was a FAME known as Biodiesel (B100). The FAME used in this study was a Rapeseed Oil Methyl Ester (RME) that conforms with EN 14214 specifications. It consists of saturated as well as unsaturated fatty acids with 12 to 22 carbon atoms. Another biomass derived fuel candidate selected for this study was Hydrogenated Vegetable Oil (HVO). HVO is a paraffinic fuel with identical properties to Fischer Tropsch Diesel (BtL / GtL). The paraffins are further isomerized to improve the cold flow properties.

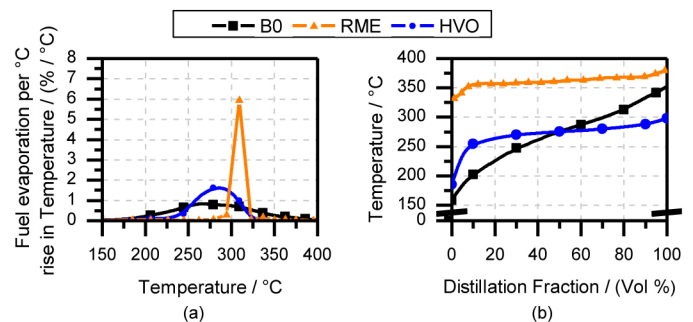


Figure 4. Distillation characteristics of investigated fuels (a) using Gas Chromatography, (b) as per EN ISO 3405 standard, prescribed in EN590 fuel specification.

The evaporation behavior of the investigated fuels was analyzed with the help of Gas Chromatography (GC) boiling curves on a db1 column, calibrated with boiling points of n-alkane as shown in Figure 4. It is very apparent from the curves that petroleum based diesel fuel (B0) evaporates over a wide temperature range. This is mainly due to the fact that petroleum diesel contains a large variety (nearly 300 different types) of different hydrocarbons [20, 21]. The final boiling point of HVO is lowest ($T_{90\%} = \sim 288^\circ\text{C}$) as compared to B0 ($T_{90\%} = \sim 330^\circ\text{C}$) and RME ($T_{90\%} = \sim 357^\circ\text{C}$), as shown in Figure 4. This is a desired feature of HVO, which may lead to enhanced spray breakup and, thus, improved mixture formation. In contrary to B0 and HVO boiling behavior, RME's boiling point is concentrated at a peak depending on its composition of certain compounds. Table 1 lists some important physico-chemical properties of the three investigated fuels.

Table 1. Physico-chemical characterization of test fuels as per prescribed specifications, (B0 and HVO analyzed as per EN590, RME/B100 as per EN 14214)

	Unit	B0 (EN 590 diesel w/o FAME)	RME (B100)	HVO (100%)
Cetane Number	-	56.5	53.9	80
Density (15°C)	kg/m ³	832.9	883.1	778.2
Carbon Content	w %	86.4	77.1	85.3
Hydrogen Content	w %	13.6	12.1	14.7
Oxygen Content	w %	0	10.8	0
Aromatic Content	w %	27	~ 0	~ 0
Molecular Weight	g/mol	~ 199	~ 285	~ 224
Lower Heating Value	MJ/kg	43	36	43.64
Evaporation Temperature (°C)	10% v/v	202.1	351.3	254.4
	50% v/v	276.1	352.8	275.2
	90% v/v	333.8	357.2	288.1

Research Engine and Operating Point

The single-cylinder diesel research engine used for the present work is optimized for improved combustion characteristics with regard to low emission levels and at the same time high fuel efficiency. Reducing the compression ratio, using a higher maximum cylinder and rail pressure, as well as improved EGR cooling resulted in the lowest engine emissions possible to meet Euro 6 standard with DPF [24]. The main specifications of the research engine are summarized in Table 2.

Table 2. Hardware specifications for the research engine.

Parameters	Units	Specifications
Displacement	cm ³	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	2000
Hydraulic Flow Rate (HFR)	cm ³ /30s	310
Nozzle hole diameter	µm	109
Number of spray holes	-	8
Spray Cone Angle	°	153
Charging	Bar	3.6

The experiments for particulate measurements were conducted at a high part load operating point, which is more relevant for the future proposed World Harmonized Light Duty Test Cycle (WHTC) and Real Drive Emission Cycles (RDE). The specifications of the engine calibration parameters are summarized in Table 3.

Table 3. Engine calibration parameters

Indicated Mean Effective Pressure (IMEP) / bar	14.8
Engine Speed / min ⁻¹	2400
Boost Pressure / bar	2.6
Exhaust Gas Back Pressure / bar	2.8
Rail Pressure / bar	1800
Charged Air Temperature / °C	45
Centre of Combustion (α_{x50}) / °CA (ATDC)	10.8

Realization of Identical Engine Operating Conditions: Demonstration of CLCC

Several studies [21, 24, 33, 34] have shown that engine operation close to the optimum efficiency can be achieved on a wide range of fuels by keeping the combustion phasing constant at a few degrees crank angle (°CA) after top dead center (aTDC). Therefore, closed loop combustion control (CLCC) with the target to keep the center of combustion (α_{x50}) constant is considered as an efficient measure in order to compensate the impact of different fuel qualities on combustion and thereby emission performance. Figure 5 demonstrates that three different fuels could be operated with identical performance. This can be achieved by continuously adjusting the start of injection (SOI) using an in-cylinder pressure sensor and by a predictive pre-control to ensure a fastest possible reaction to transient changes. This approach can successfully maintain the center of combustion within a very narrow range, even with major changes in fuel properties and EGR. The desired " α_{x50} " set point is generally defined in the base calibration.

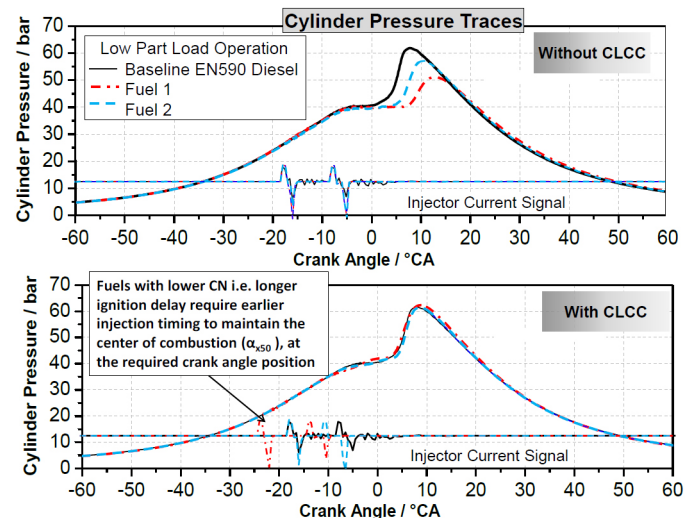


Figure 5. An example of the implementation of closed loop combustion control (CLCC) methodology to realize identical engine operating boundary conditions using fuels with different ignition delay characteristics.