

Impact of Biomass-Derived Fuels on Soot Oxidation and DPF Regeneration Behavior

Om Parkash Bhardwaj, Florian Kremer and Stefan Pischinger
VKA, RWTH Aachen University

Bernhard Lüers, Andreas F. Kolbeck and Thomas Koerfer
FEV GmbH

ABSTRACT

To comply with the new regulations on particulate matter emissions, the manufacturers of light duty as well as heavy duty vehicles more commonly use diesel particulate filters (DPF). The regeneration of DPF depends to a significant extent on the properties of the soot stored.

Within the Cluster of Excellence "Tailor-Made Fuels from Biomass (TMFB)" at RWTH Aachen University, the Institute for Combustion Engines carried out a detailed investigation program to explore the potential of future biofuel candidates for optimized combustion systems. The experiments for particulate measurements and analysis were conducted on a EURO 6 compliant High Efficiency Diesel Combustion System (HECS) with petroleum based diesel fuel as reference and a today's commercial biofuel (i.e. FAME) as well as a potential future biomass derived fuel candidate (i.e. 2-MTHF / DBE).

Thermo gravimetric analyzer (TGA) was used in this study to evaluate the oxidative reactivity of the soot. A "Laboratory Gas Test Bench (LGB)" was used to determine the kinetics of soot oxidation mechanism considering impact of soot properties on its burning behavior inside a DPF. The kinetics of soot oxidation with O₂ was studied as well as the oxidation with NO₂ in order to cover thermal filter regeneration as well as CRT[®] regeneration.

Experimental results from LGB and TGA suggest that the soot from future biomass derived fuel candidate has lower activation energy, thereby; lower oxidation temperatures compared to petroleum based diesel fuel.

CITATION: Bhardwaj, O., Kremer, F., Pischinger, S., Lüers, B. et al., "Impact of Biomass-Derived Fuels on Soot Oxidation and DPF Regeneration Behavior," *SAE Int. J. Fuels Lubr.* 6(2):2013, doi:10.4271/2013-01-1551.

INTRODUCTION

Motor vehicle emissions have been identified as a major source of particulates. Amongst the various control strategies, the use of diesel particulate filters is identified as most effective and viable solution to reduce the emissions of particulate matter.

Concurrently, the focus of research is shifting towards the development and usage of bio-fuels as alternatives for fossil fuels. Renewable biological fuels have the potential to permanently reduce greenhouse gas emissions. These fuels can be tailored to the demands of modern engines taking into account the catalytic production processes. Even a simultaneous optimization of the engine and fuel is possible.

The aim of the TMFB research group is to develop new biofuels in an integrated process, combining chemistry, process engineering and combustion science. It adopts an

interdisciplinary approach, through the application of optimized synthesis processes, towards research of new, biomass-based synthetic fuels, in order to verify their potential, with regard to modern combustion technologies, while simultaneously reducing the dependence on fossil fuels. Such a tailor-made fuel is a well-defined blend of distinct molecular components with optimized physicochemical properties for future combustion systems, which can be produced by sustainable and economical production processes. These fuels show a great potential of improvement in engine out soot emissions [1, 2].

Under the framework of this comprehensive research program, the engine investigations were also extended to understand the impact of these novel biofuel candidates on the characteristics of diesel particulate matter and its combustion behavior inside DPF.

In recent years significant efforts have been made to investigate the process of regeneration of diesel particulate filter. But very less attention has been paid to understand the influence of fuel properties on soot characteristics and thereby DPF operation. The importance of such an investigation is further increased in view of development of potential biomass derived fuel candidates for future low temperature combustion systems. Previous studies have reported significant variations in the structure and oxidative reactivity of the soot derived from different petroleum based diesel fuels and biofuels [3, 4]. In the present research the primary focus is to investigate the influence of today's biofuels and potential future biomass derived fuels on regeneration performance of DPF. A number of tools have been employed to investigate the PM emissions, PM composition and its combustion behavior in DPF. The methodology of TGA was optimized to get a better approximation of the soot oxidation behavior from a charged particulate filter.

In order to assess the impact of different generation of fuels on particulate matter characteristics and DPF behavior, the main results have been presented in the following manner:

- PM emissions and DPF soot loading behavior
- Elemental composition (C:H:O) of soot samples extracted from loaded DPF
- Analysis of oxidative reactivity using improved TGA methodology
- Evaluation of DPF regeneration behavior using measurement of soot oxidation kinetics on a Laboratory Gas Test Bench (LGB) using soot loaded DPF samples

Effect of Biomass Derived Fuels on Base Engine Results and DPF Regeneration Behavior - A Brief Review

Previous studies on first generation biodiesel show that the impact of use of biodiesel on exhaust gas emissions largely depends on the engine technology and duty cycle. Concerning particulate matter emissions, a decreasing trend is observed with neat biodiesel. While emission of NO_x showed a slightly increased trend. Different researches have shown that the combustion with increasing fuel oxygenation results in significant reduction of particulate emissions [1, 2, 5,6,7,8,9,10]

Concerning the influence of biodiesel and PM characteristics, thereby, its impact on DPF regeneration behaviour, several previous studies have reported:

- An increase in soluble organic fractions (SOF) and volatile fractions were observed with biodiesel. It was reported that these additional SOF provides reactive hydrocarbons to oxidize catalytically in the DPF [9, 11]. However, Yezerets and co-workers have reported that high initial reaction rates

are not contributed from adsorbed SOF of soot since the results from Thermal Programmed Desorption experiment of the samples, showed little deviation from samples untreated by this process, all of which were subjected to temperature programmed oxidation process [12].

- A reduced DPF soot loading rate and increased regeneration interval was observed by [13] with using biodiesel fuels. In another study, authors have observed an enhanced DPF regeneration rate with biodiesel fuelling. It was reported that the soot from biodiesel fuel has less ordered (more amorphous) nanostructure which lead to early DPF light-off temperatures and increased rate of oxidation when compared to conventional diesel fuel [9]. These results are also supported by findings of Vander Wal and Tomasek and other researchers that there is a relationship between the initial nanostructure of soot and its oxidative reactivity [3, 4, 14, 15]
- Williams et al. [10] has suggested that the Balance Point Temperature is 45°C lower for B20 & 112°C lower for B100 than conventional diesel fuel. In another study, authors have emphasized that the presence and form of fuel oxygen proved to be the dominant contributor to faster DPF regeneration times and soot reactivity. The form of the oxygen functional group proved to play a role in DPF performance. A long-chain alcohol (a carbon bonded to a single oxygen atom) provided a more effective form of oxygen than the methyl-esters of biodiesel (a carbon bonded to two oxygen atoms) for improving soot reactivity [16]. In contrast, Yezerets et al have demonstrated that the change in reactivity of soot is mainly due to formation of reactive groups on the carbon surface and not due to morphological reasons [12]
- Storey and co-workers have reported a variation in composition of soot depending on the sampling conditions. Particulate samples collected in a DPF tends to have higher fractions of heavy paraffins and aromatics compared to dilute exhaust particulate, which may change the oxidation behaviour [17]

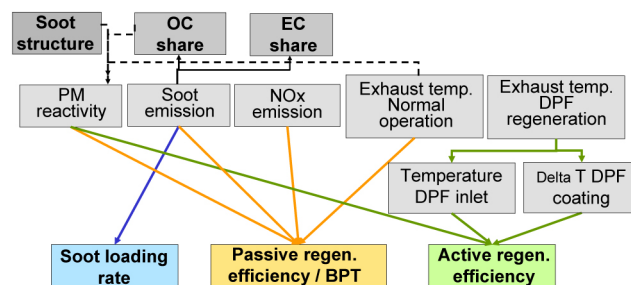


Figure 1. Impact factors of biodiesel DPF regeneration [18]

Keeping in view the above discussed findings and observations regarding the application of biodiesel to engines equipped with DPF, several interactions between the individual effects have to be considered. Figure 1 shows the

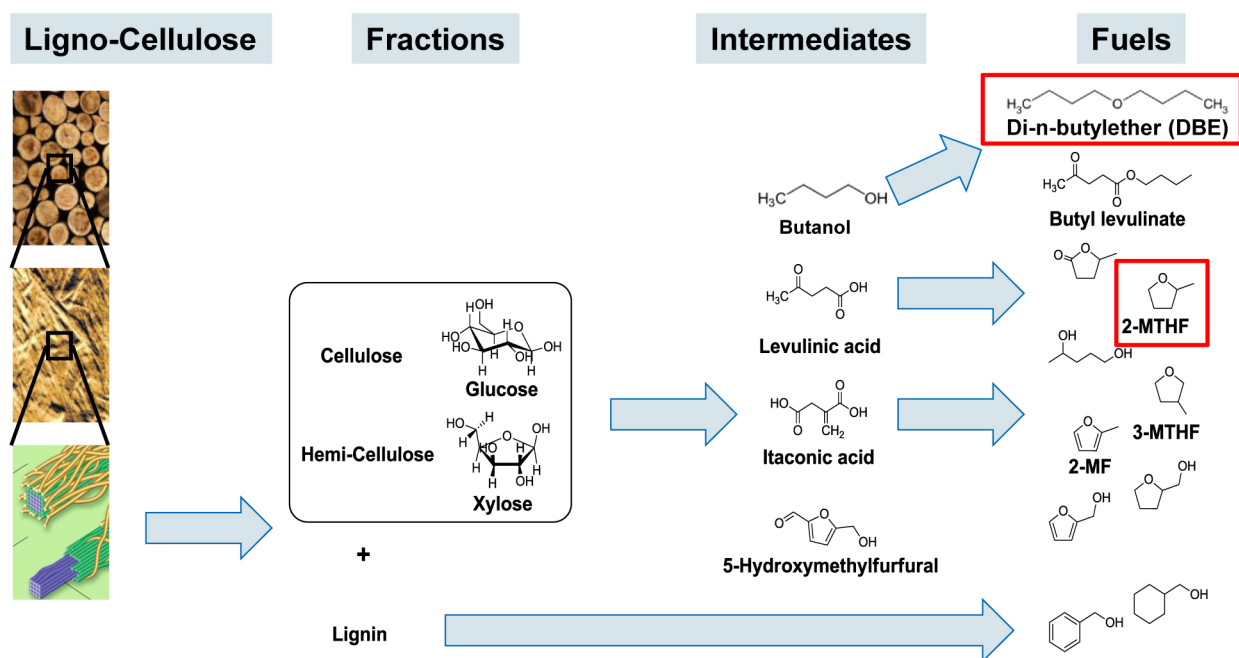


Figure 2. Possible pathways for biofuel production within the TMFB research group [20]

various interactions of individual biodiesel effects on DPF regeneration behavior.

In the nut shell it's obvious that the characteristic of soot has a significant influence on the DPF behaviour. Furthermore the wide use of biofuels will require re-calibration of DPF control strategy to take into account the important factors such as soot loading rates /back pressure behaviour, reactivity of soot, exhaust temperatures, DOC exothermic and thermal shock behaviour.

Production of Biofuels

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. However, cultivating crops for making biodiesel stands in direct competition with the production of food and feed plants, plus only the fruit and seeds of the plants are being used. Due to this reason recently (Oct 2012) EU Commission has issued guidelines to restrict the use of first generation biodiesel to maximum 5 % vol [19].

To utilize waste biomass and to increase the yield per area, future concepts include the complete utilization of plant material that is not used as a food source.

Plant material such as grasses, stalks, or wood consists of lignocellulose. This is a complex composite material consisting of the three biopolymers cellulose, hemicellulose, and lignin. Methods using lignocellulose are producing the so-called second generation biofuels. The production of these fuels are currently still at the state where they undergo technical testing. In the so-called "Biomass-to-Liquid" (BTL) method, the highly complex structures of the plant material

are decomposed into a mixture of carbon monoxide and hydrogen (syngas) at high temperatures. The syngas is converted in catalysts into hydrocarbons with longer chains (Fischer-Tropsch synthesis), which can be directly used as fuels or further processed in refinery processes.

Within TMFB research group, an innovative approach of using nature's synthesis capability to convert and modify these biopolymers only as far as it is needed for using them as fuel is pursued. To do so, methods are developed for the specific chemical conversion of biomass. First of all, the lignocellulose must be split up into its components cellulose, hemicellulose, and lignin. Reaction media such as ionic liquids are used to break up these components. Ionic liquids are compounds that - such as table salt - are made up of positively and negatively charged ions, but have a melting point of below 100 °C due to their molecular structure. Using various catalytic conversion methods, the individual components can then be converted into the desired fuel molecules. Figure 2 shows possible methods of converting organic matter into possible fuel compounds [2, 20].

From the schematic it becomes clear that, depending on the chosen pathway and the targeted intermediate/platform molecule a large variety of different fuel compounds can be produced from cellulosic biomass. The here discussed fuel candidate 2-methyltetrahydrofuran (2-MTHF) can be produced catalytically via itaconic acid, while di-n-butylether (DBE) can be etherified from butanol.

METHODOLOGY AND APPROACH

The primary aim of this work is to understand the impact of different generations of pure biofuel candidates on oxidative reactivity of soot and its combustion behaviour

inside Diesel Particulate Filters (DPF). The soot samples were collected from a modern high efficiency diesel combustion system, conforming the requirements set for EU 6 emission limits (this combustion systems meets Euro 6 emissions for engine out raw NO_x and an application of DPF is necessary for meeting PM emissions). The DPF samples loaded with soot on the engine test bench were subjected to Thermo-Gravimetric Analysis (TGA) for studying its oxidative reactivity. Furthermore in order to understand the kinetics of soot oxidation behavior, the soot loaded DPF samples were subjected to Temperature Programmed Oxidation (TPO) in a Laboratory Gas Test Bench (LGB). The fuels, engine, and sample acquisition procedures are described in following section.

Experimental Apparatus and Test Conditions

Single cylinder research engine

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. This is a technology demonstrator from FEV to represent a High Efficiency Combustion System (HECS), designed for future passenger car applications [22, 23, 24]. The hardware enhancements include high fuel injection pressures, as well as stronger charge air and exhaust gas recirculation cooling, in order to achieve low intake charge temperatures even at the highest EGR rates.

To optimize the flow characteristics, one intake port is designed as a filling port, the second one as a tangential port. Creating the charge movement is supported by seat swirl chamfers on both intake valves. The layout of the combustion chamber geometry shows a conventional recess shape, which was further optimized together with the nozzle geometry (8-hole, $ks=1.5$) in order to achieve the optimum air utilization. The recessed valves make it possible to eliminate valve pockets in the piston and thus further improve the flow quality near the recess. A compression ratio of 15:1 was selected to represent acceptable peak pressures in spite of the increased charge density. The combustion system reaches a specific output of 80 kW/l at maximum peak firing pressures under 190 bar. An advanced common rail system is used as fuel injection system; the injector can quickly open and close the nozzle needle at a maximum injection pressure of 2000 bar. For the engine bench investigations with using 2-MTHF, a Bosch-CP3 high pressure fuel pump was used. Due to the polarity of the fuel, rubber seals and O-rings were replaced with Viton®. Furthermore, a lubricity additive was used to account for poor lubrication and corrosive characteristics of the fuel. With these measures, no further problems were observed in the fuel injection system during the present investigations. [21]. Reducing compression ratio, using a higher maximum cylinder and rail pressure, as well as

improved EGR cooling makes lowest particulate emissions possible, and as a result the research engine meets the Euro 6 standard. (Engine out raw NO_x emissions Euro 6 level and an application of DPF is necessary for meeting PM emission limit) The performance of the single-cylinder diesel engine thus exceeds that of currently available production engines. These technical enhancements will also be implemented in future diesel engines. Table 1 shows a summary of the details of the test engine used. Additional information on the single-cylinder research engine can be found in various publications [22, 23, 24].

Table 1. Hardware specifications for the research engine

Parameter	Units	Specificatio
Emission Status	-	Euro 6
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

Engine operation

The experiments for particulate measurements and sampling were conducted under constant engine operating conditions. Based on the New European Driving Cycle (NEDC), the maximum Indicated Specific NO_x (ISNO_x) emissions were estimated for stated part-load point. For all the fuels the rate of recirculated exhaust gas was chosen in a way that an identical indicated specific raw NO_x-emission level of Euro 6 (0.75 g/kWh) is achieved. This level represents a modern, Euro 6 conform combustion. Investigations on a chassis dynamometer confirmed these estimated targets [24].

The centre of combustion was maintained constant for all the fuels. This was done by adjusting the fuel injection timing for each fuel so that the centre of combustion (CA₅₀) was always located at the same degree crank angle in the engine cycle, chosen to maximise the engine efficiency, regardless of the fuel properties. In general, fuels with lower cetane number (CN) and longer ignition delay require earlier fuel injection timing to maintain the centre of combustion (CA₅₀) at the required crank angle position.

Both the equal CA₅₀ as well as the identical raw ISNO_x-level guaranteed, from an emission standpoint, constant boundary conditions that allow a basic analysis of the different behavior of all the investigated fuels. The boundary conditions for the mentioned load point are listed in Table 2.

Table 2. 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 (CA ₅₀) / °CA (ATDC)	10.8
Estimated Euro 6 NOx Emissions/ g/kWh	0.75

Table 3. Designation of investigated fuel compounds

Designation of Fuel	Details of Fuel Compounds
B0	100 % European diesel (w/o FAME)
RME	100% Rape-seed oil methyl ester (B100)
2-MTHF/DBE	70 % v./v. 2-Methyl-tetrahydrofuran (2-MTHF) + 30 % v./v. Di-n-butyl ether (DBE)

Test fuels

Three different diesel fuels were used for the present investigations. Petroleum based diesel fuel was used as reference for baseline tests and other two fuels are derived from biogenic sources.

EN 590 Diesel available in Germany at fuelling stations contains approximately 5-7% FAME. However, for the present studies we used european quality diesel (without FAME) as baseline reference fuel instead of EN 590 diesel fuel to avoid any influence of FAME content (in particular oxygen content) on particulate matter characteristics.

First biogenic fuel candidate selected for this study is a commercially available first generation of biofuel also known as biodiesel or FAME. For the present investigations FAME used, was a Rapeseed Oil Methyl Ester (RME) that conform to EN 14214 specifications. It consists of saturated as well as unsaturated fatty acids with 12 to 22 carbon atoms. RME is already used as fuel either in pure form or as blend with petroleum based diesel.

The second biogenic fuel candidate chosen for this study is a third generation of potential biofuel candidate named 2-methyltetrahydrofuran (2-MTHF). This molecule forms an aliphatic ring structure and contains oxygen that directly originates from the glucose the fuel was derived from. Due to its very low self-ignitability (Cetane Number 15) it was blended with 30 vol% of Di-n-Butyl Ether (DBE, Cetane Number 100) to improve its ignition behavior. With regard to the toxicity and biodegradability of 2-MTHF and DBE, some previous studies on “rats and mice” as well as the investigations conducted by TMFB research group have revealed that these fuels have no detectable toxicity issues.

The toxicity of these fuels is lower than gasoline fuel derived from crude petroleum oil [25-26].

The above described fuel compounds used in the test program is designated as shown in Table 3:

Figure 3 illustrates the main fuel properties of the investigated test fuels. Petroleum based diesel fuel (B0) and RME (B100) has similar cetane numbers. However biofuel candidate 2-MTHF/DBE has lowest cetane number, which will lead to higher ignition delay periods and hence more homogeneous mixture formation is expected with this fuel. With regard to oxygen content in the fuel, B0 fuel has ~0% oxygen whereas both the biofuel candidates contain oxygen in their molecular structures. RME (B100) has typically 10.8 w% oxygen whereas 2-MTHF/DBE fuel has higher oxygen content (~ 15.5 w%). The higher oxygen content in the fuel molecule helps to achieve higher soot reduction potential. Amongst the investigated fuels only B0 has aromatics. Both the biofuel candidates used in the present work do not contain any aromatics. This will offers further advantages in soot reduction potential of biomass derived fuel candidates.

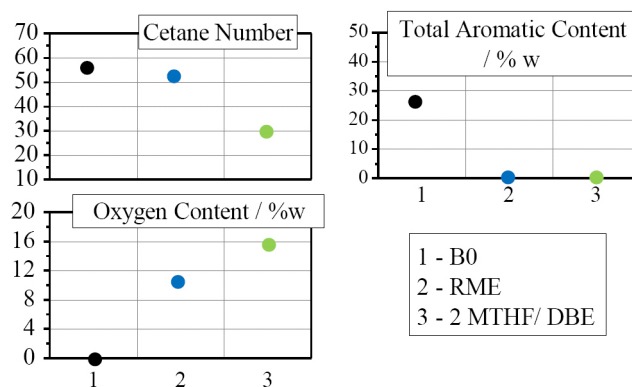


Figure 3. Main properties of investigated fuels as per standards prescribed in EN 590 specification

The distillation curve of a fuel describes its evaporation behavior at different temperatures. Figure 4 illustrates the boiling behavior of investigated test fuels. It is evident that B0 fuel has a wide range of distillation (~ 200°C-330°C) behavior. This is mainly due to the fact that petroleum based diesel fuel (B0) is composed of a mixture of approximately 200 different types of hydrocarbons. On the other hand RME (B100) shows a flat distillation behavior (~ 350°C-360°C) with highest boiling temperatures amongst all the test fuels. This may lead to relatively poor evaporation characteristic of