

Effects of Oxygenated Fuels on Combustion and Soot Formation/Oxidation Processes

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ABSTRACT

The Leaner Lifted-Flame Combustion (LLFC) strategy offers a possible alternative to low temperature combustion or other globally lean, premixed operation strategies to reduce soot directly in the flame, while maintaining mixing-controlled combustion. Adjustments to fuel properties, especially fuel oxygenation, have been reported to have potentially beneficial effects for LLFC applications. Six fuels were selected or blended based on cetane number, oxygen content, molecular structure, and the presence of an aromatic hydrocarbon. The experiments compared different fuel blends made of n-hexadecane, n-dodecane, methyl decanoate, tri-propylene glycol monomethyl ether (TPGME), as well as m-xylene. Several optical diagnostics have been used simultaneously to monitor the ignition, combustion and soot formation/oxidation processes from spray flames in a constant-volume combustion vessel. Ignition delay times, lift-off lengths and soot KL extinction levels for the six fuels have been measured at in-cylinder conditions relevant to modern diesel engines.

The results show that blending an alkane with an oxygenated fuel of similar cetane number has no noticeable impact on ignition delay while only slightly affecting lift-off length, with longer flame stabilization distance for blends with higher oxygen content. Longer ignition delays and lift-off lengths were observed when m-xylene was added to an oxygenated blend. Methyl decanoate showed both longer ignition delays and longer lift-off lengths than the other fuels, consistent with its lower cetane number. These experiments show that there is no direct linear relationship between ignition and flame stabilization when burning fuels with different chemical compositions. Blends using TPGME as oxygenated component achieved lower soot levels compared to methyl decanoate, with the best performance as soot is concerned being achieved with a 50/50 blend of TPGME and n-hexadecane. Aromatic hydrocarbons (here m-xylene), rather than paraffinic hydrocarbons, blended with an oxygenated fuel can negate the benefit of oxygenation with regard to a reduction in soot levels, despite producing longer lift-off lengths.

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INTRODUCTION

Direct-injection (DI) diesel engines offer great potential for high-efficiency operation. However, engine manufacturers are facing difficulties to meet the emission regulations set by the different governments. A large part of the problem comes from particulate matter (PM) emissions (mainly soot) formed in the fuel-rich regions of the combusting fuel jets. Regulations calling for PM, nitrogen oxides (NO_x), unburned hydrocarbon (UHC) and carbon monoxide (CO) emission reductions have led engine manufacturers to use exhaust after-treatment systems, with diesel particulate filters to control PM emissions and other complex and expensive systems to control NO_x , HC and CO emissions. These systems not only increase the cost of diesel engines, but have also been reported to negatively impact fuel economy [1].

Advanced combustion strategies that eliminate soot or exhaust PM directly in the combustion chamber have therefore been actively pursued over the past decade. A significant amount of research has been conducted on Low Temperature Combustion (LTC) due to significant benefits in PM and NO_x emissions. But despite some clear advantages, the technology showed significant challenges with load and noise limitations as well as increased HC and CO emissions [2]. Homogenous Charge Compression Ignition (HCCI) has also received vast interest in the last decade because of the mainly soot-free combustion the strategy can achieve. The main problem of HCCI comes from control because in this mode of combustion, fuel injection and combustion are no longer connected. This loss of control on combustion can result in unacceptable

combustion noise and stability issues [3], requiring the engine control designer to switch to conventional diesel combustion in order to achieve the desired loads.

Leaner lifted-flame combustion (LLFC) [4] is a promising alternative strategy to LTC involving mixing-controlled diesel combustion that achieves soot-free flames by controlling the fuel - charge gas equivalence ratio of the standing premixed auto-ignition zone. Experiments have shown that LLFC can produce a soot-free flame when the combustion occurs at equivalence ratios less than or equal to approximately two on the fuel jet centerline [4]. One of the unique features of LLFC, with respect to LTC for example, is that heat release remains directly coupled to the rate of mixing. In other words, heat release with LLFC can still be controlled by adjusting injection timing and rate whereas LTC heat release is mostly affected by chemical kinetics. Better control of the combustion event is achieved when injection and ignition are coupled, whereas limited control is encountered when combustion starts after the end of fuel injection for instance, as can happen in LTC operation.

Pickett and Siebers [5] provided the basis for LLFC, as they found that enhanced mixing upstream of the point of high-temperature combustion (the lift-off length) can produce completely soot-free diesel combustion. The LLFC strategy also showed promise in overcoming the well-known soot/ NO_x tradeoff. Specifically, exhaust gas recirculation (EGR) was used to reduce in-cylinder oxygen concentration thereby lowering the diffusion flame temperature. The lower temperature resulted in less NO_x as well as a longer flame lift-off length. Regardless of the lower oxygen concentration, the longer lift-off length improved fuel-to-oxidizer mixing, resulting in soot-free combustion. The simultaneous attainment of soot-free conditions at reduced flame temperatures offers the potential for simultaneous soot and NO_x reduction in the combustion chamber, much like premixed LTC such as HCCI or PCCI. However, because the heat release remains controlled by the injection event, rather than chemistry, LLFC is expected to extend the operating range beyond that achievable by the other strategies cited above thanks to the robustness of this strategy to noise factors influencing ignition delay and combustion.

Figure 1 is a schematic of the conceptual model of the LLFC strategy. Because it is a requirement of LLFC to extend the lift-off length, the maximum liquid penetration distance of the spray (LL) is expected to be shorter than the flame stabilization height (H). The mixture preparation to achieve equivalence ratios below two is promoted by parameters that move the flame farther downstream. Lowering the ambient temperature and oxygen concentration, or increasing the fuel injection pressure may lower equivalence ratio and allow successful LLFC operation. The use of small injector nozzle orifices has also been observed to help achieving LLFC condition by increasing the entrainment of air relative to the rate of the fuel injected [6].

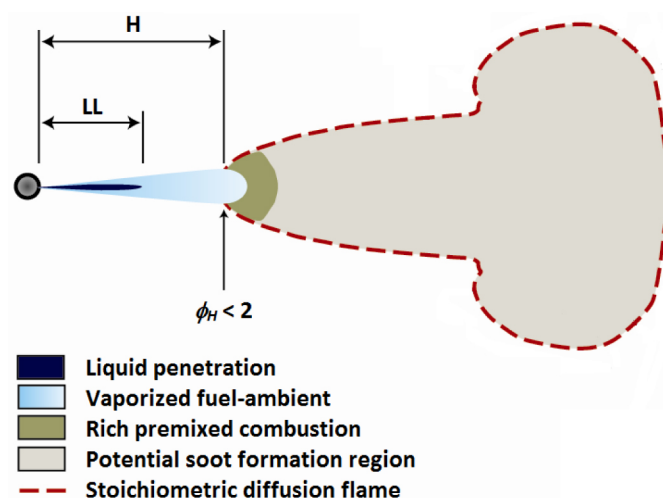


Figure 1. Schematic of the conceptual model of the Leaner Lifted-Flame Combustion (LLFC) strategy. H is the lift-off length, LL the maximum liquid penetration distance and ϕ_H is the jet centerline equivalence ratio at the lift-off position (H).

Polonowski et al. [4] investigated the applicability of the LLFC strategy in a heavy-duty diesel engine. They noted that sustained soot-free LLFC was challenging to achieve in the engine, but that the use of moderate to high EGR rates with a two-hole injector attained sustained soot-free LLFC. For higher flow injectors (6 and 10 holes), LLFC was approached but not sustained because of the re-entrainment of hot combustion products and the proximity coupling of the reacting jets. These two parameters effectively reduced the lift-off length, thus increasing equivalence ratio at H, inducing soot formation.

Fuel properties affect combustion and thus may help extend the possible engine operating range under LLFC mode. For example, fuel oxygenation changes the equivalence ratio of the fuel - gas mixture because of the oxygen available in the injected fuel and may offer another pathway to reducing soot formation or enhancing soot oxidation. As an example, low PM and NO_x levels, compatible with current emission standards, have been demonstrated with a fuel with an oxygenation level of almost 30 % by mass [7]. This was achieved by using high EGR levels, possible because oxygenated fuels have been seen to present high tolerance to EGR. Combustion control is also affected by fuel properties; the degree of stability or control of combustion depends upon ignition delay, with shorter ignition delays directly correlating with better combustion control. At the same time, Pickett and Siebers [8] observed that ignition quality of jet flames generally affects flame stabilization. Longer ignition delays tend to correspond to longer lift-off lengths and vice-versa, even though a direct correlation has not been found. In summary, the ideal fuel for successful LLFC application would yield a relatively short ignition delay to enhance control of combustion, but it would maintain a long lift-off length to make combustion leaner. Fuel oxygenation can also enhance LLFC by driving mixtures at the lift-off length to lower equivalence ratios.

The first objective of the present study was to test different oxygenated fuels in a constant volume combustion vessel and compare them to a baseline (normal alkane) fuel. Another goal was to identify and understand the fuel properties that inherently extend the operating range within the LLFC requirements. The combustion vessel was optically accessible and capable of simulating high temperatures and pressures typical of current diesel engine in-cylinder conditions. Several simultaneous optical diagnostics were employed to measure ignition delay, lift-off length as well as soot levels in the flame. The results of the different experiments (parameters) are presented and discussed for the six fuels tested under a wide range of ambient temperatures.

EXPERIMENTAL SETUP AND PROCEDURES

This section presents the experimental approach applied to this study, detailing the different fuels used. Then, the combustion vessel and injection system employed to introduce the fuel into well-controlled ambient conditions relevant to diesel combustion, with specific focus on the applicability of the LLFC mode of operation are described. Finally, the diagnostics applied in this study to understand the impact of the different fuels on commonly used parameters as well as time resolved soot data are detailed.

Fuels

Six different fuels were used to help understand which fuel properties are most likely to produce leaner mixtures at the flame lift-off length that fall within the LLFC requirements. Three fuels were blends of tri(propylene glycol) monomethyl ether (TPGME) and n-hexadecane, identified as G15, G33 and G50; with the last two digits indicating the percentage of TPGME in the blend, by volume. A fourth fuel included an aromatic hydrocarbon (identified as G50A), consisting of a 50/50 volume percent blend of TPGME and a diesel surrogate fuel, the latter composed of 77 % n-dodecane and 23 % m-xylene by volume. This diesel surrogate fuel was previously characterized by Kook and Pickett under similar conditions [9]. A fifth fuel, methyl decanoate (MD), provided a different oxygenate chemical structure and was a surrogate for traditional biodiesel fuel. The sixth fuel was a neat n-alkane without oxygenate: n-dodecane (identified as C12); this fuel served as the baseline reference fuel in this study. The molecular structures, names, abbreviations used in this document and chemical formulae of the different fuel compounds used in this work are shown in Fig. 2.

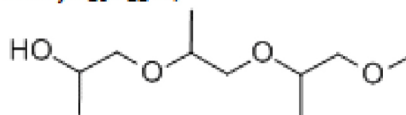
Selected fuel properties relevant to this study are presented in Table 1. The values of the boiling point listed here refer to the boiling temperature of the heaviest component (with the highest boiling temperature) of the fuel blend. The cetane ratings listed in this table were derived using a Fuel Ignition Tester (FIT - ASTM D7170). The derived cetane number (DCN) values for the n-hexadecane - TPGME fuel blends are quite similar, and higher than the rest of the fuels tested. G50A and

n-dodecane have similar DCN, while methyl decanoate has the lowest DCN of all fuels. The oxygen ratio (Ω) of a fuel is defined as the amount of oxygen (moles or mass) in the fuel divided by the amount of oxygen required to convert all fuel elements to products of complete stoichiometric oxidation, also called saturated stoichiometric products (SSPs) [10]:

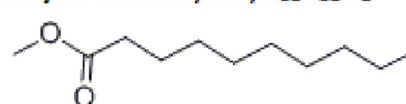
$$\Omega = \frac{n_O}{2n_C + \frac{1}{2}n_H} \quad (1)$$

With n_C , n_O and n_H the number of carbon, oxygen and hydrogen atoms in the molecule, respectively. Note that the fuel selection was partly driven by varying oxygen content (oxygen ratio) for the alkane - oxygenated fuels, while keeping similar cetane numbers.

Tripropylene Glycol Monomethyl Ether TPGME, C₁₀H₂₂O₄



Methyl Decanoate, MD, C₁₁H₂₂O₂



n-hexadecane, C16, C₁₆H₃₄



n-dodecane, C12, C₁₂H₂₄



m-xylene, A, C₈H₁₀

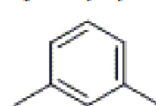


Figure 2. Names, abbreviated names, chemical formulae and molecular structures of the fuel molecules used in this work.

The carbon-to-hydrogen ratio (C/H) is another useful metric when comparing fuel impact on combustion processes. Because of the presence of oxygen atoms in an oxygenated fuel, one or more C-atoms are partially oxidized. To take this partial oxidation process into account and still deliver a comparable measure of C/H ratio, Mueller et al. [11] proposed an effective carbon-to-hydrogen ratio (C/H)_{eff}, defined as follows:

$$\left(\frac{C}{H}\right)_{eff} = \frac{n_C - \frac{1}{4}n_{O_2} - \frac{1}{2}n_{O_2=}}{n_H} \quad (2)$$

In Eq. 2, n_{O_2} and $n_{O_2=}$ represent the single and double-bonded oxygen atoms, in that order.

Table 1. Fuel properties at 20°C - 1 atm. relevant to the study. MW is the molecular weight, LHV is the lower heating value and DCN is the derived cetane number obtained by Fuel Ignition Tester (FIT) measurements.

FUELS	G15	G33	G50	G50A	MD	C12
MW [g/mol]	223	219	216	169	186	170
Density [g/cm ³]	800	835	869	859	871	749
Boiling point [†] [°C]	287	287	287	287	224	216
LHV [MJ/kg]	41.5	38.5	35.8	35.5	37.5	44.1
DCN (FIT)	108	110	112	88	48	87
O ₂ ratio (Ω) [%]	1.9	4.3	6.5	5.0	6.1	0.0
(C/H) _{eff}	0.46	0.45	0.44	0.53	0.47	0.50

[†] Boiling point refers here to the boiling temperature of the heaviest component in the fuel blend.

Combustion Vessel and Injection System

The fuels were investigated by visualization of the fuel injection and combustion processes of the spray flames in a high-pressure (up to 35 MPa), high-temperature (up to 1400 K), optically-accessible constant-volume combustion vessel. The targeted operating conditions of this study are typical of those encountered inside the combustion chamber of modern diesel engines, spanning the different operating conditions found in the common diesel combustion strategies (conventional, LTC, LLFC, etc.). The vessel is a cube with dimensions of approximately 100 mm on each side, each side being fitted with a modular window. Sapphire windows provide optical access to the spray event from four sides, offering multiple perspectives for simultaneous diagnostic operations. The other sides of the cube are for the injector and the spark plug

system. While in operation, the temperature of the entire vessel is maintained at 188 °C by electric heaters. The elevated temperature and pressure conditions present in the chamber are achieved by spark-igniting a combustible gas mixture, as done in other pre-burn type vessels. The spray event (i.e., fuel injection) takes place when the desired thermodynamic conditions are achieved after a short cool-down period.

The fuel was injected via a common-rail, solenoid actuated diesel fuel injector equipped with a single, axially-drilled 90-μm diameter orifice (# 210370) belonging to the set of Spray A injectors from the Engine Combustion Network (ECN). The nozzle features a conically-shaped orifice with a *k*-factor of 1.5. More information about the full geometry and hydraulic characteristics of the ECN Spray A injectors is available in Kastengren et al. [12] or on the ECN website (<http://www.sandia.gov/ecn/cvdata/targetCondition/injectorNozGeom.php>). The injection pressure was set to 150 MPa and the electronic command to the injector was kept constant at 4000 μs long, corresponding to an actual injection hydraulic duration of approximately 6 ms.

In addition to the standard ambient condition recommended by the ECN: Spray A (Temperature: 900 K - Density: 22.8 kg/m³ - Oxygen concentration (vol.):15 %), we performed a parametric study by changing ambient temperature (from 750 to 1200 K) and density (from 7.6 to 22.8 kg/m³) to evaluate the effects on combustion and soot formation/oxidation. Other conditions such as varying injector orifice diameter or oxygen concentration were also tested.

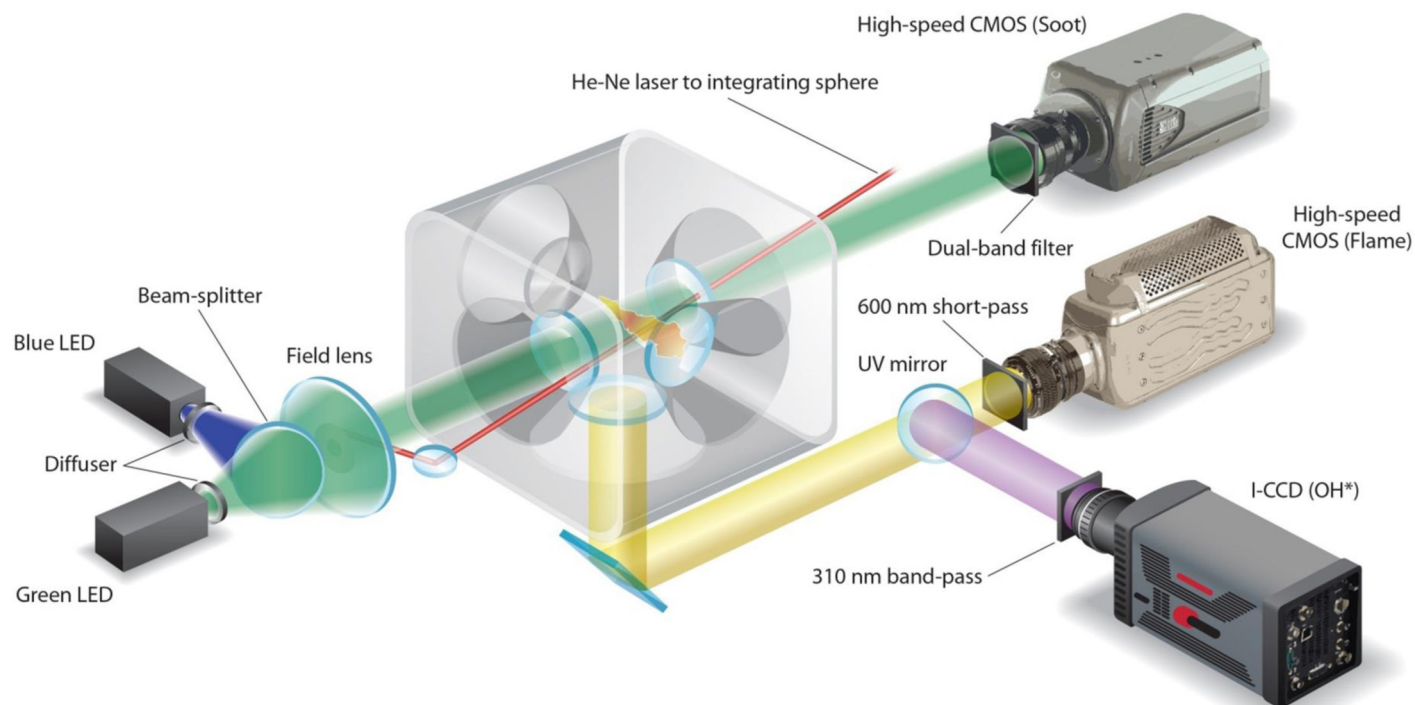


Figure 3. Schematic of the experimental arrangement showing the vessel in the center, the diffused back-illumination lighting system, and multiple cameras on the right.

Optical Diagnostics

Several diagnostics have been used simultaneously to visualize and understand the relationship between high temperature reactions and soot formation/oxidation for different fuels. Commonly used parameters to describe lifted-flame combustion, such as ignition delay or lift-off length were measured while a quantitative imaging diagnostic was used to measure soot levels in the flame as a function of time. A schematic of the multiple optical diagnostics applied in this study is provided in [Figure 3](#).

OH-Chemiluminescence Imaging

An intensified CCD camera (Princeton Instruments, PI-Max) equipped with a 308 nm (10 nm FWHM) band-pass filter measured excited state OH-chemiluminescence (OH*) in the spray flames [13]. The short-lived chemiluminescent emission of the OH molecules dominates in the lift-off length region as it results from the high-heat-release reactions, which are representative of the lifted diffusion flame [14], making the OH* a useful metric to detect the location of the flame. The camera and intensifier gates were left open for approximately 4 ms, starting after auto-ignition of the fuel jet and lasting until the end of injection. This resulted in time-averaged images without the impression of turbulent fluctuations.

In accordance with previous results from similar spray flames, OH-chemiluminescence stabilizes at a defined distance from the injector orifice, called the lift-off length. The intensity signal along the spray axis is characterized by a steep gradient followed by a plateau region [14]. As it has been defined in the past, the lift-off length corresponds to the axial distance between the orifice exit and the location where the intensity of the OH-chemiluminescence is 50% of the maximum prior to this "plateau" or "knee" region. One condition was taken as reference (Spray A) and the 50% threshold from this condition was used as the OH-chemiluminescence intensity threshold when evaluating sprays combusting under different temperature conditions, as suggested by Higgins and Siebers [14].

High-Speed Flame Luminosity

Natural luminosity emitted by the flame reactions and soot radiation has been acquired with a high-speed CMOS camera capturing the event at 30,000 frames per second (fps). The camera was equipped with a 600-nm short-pass filter and a heat absorption (KG3) filter to suppress the high intensity soot luminosity. Note that the acquired wavelength range is wide and a large amount of soot radiation is recorded by the camera, but the objective of the filters is to take advantage of the camera's dynamic range to detect ignition and resolve lift-off length with time. The results of the high-speed flame luminosity can be used to support the results from the OH-chemiluminescence imaging for the lift-off length, in addition to providing a time-resolved flame stabilization location. Because of the sensitivity of the high-speed camera, ignition location and timing were obtained by extending the exposure time to the maximum available at the

camera frame rate (32.3 μ s). Ignition location and timing with high-speed CMOS cameras have been demonstrated in past works under similar conditions [13].

The image processing methodology to detect ignition location and timing as well as lift-off length as a function of time is quite straightforward. The analysis carried out by our group [13, 15] showed that low-temperature reactions preceding high-temperature ignition would either be below the detection limit of the instrument or in the very low dynamic range of the camera with similar optics to those used in this study. In addition, they observed that the intensity of the broadband luminosity emission increased by about three orders of magnitude from cool-flame to high-temperature ignition. The results presented further have been processed using the threshold defined as 50 % of the levelling-off intensity in the lift-off region to detect ignition. With dynamic background correction outside of the flame, this same 50 % threshold was used to detect flame boundary and extract flame lift-off location as well as flame propagation and length, provided the global flame is kept within the visualization window. This method has been seen to provide good agreement with the processing technique applied to the OH-chemiluminescence imaging to quantify lift-off length.

Diffused Back-Illumination Extinction Imaging

Flame generated soot particles have been measured using a high-speed, two-dimensional extinction method. Even though the dual wavelength capabilities of the technique have not been used in this work, the diagnostic has been designed and operated with two illumination wavelengths. The main components of this diagnostic consist of high-output, ultra-fast, deep blue (406 nm, 17 nm FWHM) and green (519 nm, 34 nm FWHM) LEDs, a dichroic beam splitter, engineered diffusers, a field lens, and a high-speed camera equipped with a combination of filters to efficiently collect the LED emission while blocking as much flame luminosity as possible. This filter combination transmits from 375 nm to 565 nm, passing the full spectra of both LEDs while blocking flame luminosity between 475 and 500 nm, resulting in a dual band-pass filter. A neutral density filter of OD 1.9 was added to further reduce the intensity of broadband flame luminosity. The engineered diffusers have a 50° circular pattern and the field lens is a Fresnel type with a focal length of 152 mm. The diffusers and Fresnel lens work together to produce a large (60-mm diameter) uniformly illuminated background of diffused light with minimal intensity losses (more than 90% transmission). This light source setup directs the diffused illumination toward the spray plane with a quasi-Lambertian distribution, resulting in minimal light extinction induced by beam steering through the chamber and spray flame because of density (temperature) gradients. Note that only the extinction measured from the shorter wavelength LED (deep blue: 406 nm) is utilized in this study. During these tests, the camera was acquiring images at a frame-rate of 82,484 fps. The ability of this diagnostic to measure extinction at two incident wavelengths along with the need to collect flame emission without LED illumination at