

Soot Volume Fraction and Morphology of Conventional, Fischer-Tropsch, Coal-Derived, and Surrogate Fuel at Diesel Conditions

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ABSTRACT

Future fuels will come from a variety of feed stocks and refinement processes. Understanding the fundamentals of combustion and pollutants formation of these fuels will help clear hurdles in developing flex-fuel combustors. To this end, we investigated the combustion, soot formation, and soot oxidation processes for various classes of fuels, each with distinct physical properties and molecular structures. The fuels considered include: conventional No. 2 diesel (D2), low-aromatics jet fuel (JC), world-average jet fuel (JW), Fischer-Tropsch synthetic fuel (JS), coal-derived fuel (JP), and a two-component surrogate fuel (SR). Fuel sprays were injected into high-temperature, high-pressure ambient conditions that were representative of a practical diesel engine. Simultaneous laser extinction measurement and planar laser-induced incandescence imaging were performed to derive the in-situ soot volume fraction. From experiments, it was found that fuels with long lift-off length generally produce less soot but fuel molecular structure also affects soot formation. For instance, JP fuel with the longest lift-off length among tested fuels showed higher soot than JS because of higher cycloparaffinic content. Attributed to variations in both lift-off length and molecular structure, the level of total soot within the fuels jet in decreasing order was D2=SR>JW>JP>JC>JS. Further details of the soot processes were clarified by sampling the soot particles from within the reacting jet by means of a thermophoretic probe, with subsequent analysis by transmission electron microscopy (TEM). Analyzed TEM images of soot particles showed a marked variation in the soot particle structures depending on the fuel type and were consistent with the soot volume fraction trend.

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INTRODUCTION

The usage of alternative fuels in diesel engines has long been of interest owing to environmental concern and fear of oil depletion. Finding affordable and sustainable feedstocks is critical in this regard. As new fuels emerge with various chemical compositions and physical properties, questions arise about how these fuels will perform in modern diesel engines. In-cylinder pressure and engine-out emissions measurement provide an assessment about the impact of fuel on overall engine performance and compatibility with existing fuel injection systems.

Of particular interest are particulate matter (PM) emissions that have negative impacts on exhaust after-treatment system [1] and, more importantly, human health and environment. Health studies have shown that diesel PM can accumulate in the respiratory system and cause various

health problems [2]. Soot particles, as a major portion of atmospheric PM [3], are also suspected to cause global warming [4]. Therefore, the need to reduce soot/PM exhaust emissions from engines is clear. Over the past 20 years, emissions regulations for diesel engines have required PM emissions reductions by a factor of 30, with simultaneous reduction in the emission of nitrogen oxides (NO_x) by a factor of 5. The recently finalized European regulations require all new diesel engines to achieve an additional emissions reduction of more than 50% compared to the Euro 5 standard by 2014 [5].

Many researchers have investigated the effect of fuel molecular structure on soot and PM emissions when alternative fuels are used in a diesel engine. For instance, tailpipe soot emissions increase with increasing aromatics content [6, 7, 8, 9, 10, 11, 12, 13, 14]. This is consistent with

the result from simplified laboratory flame where single carbon bonds are found to produce less soot than fuels with double or triple carbon-carbon bonds [15]. Typically in low aromatics fuels, the aromatics are replaced by paraffins that have lower sooting tendency [6, 7, 8, 9]. Among paraffins, cyclo-paraffin (e.g. naphthenes) produces more soot than iso- or normal-paraffin [6].

Despite numerous efforts, fuels effects on engine-out soot emissions require further investigations because of the complexity of diesel engine combustion. Differences in molecular structure and chemical composition from various fuels not only impact in-cylinder soot formation directly, but the distillation characteristics and ignition quality (e.g. cetane number). Fuels with high cetane number have shorter ignition delays resulting in increased soot formation due to insufficient fuel-ambient mixing before the onset of combustion [10]. This complexity produces uncertainty as to which effect is more significant for soot formation. For example, lowering aromatic content causes a cetane number increase, if replaced with normal paraffins [6]; lighter hydrocarbon components generally have lower cetane number [11]; and the position of hydrogen on hydrocarbon molecules affects the cetane number [15]. As such, the fuel molecular structure and cetane number cannot be considered separately. This may explain why there are different results from engine-out emission tests, some of them are directly opposite to each other. For instance, many studies show lower NO_x emissions when using a higher cetane number fuel [10, 11], which prompted fuel regulations in California, Asia, and Europe to require a higher cetane number. Considering a soot-NO_x trade-off, the high cetane number fuel should cause increased soot emissions as in Refs [9, 16, 17]. However, a reduction in soot emissions [7, 18] and unburned hydrocarbon [8, 15] with high cetane number fuels is also reported, likely due to fuel molecular structure effects. For example, highly oxygenated fuels with low sooting tendency appear to show no tradeoff in soot emissions, allowing the use of very high exhaust gas recirculation (EGR) to control NO_x emissions below regulation levels [19, 20]. Accordingly, care should be taken to interpret the results from the engine tests due to confounding effect of fuel molecular structure on soot formation and cetane number. Moreover, engine operating conditions such as combustion phasing, compression ratio, engine size, and load condition should be considered all at the same time.

While the importance of engine tests in fuels research cannot be discounted, there are difficulties drawing conclusions from a change to a single fuel property that simultaneously changes other fuel properties. Therefore, lack of fundamental understanding in fuel jet flame and its soot process leaves many details unknown, which requires another iteration of a trial-and-error-type engine test. To address this issue, laser-based diagnostics of in-cylinder combustion and soot formation have been applied. For example, using a laser extinction technique, Musculus *et al.* [21] reported that diesel

fuel yields much higher in-cylinder soot than paraffinic fuels or oxygenated fuels, consistent with the aforementioned soot emissions trend. Pickett and Siebers [22, 23] studied the fundamental details of fuel jet soot distribution at diesel-like ambient conditions using laser extinction and planar laser-induced incandescence (PLII). This direct optical soot measurement determines the in-situ soot volume fraction of reacting fuel jet. For example, the fuel jet soot level increases with increasing ambient temperature, increasing ambient density, decreasing injection pressure [22], or increasing nozzle-hole size [23] when using regular diesel fuel. Flame lift-off length, which allows different levels of fuel-oxygen partial premixing, has an important effect on downstream soot formation, coupled with strong effects of temperature, pressure, and residence time on soot formation chemistry [22].

This database obtained for diesel fuel was extended later to include the effect of fuel type on soot processes [24, 25, 26]. In addition to lift-off length itself, the first-soot length (distance from the nozzle to the region of first soot formation) and soot inception time depend strongly on fuel molecular structure. These findings are summarized in Fig. 1, which illustrates the general soot processes in turbulent lifted jet flame [26], similar to that offered by Refs. [27, 28, 29]. This model is relevant to reacting fuel jets during the mixing-controlled combustion phase in a diesel engine. The schematic shows premixed combustion zones where high-temperature heat release is initiated, followed by a soot-precursor formation region and a soot-formation region. The mixing layer depicted as a dashed line shows regions of the jet where mixing with hot combustion products occur. A diffusion flame is formed at the stoichiometric location at the jet edge where reactions are the most intense and temperature is maximum. A region of soot-precursor oxidation or soot oxidation is shown between the diffusion flame and the soot-precursor formation or soot-formation regions. The distance between the lift-off length and the first soot formation displays significant fuel molecular structure effects that follow known trends for sooting tendency. An oxygenated fuel, which has no double carbon bonds but contains carbon-oxygen bonds, forms less soot precursors and requires longer time and distance before soot formation. Similarly, paraffinic fuel forms much less soot than diesel because paraffinic hydrocarbon fuels contain no aromatics or carbon double-bonded molecular species. Hence, paraffinic fuels have a larger difference between the lift-off length and first soot than that of diesel.

OBJECTIVES AND CONTRIBUTIONS

The preceding literature review has established that fuel composition *simultaneously* affects many different aspects of diesel combustion, including spray development and vaporization, ignition, lift-off length, soot precursor formation, soot formation, and so forth. Because of the existence of many confounding factors, one variable cannot

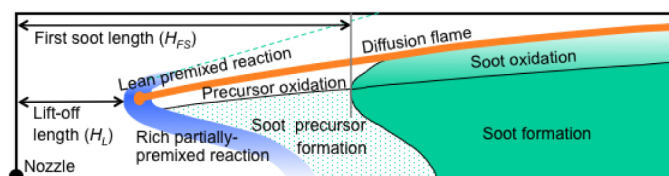


Figure 1. Conceptual sketch of soot processes near the lift-off length in turbulent lifted jet flame adapted from Pickett and Siebers' model [26]. The schematic shows one-half of an axisymmetric jet.

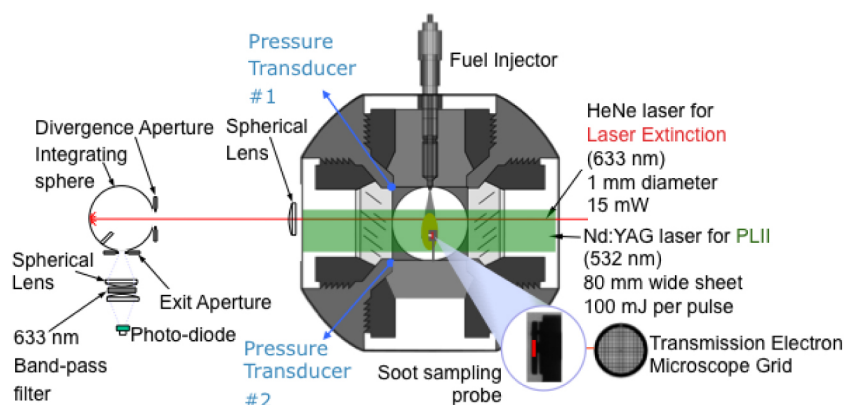


Figure 2. Schematic illustrating the combustion chamber, position of the fuel injector and pressure transducers, optical soot diagnostics setup of laser extinction and planar laser-induced incandescence, and soot sampling setup using the probe positioned inside the chamber and transmission electron microscope grid.

be changed without affecting the other, and it therefore becomes important to understand the entire pathway leading to soot formation and emissions. Ideally, the ambient and fuel injector conditions would be tightly controlled so as to focus solely on fuel effects. Furthermore, the study should include fuels from what are expected to be feedstocks of the future. Predictions show that synthetic fuels produced from gas and coal will account for about 25% of the transportation fuel supply in 2050 [30]. Thus, Gas-To-Liquid (GTL) and Coal-To-Liquid (CTL) fuels, with different resulting fuel structure, are of interest. Another example for diesel applications is kerosene-based jet fuels that have gained interest as a single fuel concept for military usage [31]. Fundamental data describing the spray and combustion processes for these fuels at controlled diesel-engine-like conditions is not yet available in the open literature. To bridge this gap, the spray development of these fuels was studied in our laboratory as detailed in Ref. [32]. In this study, we investigate the combustion and soot processes for the same fuels by offering the following experimentation:

1. Ignition, and lift-off length measurements in a well-controlled spray at relevant engine conditions.
2. Quantitative soot volume fraction and particle structure distributions within the reacting spray using optical and sampling techniques. Similar to Refs. [33, 34], direct soot particle sampling out of the reacting fuel jet is performed to develop a relationship between optically derived soot volume fraction and the morphology of soot particles.

Particularly for the quantitative soot volume fraction data and soot particle size and morphology, these data are unique because of the application at high-temperature, high-pressure conditions relevant to diesel combustion. The measurements also form a valuable database for improved combustion and soot modeling at relevant diesel conditions, and join with a previous database [24, 25, 26] built using the same facility over the last decade.

EXPERIMENTS

Experiments were performed using an optically-accessible, preburn-type, constant-volume combustion vessel where the ambient gases were controlled to mimic high-temperature and high-pressure conditions of practical diesel engines. Optical access allows measurements of OH chemiluminescence for lift-off length as well as laser extinction and planar laser-induced incandescence for soot volume fraction. Easy opening/closing of the chamber windows using a large-thread-type window holder also enabled to perform soot particle sampling using a probe containing transmission electron microscope (TEM) grid. The schematic in Fig. 2 depicts the combustion chamber, optical diagnostics setup, and soot sampling method.

FUELS

Six different fuels were tested at fixed injection and ambient conditions. The fuels consisted of the following: 1) No. 2 diesel ("D2"), an emissions-certification fuel with a

Table 1. Property of the fuels studied

FUELS	D2	JC	JW	JS	JP	SR*
	No. 2 Diesel	JP-8	World Average Jet A Blend	Fischer-Tropsch Fuel	Coal-Derived Fuel	Surrogate Fuel
T ₁₀ [°C]	211	170	180	167	192	
T ₅₀ [°C]	315	240	251	254	243	
T ₁₀₀ [°C]	350	266	274	276	270	216
Cetane Number	46	38	46	62	34	70
Lower heating value [MJ/kg]	42.975	43.228	43.2	44.138	42.801	43.33
Density at 15°C [kg/m ³]	843	812	806	755.9	870.2	778.9
C/H mass ratio	6.53	6.19	6.19	5.49	6.58	5.96
Stoichiometric Air/Fuel ratio	14.47	14.62	14.62	14.96	14.46	14.73
Aromatics volume %	27	11	19	0.4	1.9	23
Sulfur [ppm]	9	1	0	0	0	
Kin. Visc. (-20°C) [mm ² /s]	-	4.465	5.2	4.6	7.5	
Kin. Visc. (40°C) [mm ² /s]	2.35	~ 1.4				
Freeze Point [°C]	-	-57	-48	-51	-65	
Flash Point [°C]	73	47	51	45	61	

*23% *m*-xylene (C₈H₁₀), 77% *n*-dodecane (C₁₂H₂₆), volume-average properties are given except T_{100%} for *n*-dodecane (*m*-xylene boiling point is 139 °C).

cetane number of 46 and 27% aromatics; 2) conventional JP-8 (“JC”), a low cetane number fuel that can also be used to assess the use of aviation fuel using diesel engine hardware at diesel engine conditions; 3) a world-average aviation fuel (“JW”) which is an equal blend of five Jet-A fuel samples from different U.S. manufacturers, and with the same cetane number as D2; 4) a Fischer-Tropsch fuel (“JS”) characterized as fuel with minimal aromatics (0.4%) and high cetane number; 5) a coal-derived fuel (“JP”), a low cetane number fuel with low 1.9% aromatics but high (>90%) cyclo-paraffinic content; and 6) a surrogate fuel (“SR”), a mixture of 23% *m*-xylene (aromatics) and 77% *n*-dodecane. A list of fuel physical properties is given in Table 1. Additional information can be found in Ref. [35] in which Holley and co-workers performed an ASTM D2425 standard analysis for JW, JS, and JP fuels and provided a detailed composition data. The summary is outlined in Table 2. For the coal-derived fuel JP, note that the fuel creation process is not Fischer-Tropsch, but rather “co-coking” to produce cyclo-paraffins that are resistant to thermal breakdown [36]. Therefore, JS and JP have fundamentally different structure. Cyclo-paraffins are also more typical for oil-sands derived fuels, another future fuel source.

Table 2. Additional fuel composition data*

	JW	JS	JP
Paraffins (n- and i-)	55.2	99.7	0.6
Cycloparaffins	17.2	<0.2	46.4
Dicycloparaffins	7.8	0.3	47
Tricycloparaffins	0.6	<0.2	4.6
Alkylbenzenes	12.7	<0.2	0.3
Indans/tetralins	4.9	<0.2	1.1
Indenes	<0.2	<0.2	<0.2
Naphthalene	<0.2	<0.2	<0.2
Naphthalenes	1.3	<0.2	<0.2
Acenaphthenes	<0.2	<0.2	<0.2
Acenaphthylenes	<0.2	<0.2	<0.2
Tricyclic aromatics	<0.2	<0.2	<0.2

*Data from ASTM D2425 analysis [35]

COMBUSTION CHAMBER AND OPERATING CONDITIONS

A constant-volume combustion vessel was used to study soot processes of various fuels while ambient and injector conditions were fixed. A schematic of the vessel and optical measurement setups are shown in Fig. 2. The vessel has a cubic combustion chamber, 108 mm on a side. Sapphire windows are installed in three sides of the chamber, enabling

optical access. The operating conditions and injector hardware are summarized in Table 3. Experiments were performed at the specified ambient gas temperature and density in an environment with 15% oxygen. The ambient gas conditions were selected to mimic operating conditions for the latest generation of diesel engines that use moderate EGR and have minimal NO_x emissions. The 900-K temperature and 6-MPa pressure condition is the so-called “Spray A” condition of the Engine Combustion Network [37]. The 1000-K temperature and 6.7-MPa pressure was also examined as some fuels tested appeared to show near-zero soot formation at 900 K. Since increased temperature ambient is known to increase soot formation [22], a 1000-K condition was examined as well. The ambient density was fixed at 22.8 kg/m³ while temperature and pressure were varied.

Fuels were injected into the center of the chamber using a solenoid-driven common-rail diesel injector (Bosch second-generation) with an axially-drilled, single-hole nozzle. The nozzle was a mini-sac type and has a convergent, hydro-ground orifice (KS1.5/86 specification by Bosch). The nominal diameter of the orifice is 90 μm, with optical microscopy imaging showing an actual diameter of 90.8 μm. The injection pressure was set to 150 MPa for all fuels studied. A long 7-ms of injection duration was used to create a quasi-steady period of injection rate and combustion. A more detailed description of the facility and method of ambient preparation can be found in [37].

Table 3. Ambient and injector conditions

Ambient conditions	
O ₂	15%
N ₂	75.15%
CO ₂	6.23%
H ₂ O	3.62%
Molecular mass	29.24 g/mol
Pressure	6 and 6.7 MPa
Temperature	900 and 1000 K
Density	22.8 kg/m ³
Injector conditions	
Type	Bosch common-rail, 2 nd generation
Nozzle	Single-hole, KS1.5/86, mini-sac
Nozzle diameter	90 μm nominal
Injection pressure	150 MPa
Injection duration	7 ms

DIAGNOSTICS

Three optical diagnostics were performed simultaneously in this study: OH chemiluminescence imaging, planar laser-induced incandescence (PLII), and laser extinction measurement (Fig. 2).

OH chemiluminescence imaging was conducted to identify lift-off location of the reacting jet (setup is not shown

but the view field is as in Fig. 2). The method has been described previously [24, 26]. By using an intensified CCD camera (Xybion ISG-250) coupled with 310-nm band-pass-filter, a line-of-sight integration of OH chemiluminescence was imaged during the quasi-steady period of fuel injection. The camera exposure time was set to 3 ms to obtain time-averaged images after fuel jet development and ignition. An ensemble average of more than 20 injection cycles was used to determine the lift-off length for each fuel.

PLII images of soot are collected to analyze the location of soot along a thin plane at the jet axis. A high energy (100 mJ) laser pulse at 532 nm (SpectraPhysics Nd:YAG laser) was used for this measurement. The laser timing was set to 4 ms after the start of injection to image the soot spatial location for a steady jet. Figure 2 shows that the 80-mm wide and 100-μm thick laser sheet passes through the jet axis, which creates the soot PLII signal. A second intensified CCD camera imaged this soot signal. A 450-nm short-pass-filter was used to block the soot luminosity and elastic scatter from other sources. The excitation wavelength and detection wavelength were selected to optimize the PLII signal-to-noise ratio, and to avoid red-shifted (wavelength) PAH fluorescence.

Simultaneous to the PLII data acquisition, a helium-neon (HeNe) laser beam is passed through the center of the fuel jet to measure the soot extinction (*i.e.* *KL* value) along this beam path. In this laser extinction measurement, beam steering due to refractive index gradients within the combustion chamber can cause the beam to diverge by a certain angle. A spherical lens and an integrating sphere were used to ensure that the entire steered beam was collected. Further details in diagnostic complexity and uncertainty of the extinction measurement are found in a previous publication [38].

The *KL* data was time-averaged over the quasi-steady period of combustion that is defined as the time after the head of the reacting jet passes a given measurement location, but before the jet wrapped around the back wall [33]. Therefore, a time-average of *KL* during this period (*e.g.*, 3–7 ms, a time after the early transient and before the end of injection) is relevant for description of the quasi-steady *KL*. This measurement was repeated for various axial locations along the jet axis. Similar to OH chemiluminescence measurement, more than 20 injection cycles were used to determine ensemble-averaged PLII and *KL* data. The quantitative *KL* data were combined with qualitative PLII showing only the soot position used to obtain quantitative, two-dimensional soot volume fraction distributions for tested fuels. Theories and setup details are found in our previous publications [22, 23, 33, 39].

The chamber pressure was also measured to acquire the ignition delay and apparent heat-release rate. To improve the accuracy of the pressure measurement, we used two pressure transducers at the same time and also enabled a two-channel measurement for each pressure transducer [39, 40]. This approach minimizes potential measurement error and also increases the data acquisition rate. An ensemble-average of

more than 20 injection cycles was calculated for each channel. The average of these four was then used for the fuel-to-fuel comparisons.

SOOT SAMPLING

A thermophoretic soot sampling technique was used to study soot morphology. Similar techniques are widely used in an open flame burner [41, 42] or diesel engine exhaust [43, 44, 45] where a fast-moving actuator places a transmission electron microscope (TEM) grid within the high-sooting gases for a very short period of time. A challenge in the high-pressure combustion chamber to apply this technique is sealing around the fast-moving sampling probe. In one application, a fast sampling valve extracts soot-laden gases from the combustion chamber of a diesel engine, and then these gases are exposed to the TEM grid [46]. Since an insertion probe is not used, only the sealing action of the valve is required; however, a critical question remains whether or not the extracted soot particles represent the soot particles within the reacting jet, since the residence time, temperature, pressure, and fuel-ambient mixture all change during the sampling process.

Recently, we implemented a technique to sample the soot particles directly from the reacting jet using a probe that is fixed inside the combustion chamber [33, 34]. As shown in Fig. 2, the probe holds a carbon-coated TEM grid (3-mm diameter) at the jet centerline. The probe is placed parallel to the jet axis to skim gas from the jet while attempting to minimize flow disturbance. Through a 1-mm diameter hole, reacting flows containing soot enter the probe and soot particles are deposited on the cooler TEM grid via thermophoresis. This restrictive passage ensures quenching of combustion and also protects the grid from excessive heating. Therefore, the sampled soot particles should correspond to soot present at that position.

This sampling approach might raise questions about potential contamination of the grid from combustion products other than soot particles. To resolve this concern, experiments were conducted outside of the sooting regions of the jet, which showed no soot particle deposition (see the Appendix). Soot loading can be another issue because variation of injection duration (or combustion period) will change amount of soot deposited on the grid. This issue was addressed by varying the fuel injection duration. As the probe is stationary, the goal is to collect soot for long injection durations to make the soot deposition dominated by the quasi-steady period of injection. However, jet wrap around from the back wall and over-loading of soot ultimately limit the injection duration. Results showed that the soot loading on the TEM grid changed with injection duration, but the soot morphology did not (as shown in the Appendix). Consequently, the injection duration was fixed at 7 ms, consistent with the other diagnostics.

RESULT AND DISCUSSION

FLAME LIFT-OFF LENGTH AND IGNITION DELAY

The flame lift-off was measured by OH chemiluminescence imaging during the quasi-steady period of injection. From previous studies [22, 23, 24, 25, 26], a strong relationship is found between changes in the amount of fuel-ambient mixing upstream of the lift-off length and soot concentrations downstream of the lift-off length. Therefore, knowledge of the lift-off length for various fuels is prerequisite to understand the soot processes.

OH chemiluminescence and lift-off results are shown in Fig. 3. The images shown are ensemble averages of more than 20 images each. The average flame lift-off length, analyzed from the mean of individual injection, is defined as the distance from the nozzle to the first axial location of the OH chemiluminescence and overlaid as a red, dashed line on the image. To show the uncertainty in this ensemble average,

an uncertainty band of $\pm 2\sigma/\sqrt{N}$ where σ is the standard deviation for N number of injections) is also annotated for each fuel. Fuel composition has an obvious effect on lift-off length. Among the tested fuels, SR shows the shortest lift-off length while JP shows the longest one. Within a temperature range examined in this study, the ordering in lift-off length with fuel types generally stays the same such as JP>JC>D2=JW>JS>SR.

Since each fuel has different physical and chemical properties, the root causes for the fuel dependency upon lift-off length are not necessarily straightforward. Recently, we have studied the lift-off length for fuels with various volatilities at the same operating conditions of this study [39]. From the Mie-scattered liquid-phase fuel sprays imaging performed in conjunction with the OH chemiluminescence imaging, results showed that liquid vaporization is completed by mixing with hot ambient gases prior to the flame lift-off. Therefore, combustion occurs without the presence of liquid droplets. Also, for the same fuels of this study, the vapor-phase spray penetrations are found to be the same regardless of fuel types [32], implying that the ordering in lift-off length is caused by ignition characteristics rather than volatility effects.

A parameter used to rate the ignition characteristics of fuels is cetane number. To determine the correlation between lift-off length and cetane number, Figure 4 shows a plot of these parameters at both 900 K and 1000 K. There is an overall trend that the lift-off length decreases with increasing cetane number. Since high cetane number fuels ignite earlier than low cetane number fuels, one might expect that the jet penetration and ignition site occur at a shorter distance from the nozzle for high cetane number fuels, thereby resulting in a shorter lift-off length [47]. While the overall trend is as expected, Fig. 4 shows some discrepancies. For example, the lift-off length dependency on the cetane number is not as