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Effects of 2-Ethylhexyl Nitrate on Diesel-Spray Processes[‡]

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ABSTRACT

Diesel fuel ignition-enhancing additives, such as 2-ethylhexyl nitrate, are known to reduce emissions from diesel engines; however, the mechanisms by which the emissions reduction occur are not understood. This report covers the first phase of a research project supported by Ethyl Corporation that is aimed at developing a detailed understanding of how 2-ethylhexyl nitrate alters in-cylinder injection, ignition, and combustion processes to reduce diesel engine emissions. The goals of the first phase were to conduct experiments to assess: (a) how diesel fuel ignition quality (as measured by cetane number) affects the physical and/or chemical processes in a developing diesel spray, (b) how 2-ethylhexyl nitrate affects these processes, and (c) whether the changes are inherent with cetane number. This first phase is aimed at providing results that will isolate the diesel spray processes affected by the additive and guide future, more-detailed research into these processes.

The experiments were conducted in an optically-accessible, constant-volume, combustion vessel that simulates top-dead-center (TDC) conditions in a direct injection (DI) diesel engine. The TDC conditions covered ambient gas temperatures and densities from 700 to 1200 K and 7.3 to 45 kg/m³, respectively. These conditions include those expected from low-load to high-load in present and proposed advanced diesel engines.

Fuels were injected with an electronically controlled, common-rail diesel fuel injector. The fuels considered were blends of three single-component fuels. Two of the fuels were blended to give cetane numbers (CN) of 45 and 55. The third fuel was made by adding 4000 ppm of 2-ethylhexyl nitrate to the CN-45 fuel blend, resulting in a second CN-55 fuel. These fuels had controlled differences in ignition characteristics with minimal differences in physical properties.

The results show that the primary effect of the 2-ethylhexyl nitrate additive is to accelerate the preignition radical-pool formation, thus shortening the autoignition period. This effect is most significant at the lowest gas temperature-density conditions and least significant at the highest temperature-density conditions. The results also show that the development of the preignition radical pool was not the same for the two CN-55 fuels. Instead, the development of the additized, CN-55 fuel resembled that of the unadditized, CN-45 parent fuel, just shifted earlier in time. Finally, the effect of this ignition improver on parameters such as flame lift-off, maximum liquid phase fuel penetration, and spray dispersion were negligible, indicating that neither the high-temperature combustion chemistry nor the mixing-controlled processes are affected by the additive.

The observations support the arguments that 2-ethylhexyl nitrate decomposes very early in the

[‡] This work was performed at the Combustion Research Facility, Sandia National Laboratories and was supported by Ethyl Corporation.

spray development and enhances the earliest phases of the radical pool formation leading up to ignition and combustion. The later stages of the radical pool formation are controlled by the parent fuel chemistry, and are not similar to a fuel which has the same natural cetane number. In other words, the changes caused by 2-ethylhexyl nitrate are not inherently described by cetane number. Overall, the results suggest that the effects of the additive on engine performance and emissions are most likely the result of changes in the timing of the various stages of diesel combustion relative to the engine cycle, and are not the result of fundamental changes in the diesel combustion process beyond the changes in the earliest stages of the ignition process.

INTRODUCTION AND BACKGROUND

Growing interest in higher efficiency engines for transportation is creating a research focus on diesel engines, especially regarding methods for improving efficiency while reducing emissions. An important factor in determining the performance of a diesel engine is the autoignition quality of the diesel fuel. The ignition quality of the fuel is characterized by a cetane number (CN), determined at one engine operating condition as defined by ASTM D613 [1]. A higher cetane number equates to better autoignition quality (*i.e.*, shorter ignition delays). Typical diesel fuels in the U.S. have cetane numbers between 42 and 50.

Research has shown that improvements in the autoignition quality of diesel fuels with ignition enhancers, such as 2-ethylhexyl nitrate, can not only improve diesel engine performance, but also reduce emissions [2-5]. In addition, small but significant decreases in NO_x emissions have been shown to correlate well with ignition-quality improvement, whether the ignition improvement was achieved by fuel blending or by the addition of 2-ethylhexyl nitrate [4]. However, the improvements are not uniform with engine load [4,5] and the mechanisms by which these ignition improvers affect performance and emissions are not understood.

A research project in collaboration with Ethyl Corporation was undertaken to begin devel-

oping a detailed understanding of how the addition of 2-ethylhexyl nitrate to diesel fuel alters in-cylinder injection, ignition, and combustion processes to reduce diesel engine emissions, as noted by others. This report covers the first phase the project. The stated goals of the first phase were to conduct experiments with simple fuel mixtures with and without ignition improvers to assess: (a) how diesel fuel ignition quality (as measured by cetane number) affects the physical and/or chemical processes of the diesel ignition and combustion (b) how ignition improvers affect these processes, and (c) whether the changes are inherent with cetane number. This phase is aimed at providing results that will isolate the diesel spray processes affected by the additive and guide future, more-detailed research into the relevant processes. To address these issues, the following were investigated: the uniformity of the ignition enhancement by 2-ethylhexyl nitrate over a range of density and temperature conditions (matching those expected at various operating conditions in an engine), the similarity of the ignition process in a fuel with the additive and one with no additive (but with the same cetane number), and the effects of the additive on diesel-spray evaporation, mixing, and combustion processes.

In the first two sections that follow, the diesel combustion simulation facility and procedure and the fuels and experimental conditions are discussed, respectively. The next three sections present the results.

DIESEL COMBUSTION SIMULATION FACILITY AND PROCEDURE

Experiments were conducted under simulated, diesel engine conditions in a constant-volume combustion vessel. Figure 1 shows a schematic cross-section of the combustion vessel. It has a cubical shaped combustion chamber with a characteristic dimension of 108 mm. Each side of this combustion chamber has a round port with a diameter of 105 mm. The fuel injector is located in the right side port in a metal insert that forms the right wall of the combustion chamber. Optical access is provided by four sapphire windows with clear apertures of 102 mm located in four of the

ports. Two are shown in the schematic: one on the left side and one on the bottom. The other two form the front and back sides of the combustion chamber in the schematic. The sapphire windows permit full access to the vessel for optical diagnostics requiring either line-of-sight or orthogonal access. The top port contains two spark plugs and a mixing fan mounted in another metal insert that forms the top wall of the chamber. (The details concerning the spark plugs and the fan are presented in Refs. [6,7].)

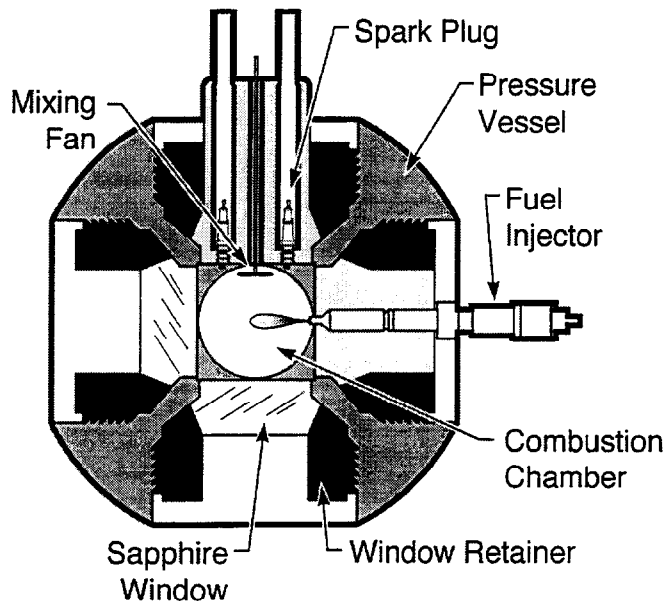


Figure 1: Schematic of cross-section of the combustion vessel.

This combustion vessel is capable of handling gas pressures more than a factor-of-two higher than current-technology diesel engines and can be used to simulate a wide range of in-cylinder conditions in diesel engines, including those in proposed new high-power-density automotive and heavy-duty diesel engines. The fuel injector used was an electronically-controlled, common-rail, solenoid-activated injector capable of an injection duration from 0.6 ms to several milliseconds. The injector had a top-hat injection profile, that is, it opened and closed rapidly ($<100 \mu\text{s}$) and had a constant injection rate throughout the injection period. Previous work provides in-depth descriptions of the combustion vessel and fuel injector [6,7].

The experimental procedure used to simulate diesel-fuel injection and combustion processes in a

constant-volume combustion vessel was developed previously [6-10] and is illustrated by the pressure history shown in Fig. 2. To summarize, the procedure begins with filling the vessel to a specified density with a premixed, combustible-gas mixture. This mixture is then spark-ignited (with the spark plugs shown in Fig. 1) and burned, creating a high-temperature, high-pressure environment in the vessel. As the combustion products cool, due to heat transfer to the vessel walls, the gas pressure inside the vessel decreases. When the desired pressure is reached, the diesel-fuel injector is triggered. Throughout the simulation the fan at the top of the combustion chamber maintains a uniform temperature environment in the combustion vessel [6,7]. The velocities induced by the fan are insignificant in comparison to the velocity of the dense liquid fuel jet from the injector [6,7].

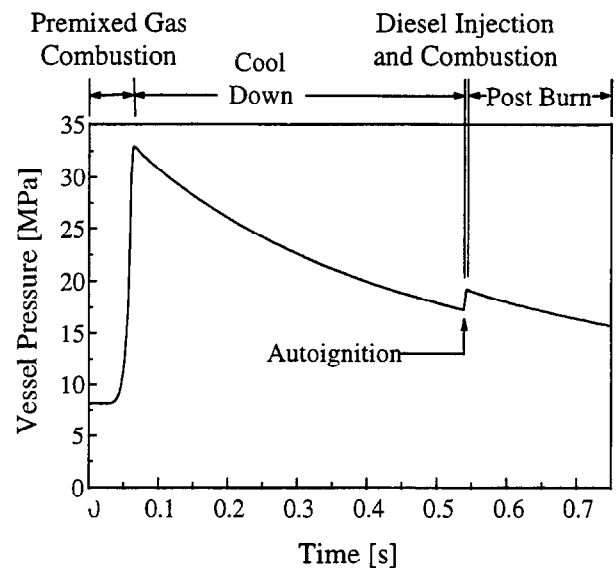


Figure 2: Pressure history for a typical diesel simulation, illustrating how the desired temperature and density conditions are achieved.

The temperature, density, and composition of the ambient gas in the vessel at the time of diesel-fuel injection can be varied widely with this simulation procedure. Temperature can be varied from 600 to 1400 K and density from 3.6 to 60 kg/m^3 . The ambient composition is determined by the combustible-gas mixture burned to create the high-pressure/temperature environment in the vessel. For these experiments, two different combustible-gas mixtures were used: the products of

one simulated air and the other generated an inert environment. The simulated air was generated with a lean mixture of 68.1% N₂, 28.4% O₂, 3.0% C₂H₂, and 0.5% H₂ that had a volumetric product composition of 69.3% N₂, 21.0% O₂, 6.1% CO₂, and 3.6% H₂O. This mixture was used for the investigation of ignition and combustion related effects of the additive on the diesel sprays. The inert environment was created with a dilute, stoichiometric mixture of 89.8% N₂, 8.4% O₂, 3.3% C₂H₂, and 0.5% H₂ which reacted to 89.8% N₂, 6.5% CO₂, and 3.8% H₂O, and was used in the investigation of the non-combustion related effects of the additive on the diesel sprays.

The start of fuel injection was determined by the attenuation of a HeNe laser beam directed across the injector orifice onto a photo diode. The output of the photo diode was used both to sequence the optical diagnostics and for all post-processing of the time-resolved, combustion-luminosity data. All time-resolved data (*i.e.*, combustion-vessel pressure, injection pressure, injection-timing signal, combustion luminosity) were sampled at 36 kHz.

FUELS AND OTHER EXPERIMENTAL CONDITIONS

The effects of 2-ethylhexyl nitrate on the diesel-spray vaporization, mixing, ignition, and combustion processes were determined by comparing results for three fuels. Each fuel was a blend of three, single-component fuels: *n*-hexadecane (cetane), decalin, and 1-methylnaphthalene. The base fuel had a cetane number (CN) of 45 and contained 33.3%, 30.0%, and 36.7% by volume of each single-component fuel, respectively. A second fuel had a CN of 55 and contained 43.3%, 30.0%, and 26.7%, respectively. These two blends provided reasonable representations of commercial diesel fuel with a controlled difference in their ignition characteristics and minimal changes in their physical properties. The third fuel was identical to the first fuel except that 4000 ppm of 2-ethylhexyl nitrate was added to raise its CN to 55. These cetane numbers are computed from the cetane numbers of the individual mixture components. Experimentally measured cetane numbers

[1] agreed with the computed values to within the accuracy of the cetane number rating procedure and were found to be 46, 53, and 55 for the base fuel, the blended fuel, and the additized fuel, respectively. In the report, the fuels will be referred to as follows using their computed cetane numbers: CN-45, blended CN-55, or additized CN-55. These fuels have controlled differences in their ignition characteristics with minimal differences in physical properties.

For all experiments, the fuel temperature, the injection pressure, the wall temperature, and the injector-orifice aspect ratio (length/diameter) and diameter were 440 K, 136 MPa, 453 K, 4.2, and 0.246 mm, respectively.

ADDITIVE EFFECTS ON THE IGNITION PROCESS

Measurements of the temporal evolution of chemiluminescence during the autoignition period of a diesel spray, up to the start of significant soot incandescence, were used to investigate the effects of the 2-ethylhexyl nitrate on ignition. The chemiluminescence during the autoignition period is from excited-state species in the developing radical pool. The initial soot incandescence occurs shortly after the beginning of significant fuel breakdown and heat release [11], or similarly, shortly after the end of the autoignition period and early in the premixed-burn phase of diesel combustion [12].

The chemiluminescence measured during the autoignition period was near 430 nm. Recent spectroscopic measurements of diesel-fuel autoignition in an engine have shown that prior to the time of initial soot formation there is a broad region of chemiluminescence between 380 nm and 500 nm with a peak at 430 nm [13]. Chemiluminescence in this spectral region is predominantly from CH and formaldehyde [13].

The chemiluminescence and the initial soot incandescence were measured with a photo-multiplier tube (PMT) and two optical filters: a narrow-band-pass interference filter (430 nm, 7.3 nm FWHM) and a band-pass colored-glass filter (BG7, Oriel). The PMT was set so that it operated

in its linear-response regime over the range of chemiluminescence intensities measured.

The intense soot incandescence during the later stages of the premixed burn phase through the end of the mixing-controlled phase of the diesel-spray combustion was measured with a photodiode in combination with two optical filters: a neutral-density filter (40% transmission) and a long-wave-pass filter (LG-725-F, Corion). The latter filter limited the measured soot incandescence to wavelengths longer than 725 nm.

Both the PMT and the photodiode were positioned near one of the combustion-vessel sapphire windows, perpendicular to the axis of the spray, which allowed light collection from the entire developing spray. Their outputs were acquired with the same 12-bit A/D used to acquire other data during the experiment, such as the vessel pressure. The time responses for the PMT and the photodiode were both measured and found to be shorter than our A/D sampling period (28 μ s). The outputs from the photodiode and the PMT were related by determining the amount of neutral-density filtering required in front of the PMT to equalize its output with the photodiode output during the later stages of combustion for one condition. The PMT and photodiode outputs are plotted in terms of a relative luminosity normalized to unity at the maximum luminosity measured for all conditions. Together, the two outputs cover seven orders of magnitude of luminosity.

Figure 3 presents the PMT and photodiode outputs during the first 1.5 ms after the start of injection for each of the fuels injected into three different ambient gas temperatures (900, 1000, and 1100 K) and a fixed density of 14.8 kg/m³. The PMT output forms the portion of each curve below a relative luminosity of 10⁻⁴. The photodiode output forms the portion of the curve above a relative intensity of 10⁻². The relative-luminosity profiles in Fig. 3 are ensemble averages of ten combustion events. Before averaging, each profile was shifted in time so that the time at which a relative luminosity of 10⁻⁵ was reached corresponded to the average time noted for the ten unshifted profiles. This method of averaging preserved the temporal evolution of the relative

luminosity for each individual experiment. A typical standard deviation for ten repeat experiments in the time required for the relative luminosity to reach a value of 10⁻⁵ was 5%.

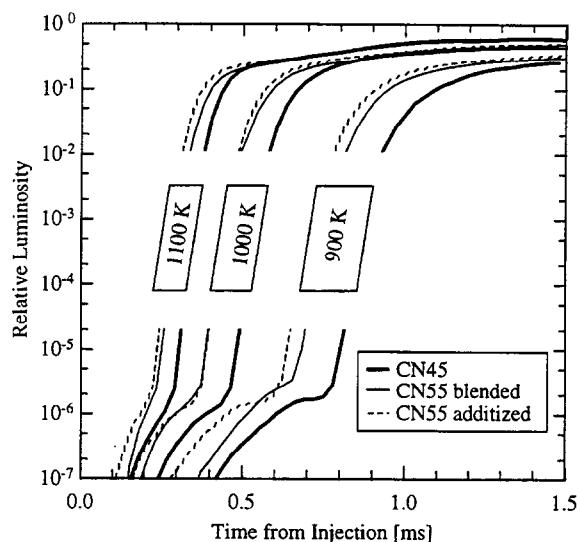


Figure 3: Relative luminosity measurements from the photo-multiplier tube (curves below 10⁻⁴) and the photodiode (curves above 10⁻²) for three ambient gas temperature conditions, three fuels, and an ambient gas density of 14.8 kg/m³. Time is relative to the start of injection.

Consider a typical profile such as the middle solid-dark line in Fig. 3, corresponding to the CN-45 fuel at 1000 K. The initial increase in the relative luminosity between 250 μ s and 450 μ s is due to the chemiluminescence (at 430 nm). The rate of increase in the chemiluminescence signal is rapid initially, but then begins to slow down at about 350 μ s, just before the sudden rise in the relative luminosity at 450 μ s. The sudden rise at 450 μ s is due to soot incandescence and indicates that significant heat release as a result of combustion has begun to occur [11], or similarly, that the autoignition phase is over. In the following discussion, the period of time up to the sharp increase in luminosity due to soot incandescence, which typically occurs near a relative luminosity of 10⁻⁶, will be referred to as the autoignition period.

Examination of the other relative luminosity profiles in the figure shows that the general description above applies for all conditions. In addition, four more detailed observations can also be

made with respect to the different fuels. First, the autoignition period is shorter for both CN-55 fuels than for the CN-45 fuel for all conditions, but this difference decreases with increasing temperature. Second, the autoignition period of the additized CN-55 fuel is similar to the blended CN-55 fuel at higher temperatures, but is shorter at 900 K. Third, the lowest detectable chemiluminescence for the additized fuel always begins as much as 50 μ s before the blended CN-55 fuel. Fourth, although shifted earlier in time, the progression of the chemiluminescence for the additized CN-55 fuel (dashed curves) is nearly identical to that of the parent CN-45 fuel (heavy solid curves), and is not similar to that of the blended CN-55 fuel.

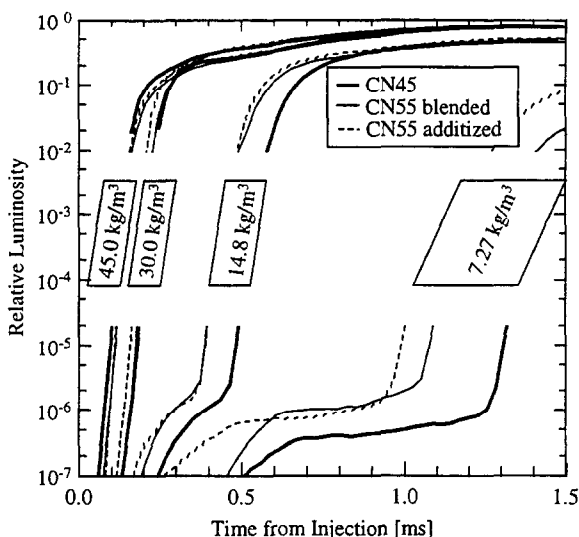


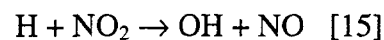
Figure 4: Relative luminosity measurements from the photo-multiplier tube (curves below 10^{-4}) and the photodiode (curves above 10^{-2}) for four ambient gas density conditions, three fuels, and an ambient gas temperature of 1000 K. Time is relative to the start of injection.

Figure 4 presents the relative-luminosity profiles for four densities at a temperature of 1000 K. The figure shows that there is little measurable difference between the ignition periods for all three fuels at the high-density conditions (30 and 45 kg/m^3), where the transition from chemiluminescence to soot incandescence appears very smooth. At the moderate-density condition (14.8 kg/m^3), the two CN-55 fuels have similar autoignition periods, while for the low-density condition (7.27 kg/m^3), the additized fuel has the

shortest ignition period of the three. Also, as noted in Fig. 3, the progression of the chemiluminescence for the additized fuel follows that of the parent CN-45 fuel shifted in time, and not that of the CN-55 blended fuel.

From the results in Figs. 3 and 4, we see that a primary effect of the additive is to shorten the autoignition period. This effect, however, is not the same for all ambient gas temperatures and densities, and therefore, cannot be accurately characterized by a rating based on a single engine operating condition, such as the cetane number. The effects of the 2-ethylhexyl nitrate are more significant at low-temperature and low-density conditions than the cetane number indicates.

These results also suggest that the 2-ethylhexyl nitrate enhances the radical pool formation early in the injection process, but once the radical pool is initiated, the parent-fuel chemistry determines the further evolution of the ignition process. This is compatible with the idea that unimolecular decomposition of 2-ethylhexyl nitrate (RO-NO_2) [14] occurs early in the injection event, providing an efficient mechanism for OH production through the reaction:



Without the additive, there are no other dominant OH generating reactions early in the injection event and more time is required to develop the radical pool. [Note: Regarding NO_x emissions, engine studies have shown that when fuel ignition quality is improved, either by blending or by the addition of 2-ethylhexyl nitrate, NO_x emissions can be reduced [2-4]. These engine results suggest that the NO_2 resulting from the unimolecular decomposition of 2-ethylhexyl nitrate (RO-NO_2) upstream of the mixing-controlled combustion zone does not lead to an increase in NO_x emissions.]

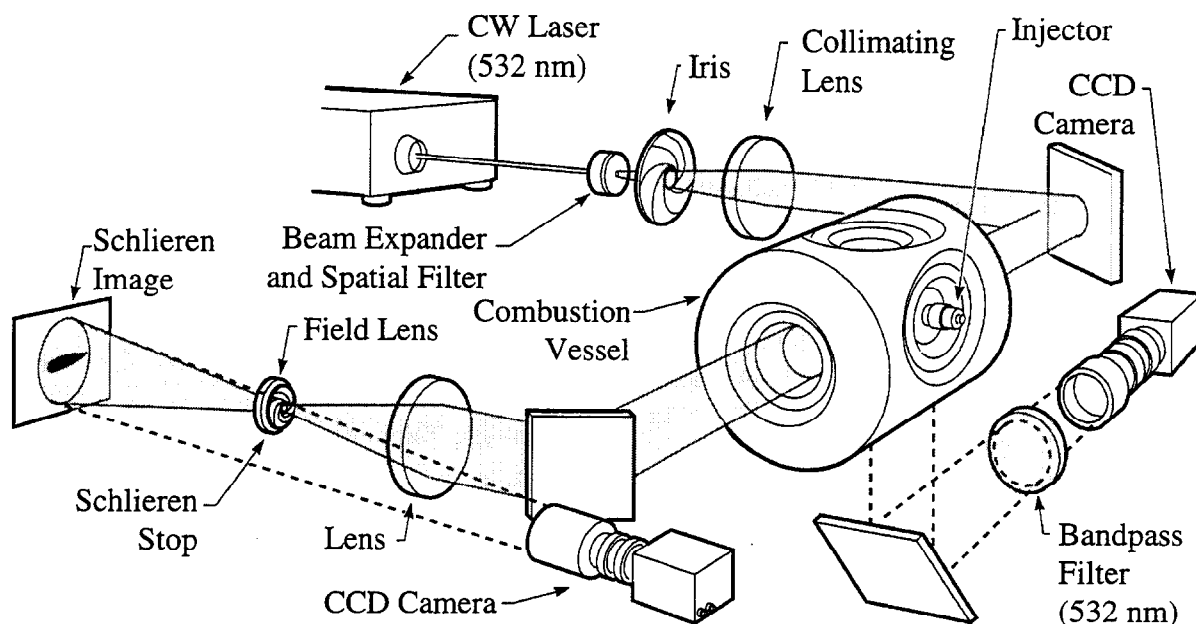


Figure 5: Schematic of the optical system for Mie-scattered light and schlieren images.

ADDITIVE EFFECTS ON PHYSICAL PROCESSES (NON-COMBUSTING CONDITIONS)

The additive effects on physical processes in the spray were investigated under inert conditions, which allowed the effects of the additive on physical processes to be isolated from effects on ignition and combustion processes. The parameters measured were the quasi-steady, maximum-axial extent of the liquid-phase fuel (*i.e.*, the liquid length [6,11]) and the overall-spreading angle of the spray. The quasi-steady liquid length is established early in the injection process [*e.g.*, 6,11] and remains throughout the entire injection event. Comparison of these liquid lengths and spreading angles for the three fuels provides a measure of the effects of the additive on the atomization, vaporization, and mixing processes in the spray.

The liquid lengths and overall spray-spreading angles were determined from time-averaged images of Mie-scattered light from the liquid-phase fuel in a spray and schlieren images of the overall spray, respectively. The Mie-scattered light and schlieren images were acquired

simultaneously for each experimental condition with two intensified, gated, CCD video cameras oriented as shown in Fig. 5. The light source for the images was a collimated laser beam passed through the vessel. The lower right camera was used to acquire the Mie scattered light images. Time-averaging was used to average the turbulent fluctuations in the outer boundary of the overall spray and the liquid region in the spray. The image integration time (*i.e.*, camera gate) was 3.0 ms. The gate was delayed 1.5 ms from the start of injection to eliminate the effects of the early transient spray development. The camera gains were held fixed throughout the experiments. Further details of the measurement techniques can be found in Ref. [6].

Analysis of the Mie-scattered light images for liquid length involved determining the maximum axial distance in the spray where the light intensity was above a threshold equal to 3% of the light intensity range measurable with the camera. Conservatively, 97% of the liquid in the spray has evaporated by this location. This definition of liquid length was found to be relatively insensitive to large changes in parameters such as the laser

power and the camera gain because of the rapid decline in the scattered light intensity at the leading edge of the liquid region [6]. For example, a factor-of-two change in the laser power, the camera gain, or the threshold used to define liquid length changes the liquid length by, at most, 4%.

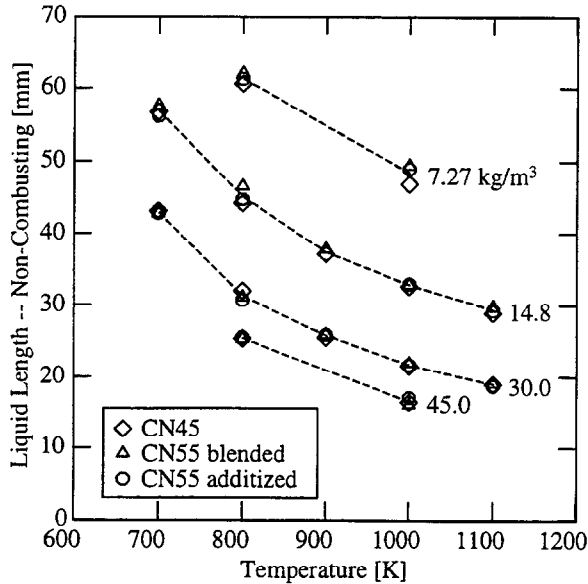


Figure 6: Liquid lengths determined from the Mie-scattered light images for non-combusting conditions versus the ambient gas temperature for four densities and three fuels.

Figure 6 shows the liquid lengths measured for the three fuels described previously. The figure is a plot of liquid length for each fuel *versus* ambient-gas temperature for four ambient-gas densities. All other conditions are held fixed. Each data point in the figure is an average of the liquid lengths determined from 3 to 10 images. The standard deviation of liquid lengths determined in this manner for one set of conditions is 2% [6].

The trends observed in Fig. 6 with respect to temperature and density are those expected; namely, as either temperature or density increases, liquid length decreases as a result of an increased rate of vaporization [6]. The important new observation is that for the range of conditions considered, the additive, as well as other fuel differences, have no systematic effect on the liquid length. At each temperature-density condition, the liquid lengths are the same for the three fuels to within the experimental error. This result indicates that neither the additive, nor the fuel differences,

have any effect on processes that might impact the liquid length, such as atomization, fuel vaporization, and turbulent mixing.

This conclusion is also supported by the overall spray spreading angles determined from the schlieren images of the spray (not shown). The spray-spreading angles, a measure of the processes controlling the entrainment and mixing in the spray, were also identical for each of the three fuels at each ambient gas temperature-density condition considered.

The spreading angle was determined from the schlieren images. In the time-averaged, schlieren images, the overall spray (liquid and gas) appears as a dark cone emanating from the injector tip in a light background. The spreading angle was determined from the angle of a cone that best fit the dark region in the image below a threshold intensity. The threshold intensity selected was halfway between the low light intensity on the spray centerline and the bright background light intensity. This definition of spray angle falls within the intermittent outer region of the spray [7].

ADDITIVE EFFECTS ON FLAME LIFT-OFF AND PHYSICAL PROCESSES (COMBUSTING CONDITIONS)

An investigation of combusting sprays was conducted to determine if the additive indirectly affects any physical processes, through enhanced combustion. For these experiments, the fuels were injected into the simulated-air environment. The parameters measured were the liquid length and the axial location of first soot incandescence. The location of first soot incandescence is a measure of the stand-off distance between the injector tip and the flame (*i.e.*, the lift-off of the turbulent diffusion flame).

The flame lift-off was determined from time-averaged images of soot incandescence from combusting sprays acquired with the camera in Fig. 5 viewing the spray from below (with the laser off). The band-pass filter in front of this camera limited the wavelength of the collected light to 532 nm. The lift-off in these images is defined as the first axial location in the spray with detectable soot

incandescence. This location corresponds to the first axial location with detectable OH [16].

The liquid lengths were determined from time-averaged images of Mie-scattered light from the liquid region in combusting sprays. These images were acquired in the same manner described in the previous section. To obtain sufficient Mie signal in the presence of the soot incandescence, the laser power was increased to 5.5 W and the beam height was compressed to approximately 1 cm with cylindrical optics.

The acquired images show two distinct regions of the spray: the liquid phase region near the injector and the combusting region of the spray based on soot incandescence at 532 nm. The combustion region in the spray begins in the vicinity of the tip of the liquid region and extends downstream from there. To determine liquid lengths from these images, the soot incandescence image with the laser off was subtracted from the image with the laser on. The image difference contained only the Mie-scattered light and was analyzed for liquid length as described for the non-combusting sprays in the previous section.

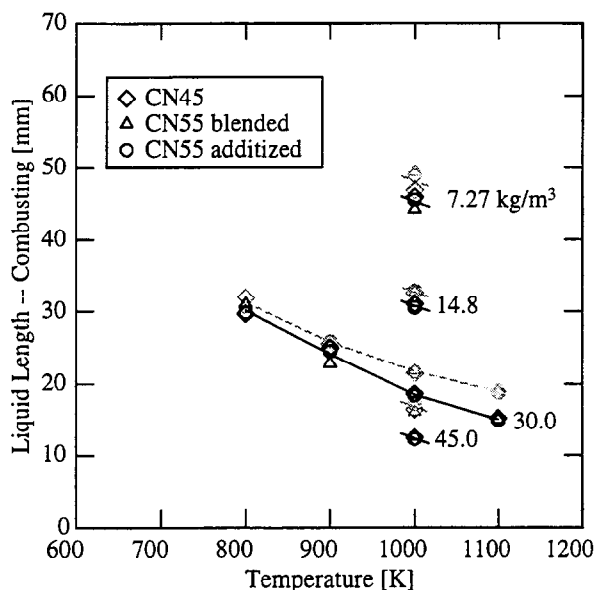


Figure 7: Liquid lengths determined from the Mie-scattered light images for combusting (black symbols) and non-combusting (gray symbols) conditions versus the ambient gas temperature for seven temperature/density conditions for all three fuels.

Figure 7 is a plot of the liquid lengths for the combusting conditions (black symbols) versus the

ambient temperature for several densities. Also shown are the corresponding liquid lengths for non-combusting conditions (gray symbols) from Fig. 6. As observed in Fig. 6 for non-combusting conditions, the figure shows that there are no observable variations in the liquid length due to the fuel or the additive; that is, at each condition the three fuels have the same liquid length. There is, however, an apparent shortening of the liquid length between the non-combusting and the combusting conditions. At this time, it is not clear if this decrease is due to a decrease in the actual liquid length or attenuation of the incident laser light and/or Mie-scattering light intensity by soot present in the vicinity of the tip of the liquid region.

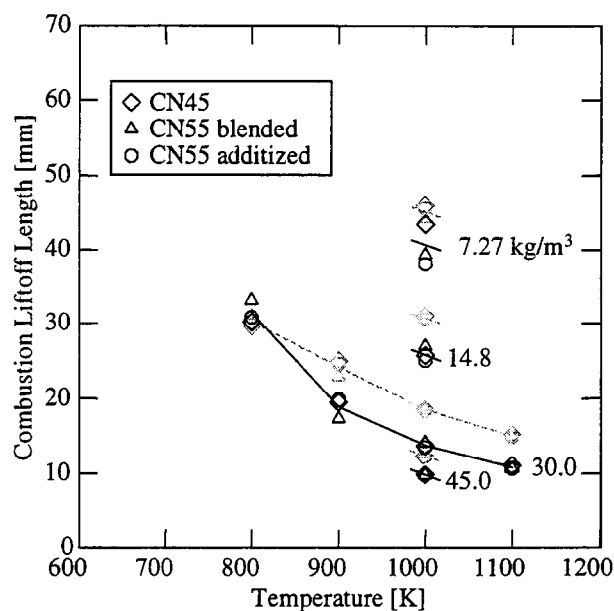


Figure 8: Flame lift-off (black symbols) based on the location of initial soot formation and liquid lengths (gray symbols) for combusting conditions versus the ambient gas temperature for seven temperature/density conditions for all three fuels.

In Fig. 8, the flame lift-off data (black symbols) measured for the same conditions shown in Fig. 7 are plotted with the liquid length data (gray symbols) from Fig. 7 for the combusting sprays. The data show that there is an overlap between the liquid and combustion regions in the spray for all but the lowest temperature condition. The overlap indicates that the combustion zone must be surrounding the centrally-located liquid

region in the spray. However, no significant variation in the flame lift-off is observable as a result of the additive or fuel for the conditions examined.

The flame liftoff results, again, indicate that the primary effect of the additive is through the initial autoignition chemistry. Once combustion is initiated, the kinetics are dominated by high temperature radical reactions, and any post-ignition increases in radical concentrations due to the additive are insignificant.

SUMMARY AND CONCLUSIONS

The effects of an ignition-improving additive, 2-ethylhexyl nitrate, on diesel-spray evaporation, mixing, ignition, and combustion processes were investigated. The results indicate that the primary effect of the additive is to increase the radical-pool formation very early in the auto-ignition period, leading to a shorter overall auto-ignition period for a diesel spray. This effect is greatest at lower temperature-density conditions, corresponding to low-load and start-up conditions in a diesel engine, and becomes negligible at the highest temperature-density conditions examined.

The investigation of the effects of the additive on other aspects of the spray such as the liquid length, the spreading angle (*i.e.*, mixing), and the combustion lift-off conclusively show that the additive does not affect physical processes in the spray, or combustion processes once the ignition phase is complete. This result is in agreement with the mixing-limited nature of diesel combustion after ignition [12] and recent research showing that fuel vaporization is also mixing limited [6].

The results support the argument that the primary effect of the additive is to decompose early in the spray development process and initiate the formation of a radical pool by providing an efficient mechanism for OH production. Specifically, unimolecular decomposition of 2-ethylhexyl nitrate creates NO₂, which then further reacts with available H atoms to produce OH radicals [14]. Once radical-pool development begins, 2-ethylhexyl nitrate appears to have an insignificant effect on the further development of the radical-pool,

since further development follows that of the parent fuel, and not that of a fuel with the same natural cetane number. In other words, the changes caused by 2-ethylhexyl nitrate are not inherently described by cetane number. After autoignition, additional radical species formed by dissociation of 2-ethylhexyl nitrate are negligible compared with those generated by the high-temperature kinetics of combustion and no significant further effects on the combustion process occur. Overall, the results suggest that the effects of the additive on engine performance and emissions are most likely the result of changes in the timing of the various stages of diesel combustion relative to the engine cycle, and except for the enhancement of the initial stage of ignition, not the result of fundamental changes in the diesel combustion process itself.

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