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Laser diagnostics of soot precursors in a heavy-duty diesel engine at low-temperature combustion conditions

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ABSTRACT

To better understand in-cylinder soot formation processes for modern, low-emissions, low-temperature combustion (LTC) operating conditions in diesel engines, soot and its precursors are imaged by laser diagnostics in a heavy duty optical engine. Virtually simultaneous images of planar laser-induced incandescence of soot (soot-PLII) using 1064 nm excitation and combined soot-PLII and planar laser-induced fluorescence of poly-cyclic aromatic hydrocarbons (PAH-PLIF) using 532 nm excitation reveal the temporal and spatial evolution of soot and its precursors during combustion. With increasing dilution of the intake air stream by various levels of nitrogen to simulate the use of exhaust-gas recirculation (EGR) to achieve LTC, the residence time of PAH increases as soot formation is delayed. At zero dilution (21% intake oxygen), soot appears nearly simultaneously with PAH, while at higher dilution (12.7% or 9.5% intake oxygen), soot formation is delayed by hundreds of microseconds to a millisecond or more. At all dilution levels, at its onset, PAH rapidly fills most of the downstream cross-section of the jet, with a relatively uniform fluorescence intensity distribution. The spatial evolution of soot, however, shifts from a relatively rapid filling of the downstream head of the jet at low dilution, to inception at the midstream periphery of the jet followed by a gradual progression downstream at high dilution. Effects of fuel-bound aromatics are also explored by comparing soot and PAH formation for a representative diesel fuel containing 27% aromatics by weight to that for neat n-heptane. The residence time of PAH before the onset of soot is slightly longer with the non-aromatic fuel, but otherwise the spatial and temporal evolution of PAH-PLIF and soot-PLII are indistinguishable from that of the diesel fuel at LTC conditions. Spectral analysis shows a characteristic soot emission spectra from 1064 nm excitation, while 532 nm excitation yields significant short-wavelength emission that cannot be attributed solely to soot incandescence, and is likely due to fluorescence of large PAH soot precursors. No narrow spectral features, such as from C_2 or C_3 emission, are apparent in the spectra, even at high laser fluence.

1. Introduction

Particulate matter (PM) is a harmful pollutant whose emission from combustion devices is restricted by worldwide air-pollution regulations. In addition to carbonaceous soot, PM in internal-combustion engine exhaust also contains poly-cyclic aromatic hydrocarbon (PAH) species. PAH molecules are formed during the incomplete combustion of hydrocarbon fuels and are soot precursor species [1]. Many PAHs are known to be carcinogenic and are to some extent adsorbed on the carbonaceous soot, comprising the soluble fraction of PM [1–3].

The two main sources of in-cylinder PAH are fuel components and products of synthesis reactions during combustion. PAH in diesel fuel are mostly relatively small (2, 3 rings), which can survive the combustion process intact or contribute to synthesis of other PAHs [1,5]. Aromatic fuel components are reported to be a dominant source of exhaust PAH in older less-efficient diesel engines where a considerable portion of the fuel-bound PAH is left intact in the exhaust [6]. While the contribution of aromatic fuel components on exhaust PAH can be significant, PAH species synthesized during combustion typically compose the largest fraction of exhaust PAH. For example, Rhead and Hardy [5] used radio-labeled PAH molecules in the fuel to quantify the fraction of fuel PAH that survived into the exhaust of a heavy-duty diesel engine. They found that at most, about one percent of the fuel-PAH survived and up to 5% contributed to other PAH. The vast majority of exhaust PAH (95–99%) was synthesized from other non-PAH fuel components. Indeed, even fuels without any fuel-bound PAH (neat n-heptane for example) can produce significant soot, albeit at a reduced rate compared to diesel fuel [7]. These data clearly show that in-cylinder pyro-synthesis is the dominant source of exhaust PAH and soot precursors, and ultimately of soot. Therefore, an investigation of in-cylinder PAH evolution and conversion to soot at LTC conditions is warranted.

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Insight into the general PAH synthesis and soot formation processes that occur during diesel combustion may be gained by extension from more tractable laboratory flames. For example, atmospheric-pressure studies in both diffusion [8,9] and premixed [10] flames show that PAHs grow larger with increasing temperature and residence time along the axis of the flame, eventually forming soot close to the flame front. In both flames, soot precursors (PAH and nano-particles) appear upstream of the soot zones, in intermediate-temperature regions (1200–1600 K for the diffusion flame, ~1900 K for the premixed flame), and extend downstream well into the sooty zones. Sampling [9,10] and inferences from red-shifting of PAH fluorescence [8] indicate that at soot inception, PAHs range from two to as many as 12 rings. Deductions from absorption and scattering measurements in the premixed flame [10] indicate that PAH in condensed ~2-nm nanoparticles, however, are primarily smaller two-ring molecules, as also concluded by others [11,12].

For advanced diesel engines using exhaust-gas recirculation (EGR) to operate at low-temperature combustion (LTC) conditions to reduce nitrogen oxides (NO_x) formation, the intermediate-temperature regions where PAH species and nano-particle soot precursors reside are likely more broadly distributed, both spatially and temporally. With high levels of EGR, ignition delays are extended in LTC diesel engines, so pre-combustion mixing is considerable. Consequently, mixture gradients are significantly shallower than in laboratory diffusion flames, or even than conventional diesel-engines. Furthermore, the diluent effect of EGR broadens the temperature history in time, with a slower, more kinetically controlled progression through auto-ignition to combustion products. Hence, the LTC diesel engine presents a unique platform for study of PAH formation where intermediate-temperature regions persist for a relatively long time. Indeed, diesel exhaust under LTC conditions can have a much larger fraction of organic (PAH) species than conventional high-temperature diesel combustion [4]. Some evidence of possible extended PAH residence time for diesel LTC conditions was also noted in previous measurements from our optical engine laboratory. Our 2-color soot thermometry measurements showed short-wavelength emission that was too strong relative to the long-wavelength emission to be attributed to thermal radiation from soot, especially near the onset of soot-formation [13]. We speculated that the short-wavelength signal could be due to chemiluminescence emission, which potentially could be from PAH and other soot precursors.

The emission and absorption spectra of PAH molecules depend on their size and structure, which can be very diverse for combustion-generated PAH. Clar proposed a sextet rule to qualitatively predict the chemical and photo-physical properties of PAH molecules based on their size and ring structure [14]. According to this rule, particularly high stabilization-energy and consequently low reactivity is observed if the π-electrons in the aromatic molecule can be grouped into sextets. For the simplest aromatic, single-ringed benzene, all of the π-electrons can be grouped into a sextet in its single ring. When additional aromatic rings are added to form larger PAHs, the additional π-electrons may or may not be grouped into sextets, depending on the structure of the PAH. Molecules where all the π-electrons can be grouped into sextets are termed fully-benzenoid PAH. After benzene itself, the smallest fully benzenoid PAH is tri-phenylene, which has three sextet rings surrounding a central non-sextet ring that has no ungrouped π-electrons. Most PAH species are not fully benzenoid, however, and the ungrouped outer π-electrons form bonds that exhibit olefinic nature and higher reactivity [15]. Hence, molecules with more ungrouped π-electrons, either due to their structure or size, are less stable, and are generally more toxic.

Ungrouped π-electrons also affect the photo-physical characteristics of PAHs. As the size and number of ungrouped π-electrons increases, the band gap between electronically excited and ground states is reduced, so that optical transitions tend to occur at longer wavelengths [15]. Perhaps the most dramatic example is the acene series, which are straight chains of aromatic rings (e.g., benzene, naphthalene, anthracene, tetracene, etc.). Only one ring of any acene can form a sextet, so that all other rings have ungrouped π-electrons. As the chain length of rings increases, the number of ungrouped π-electrons increases, and the absorption (and emission) spectra shift to longer wavelengths. For the acene series, the long-wavelength edge of the absorption spectrum shifts by 60–120 nm with each additional ring, from approximately 260 nm for benzene (one ring) to 850 nm for extremely unstable heptacene (seven rings) [14,15]. PAH structures other than the acene series can have more than one sextet, and the wavelength shift with each additional ring is generally not so dramatic for most PAHs. Large sheet-like PAH soot precursors, for instance, reach a red-shift threshold near 600 nm, even with 30 or more rings [15]. Nevertheless, for a given structural class, the size of a PAH molecule can be determined to some degree by the red-shift of its absorption (or emission) spectrum. This is evident from emission spectra recorded in atmospheric diffusion-flames, where the emission peak gradually shifts to longer wavelengths as the PAH molecules grow downstream [8]. Even though PAH absorption and emission spectra are affected by both structure and size, the spectra are broad, with few distinct features, especially for larger PAH species. Consequently, selective excitation and/or identification of individual PAH becomes increasingly difficult or impossible as the pool of PAH becomes more diverse or includes larger PAHs. Even so, the red-shift in the excitation and emission spectra of PAH has been exploited by many researchers to map the distribution of PAH molecules of different sizes in atmospheric-pressure flames [8,16,17]. Based on the size dependence described above, as well as other works [8], laser-induced fluorescence (LIF) with ultraviolet excitation should excite small PAH species, either present in the fuel or synthesized by combustion. Visible excitation at 532-nm should excite larger PAH molecules with at least five rings [8]. Such large PAHs must be synthesized in-cylinder during combustion, since such large PAH are not present in the diesel fuel. Indeed, 5-ring and larger PAH species have been observed in diesel exhaust [1].

Previous work in diesel sprays using ultraviolet excitation show that combustion generates PAH prior to the onset of soot in transient jets [18,19], and upstream of soot in quasi-steady jets [18–20]. Spectral analysis of the PAH LIF emission shows a transient red-shift prior to the onset of soot formation, implying a growth of PAH size [18]. In these previous studies, interpretation of the late PAH LIF emission was hampered to some degree by interference from laser-induced incandescence (LII) of soot. The influence of soot LII was observed as either a sudden brightening and red shifting of the emission spectra [18], a sudden localized signal increase in images [19], or by spatial comparisons with images acquired upon longer wavelength (532-nm) excitation [20]. The size dependence of PAH absorption described above, however, indicates that fluorescence of large PAH, along with LII, may be excited even with visible excitation at 532 nm. Indeed, it is well recognized that soot LII signals using 532-nm excitation may be contaminated by PAH fluorescence [17]. Hence, a clear distinction between PAH and soot under both conventional high-temperature and advanced low-temperature diesel combustion conditions remains to be established. Furthermore, the possibility of significant PAH fluorescence upon 532-nm excitation calls into question established understanding of diesel combustion based on 532-nm LII [19].

Here, we use virtually simultaneous excitation at both 532 nm and 1064 nm to discriminate between fluorescence of large PAH and LII of soot. We selected 1064 nm excitation for soot LII because