

Using Extreme Compression to Promote Fuel Reformation within a Reacting Jet: The Path Towards a Sootless Diesel Engine

Investigators

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Abstract

Direct injection Diesel-style engines emit solid-phase carbonaceous particulate matter (i.e. soot) at levels that negatively impact both climate change and personal health. Although advances in injection technology have increased atomization and mixing of the injected fuel jet, which reduces local equivalence ratios and decreases soot formation, aftertreatment is still required. This in turn has associated efficiency and cost penalties. Our research is aimed at eliminating cylinder-out soot particles entirely. Extremely high compression of air has the potential to provide an environment where in-plume fuel reformation can occur. It is well understood that soot formation is kinetically controlled. By achieving extremely high temperatures within the fuel jet, it is possible to reach the equilibrium state of the mixture locally before getting kinetically constrained and building significant populations of soot precursor species. By adding a moderator species to the fuel, control over atom ratios – and thus composition of the equilibrium state – may be adjusted such that the resulting reformed fuel will then combust without forming soot. To date, numerical tools have been built that allow analysis of chemical kinetics of crucial soot precursor species, namely Polycyclic Aromatic Hydrocarbons (PAHs). Some initial experimental investigations have been carried out with direct-injected, ethanol/water mixtures. Optical access and a high frame-rate camera allows for visible detection of luminous soot formation. Work is underway to systematically investigate variations on mixture composition and initial air temperature (at start of injection) in order to observe and measure the effects on soot formation within the reacting jet. Numerical modeling and analysis is carried out to understand and explain experimental results.

Introduction

The primary goal of this research is to eliminate in-plume, jet-core soot production by using extremely high temperature air and modifying the local atom ratios with a moderator species added to the fuel. High temperature is achieved by using a piston-cylinder device that is capable of a geometric compression ratio of 100:1. By pre-heating the air, on the order of 100 °C or more, the air temperature at the Start of Injection (SOI) can be upwards of 2000 K. Since chemical kinetic rates are exponentially dependent on temperature, this extremely high air temperature drastically decreases the time to reach equilibrium. And with the use of a moderator species, the equilibrium state

can be manipulated such that the reformed-fuel species are non-sooting: primarily carbon monoxide and hydrogen. The importance of approaching equilibrium comes from the fact that soot formation is a kinetically constrained process. Through the chemical pathways that are taken from fuel/air reactants to products, a bottle neck exists under typical Diesel engine operating conditions whereby a large population of PAHs are formed and subsequently nucleate a condensed phase. These nanoparticles then grow in size and agglomerate, and ultimately form particulate matter that is emitted from the engine.

Initial numerical analyses have been made that indicate the propensity for various premixed, rich mixtures to form soot. Chemical kinetic computations are made using a mechanism that has been developed with the specific inclusion of PAH gas-phase species and their respective radical species [1].

In parallel, experimental work is being done to obtain images of the injection and combustion of ethanol/water mixtures in the extreme compression device. These images provide a clear, qualitative indication of where and when soot is present due to the visible luminosity of soot particles. Ethanol has been chosen as the starting point for fuel since it is lightly sooting and miscible with water, a simple moderator species (and O-atom donor). Beyond this, we have plans to work with higher alcohols, such as propanol and butanol, combined with water or other moderators.

Background

The Significance of Soot

Particulate matter emissions are of critical importance to both global climate change and human health. Studies have shown that human exposure to carbon-based ambient aerosols increases the odds of developing pulmonary and cardiac problems which can lead to lung and heart diseases, and in the long-term may be fatal [2]. With regards to climate effects, carbon aerosols have the ability to absorb and scatter solar radiation. Recent modeling efforts have indicated the propensity for carbon particulates to increase the global mean surface air temperature by 0.2 to 0.37 K per year, and the radiative forcing is estimated to be 70% that of CO₂ in the atmosphere [3]. The largest effects occur in regions with high fossil fuel emissions and burning of biomass. Clearly there is an urgent need to curb carbon particulate emissions.

Current Approaches to Mitigating Diesel Soot Formation

Within a direct-injection Diesel engine, soot formation occurs in regions of locally high equivalence ratios and favorable temperatures. There exist both low- and high-temperature limits, although a change in the combustion strategy is required to move beyond these limits. Other research and development efforts in the field have

moved towards the direction of staying below the low temperature limit, and this has the additional benefit of avoiding high thermal NO_x production. Figure 1 below shows a graph of equivalence ratio versus temperature, indicating how a typical Diesel engine fuel jet occupies several regions.

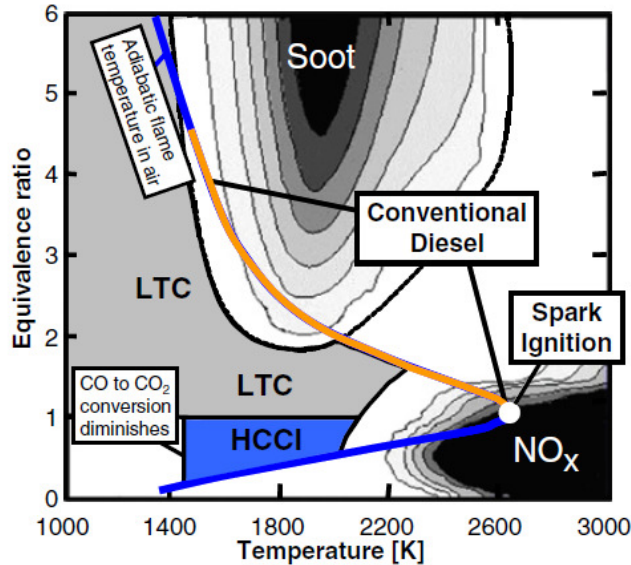


Figure 1: Local equivalence ratio versus temperature, with reference to regions that describe a conventional Diesel fuel jet [4].

The method by which a Low Temperature Combustion (LTC) strategy is implemented usually involves the use of Exhaust Gas Recirculation (EGR). This has the disadvantage of reducing engine load capability. Our approach of using an injected fuel/moderator mixture and going to extremely high temperatures is aimed at keeping engine load capabilities at their highest while simultaneously avoiding particulate emissions.

Using an Appropriate Chemical Mechanism

Much work within the combustion community has been done investigating the development of chemical mechanisms that can predict both the nucleation and growth of a condensed phase. The type of species called Polycyclic Aromatic Hydrocarbons (PAHs) has been identified experimentally as being critical to initiating soot inception.

A chemical mechanism has been developed by Blanquart [1] that includes up to 4-ringed aromatic species, inclusive of many aromatic radicals. It was designed to validate the combustion of large hydrocarbon fuels, namely n-heptane and iso-octane, although a number of smaller hydrocarbon species have been validated against experimental data as well. It contains ~1650 elementary reactions and ~150 species, and

includes both transport as well as thermodynamic data. This mechanism is being used to study gas-phase kinetics, in particular the temporal growth of PAH species, in order to predict soot formation tendencies.

Equilibrium and Forming a Condensed Phase

Within a direct-injected jet the formation of soot is kinetically controlled; that is, there are regions within the fuel jet where specific species are formed, and given little oxygen and favorable temperatures, a condensed phase is formed. In other words, equilibrium is not reached. The goal of this research is to both control the equilibrium state and to reach it, all within the reacting jet. It is thus informative to have a clear idea of what thermodynamic equilibrium indicates about the product composition of a particular mixture.

The following graph shows the equilibrium composition for various n-heptane/air mixtures, where n-heptane is chosen as a diesel fuel surrogate. The C/O atom ratio is varied by adjusting the fuel/air equivalence ratio. The vertical dashed line indicates where the stoichiometric condition exists. It is noted that nitrogen chemistry is not included in the aforementioned chemical mechanism.

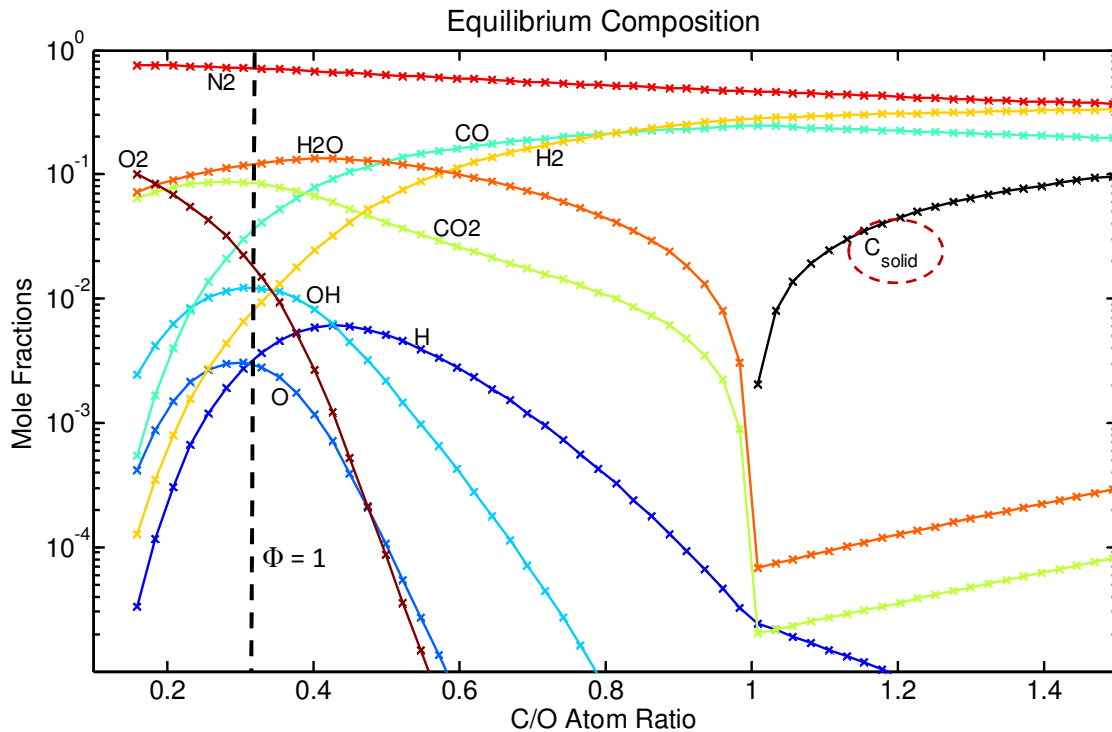


Figure 2: Thermodynamic equilibrium composition as a function of overall C/O atom ratio for n-heptane/air (21% oxygen, 79% nitrogen) mixtures.

This figure shows that not until a C/O atom ratio of unity is reached does a solid phase form in equilibrium. A couple things to note: for one, the solid phase permitted here is graphite, and soot is not pure carbon but has some hydrogen bound inside of it such that the C/H atom ratios are typically on the order of 1 to 2. Secondly, other species that are permitted include aromatics benzene (A1), naphthalene (A2), anthracene (A3) and pyrene (A4) as well as a number of their respective radicals, all of which have insignificant equilibrium mole fractions (e.g. $< 10^{-12}$). This information is compared to experimental observations of soot formation occurring locally in environments with C/O ratios as low as ~ 0.5 . Thus, soot formation is a kinetically, and not thermodynamically, controlled process.

Understanding the Opportunity

With regards to modeling a direct-injected fuel, some simplifications are made in order to make initial efforts tractable. By disregarding fluid dynamics and droplet evaporation processes, a one-dimensional homogeneous adiabatic mixture is the appropriate starting point. The basis for this simplification comes from experimental studies of soot-producing fuel jets performed at conventional Diesel engine operating conditions.

Work done by Dec [5] using laser-sheet imaging produced a model that defines specific regions where different phenomena occur. Most notably, it is postulated that just downstream of the liquid jet there exists a region of a rich, premixed fuel/air mixture and subsequent combustion zone. The products of this fuel-rich reaction zone have a high concentration of soot precursors (i.e. PAHs) which quickly lead to soot formation. Figure 3 below shows a graphic of the mixing controlled jet with these regions indicated by color.

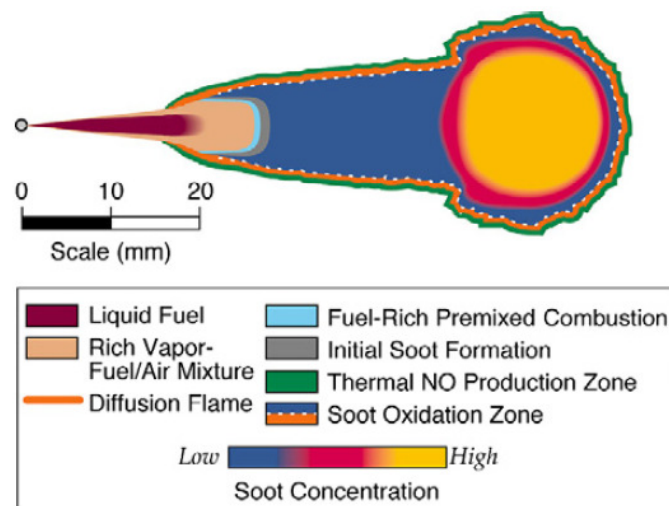


Figure 3: Conceptual model of a quasi-steady-state mixing controlled reacting jet [5].

It is the premixed fuel/air reaction zone that is of particular interest. Here is where an opportunity exists. There are two distinct aspects that can be controlled: the atoms at play within the gaseous fuel/air mixture, and the temperature and pressure within this region. Both of these properties define the equilibrium state. And if the temperature is high enough, then equilibrium can be reached within the physically confined space of a reacting jet. The atoms present within this region are due to three factors: the fuel, the air that has been entrained into the jet, and a moderator species that can be added to the fuel prior to injection. Given a particular injection system setup and fuel choice, then it is the moderator that provides the most flexibility. The temperature of the mixture can be controlled by going to extreme states. One way of reaching extreme states is by using a high compression ratio piston-cylinder device, which has been built in our laboratory.

A single-shot free piston combustion apparatus has been designed under a previous GCEP project [6]. It can provide compressed air temperatures on the order of 1000 to 2000 K and pressures of 100 to 500 bar. The highest temperatures are attainable by pre-heating the air before compression by the use of band heaters placed around the cylinder. The experimental apparatus is shown in the figure below.

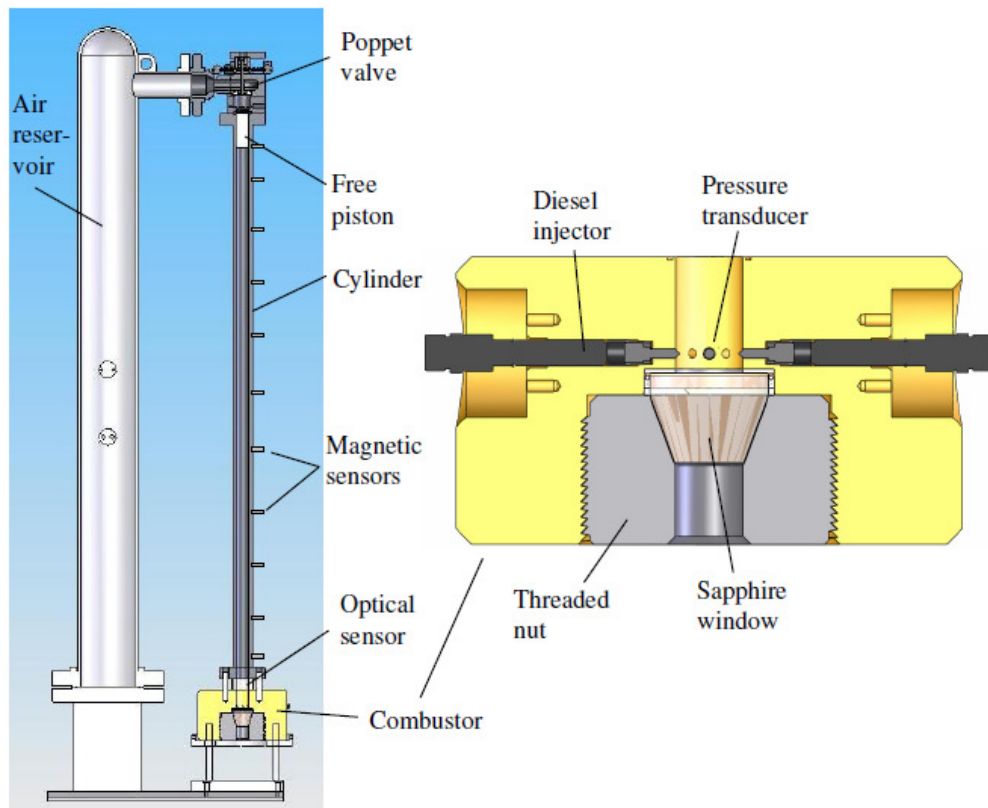


Figure 4: A single shot free-piston extreme compression piston-cylinder device with optical access [7].

The device is operated by filling the air reservoir to a desired pressure, and opening the poppet valve to actuate. The free piston is then forced down the cylinder and compresses air into the combustion chamber. Once triggered, the Diesel injectors deliver the fuel which is auto-ignited within the combustor. Figure 4 also shows how optical access is provided by a sapphire window placed at the bottom end of the combustion chamber. An argon laser is used for illumination, whereby the beam passes through the window, off of a mirror-faced piston, and is captured by a high frame rate camera. This allows for clear observation of soot formation due to yellow luminosity. A sample image is provided below in the results section. There exists an additional capability (not shown in Figure 4) that uses a broadband light extinction measurement that can be calibrated to measure the final soot volume fraction.

Results

Premixed Reaction Zone Computations

Given that the gaseous fuel/moderator/air mixture is an appropriate starting point for chemical kinetic analysis, there lies the question: is axial thermal and mass diffusion a significant transport mechanism? Typically, low temperature premixed flames rely on transport mechanisms for stability or flame propagation. However, in this environment of high temperature and pressure, this may not be the case. Numerical simulations of the chemical kinetics are carried out that compare two different scenarios for a rich, premixed n-heptane/air mixture with enthalpy and pressure held constant: 1) thermal and mass diffusion are allowed along the axial dimension, and 2) a closed system. The first situation is simulated using the Cantera toolbox [8] via a Python script and calls upon an iterative solution procedure that solves the nonlinear energy and mass differential equations provided with appropriate spatial boundary conditions. The output of this solution includes a flow velocity that is used to map to the time domain. The second scenario is solved with Cantera by letting the mixture approach equilibrium in time as per the chemical kinetics. The results of this comparison are shown in the following figure.

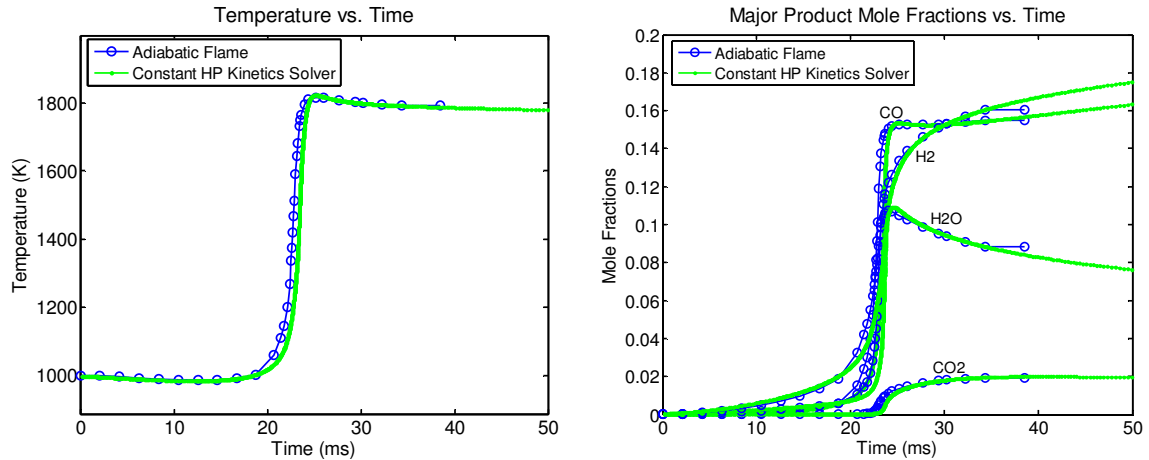


Figure 5: Temperature and major product species mole fractions versus time for comparing combustion processes with and without thermal and mass diffusion.

The graph on the left of Figure 5 shows the temperature profile comparison. The blue points labeled “Adiabatic Flame” correspond to scenario 1 outlined above, a freely propagating flame, and this profile is very nearly identical to the closed system solution. The major product species in the graph on the right also agree very well. It is noted that the flat lines at the end of the flame solution are due to a zero-gradient boundary condition imposed by the solver.

Of particular importance is the buildup of soot precursor species, namely the PAHs. Benzene is the first of such aromatic species, and the formation of benzene is a necessary but not sufficient condition for soot formation [9]. The following graph shows the same two scenarios compared for benzene (A1) and naphthalene (A2), the first and second ringed aromatic species.

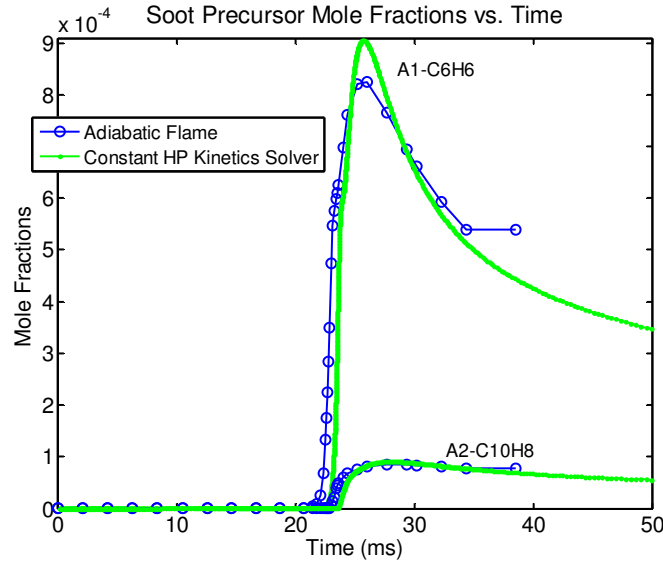


Figure 6: Benzene (A1) and naphthalene (A2) mole fractions versus time, comparing combustion solutions from scenarios with and without thermal and mass diffusion.

Given the results of this analysis, it is assumed then that axial diffusion is an insignificant transport mechanism. This is desirable since computations requiring iterative solutions, especially when using a chemical mechanism with 150 species, can take significant amounts of time.

Indications of Soot Formation for a Typical Diesel Jet

From the laser-sheet fuel spray imaging study previously mentioned [5], it is estimated that the state of the premixed fuel/air vapor region just downstream of the liquid jet is roughly 1000 K, 40 bar and has an equivalence ratio of 3. A simulation is run that solves the chemical kinetics for a closed n-heptane/air system, with enthalpy and pressure held constant. This corresponds to a model of an adiabatic, rich fuel/air parcel traveling from the end of the liquid region and through the reaction zone within the jet. It is noted that the C/O atom ratio for this mixture is 0.95, very near the thermodynamic equilibrium limit of forming solid graphite (see Figure 2). The following graphs show the temperature and selected species mole fractions versus time.

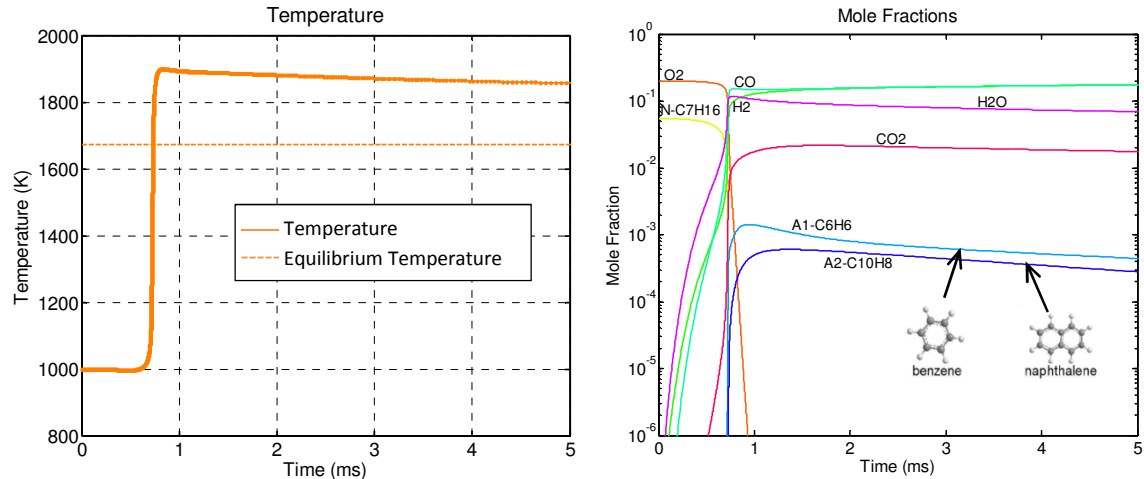


Figure 7: Temperature and selected mole fractions versus time for constant enthalpy-pressure combustion of rich ($\Phi=3$) n-heptane/air system.

The left graph in the above figure shows the temperature profile for the first 5 ms. Given a flow velocity estimate of ~ 20 mm/ms (estimated from liquid penetration depth versus time [7]) and a spatial distance of ~ 10 mm between the end of the liquid region and the reaction zone of the premixed flame [5], a time of ~ 0.5 ms to the reaction zone is in good agreement with the simulation results. If achievement of equilibrium is defined by reaching the equilibrium temperature to within 1%, then it takes ~ 10 sec (10,000 ms) to reach equilibrium, which is clearly unachievable under normal engine operating conditions. Select species mole fractions are shown in the graph on the right. Both fuel and oxygen are shown to be consumed within the reaction zone, and mostly CO and H₂ are produced, corresponding to rich combustion. It is noted that the equilibrium CO and H₂ mole fractions are both ~ 0.25 , and within the 5 ms shown these species are approximately halfway to their equilibrium values. The benzene and naphthalene species, however, are far from their equilibrium values (both $< 10^{-12}$). After this premixed reaction zone, the PAH species have a relatively large region (see Figure 3) within the jet to grow in size (i.e. create larger rings), bond to one another, and subsequently form small condensed phase nanoparticles. Although this model does not include the formation and growth of a condensed phase, the presence of such a large concentration of soot precursors indicates that this situation very likely represents soot-forming combustion.

The next step is to use both high temperatures (achievable through extreme compression) and a moderator species added to the fuel prior to injection in order to manipulate the chemical pathway towards reaching equilibrium. Experimentally, we are using ethanol as a starting fuel species. This is chosen because it does form soot, albeit very little compared to diesel fuel, and because it is miscible with water. A numerical

analysis of this situation is presently underway. Some initial experimental results will be discussed in the following section.

Initial Experimental Results

A brief series of initial experimental runs have been conducted by injecting equimolar ethanol/water mixtures. This mixture ratio was chosen such that the maximum local C/O atom ratio is unity, and that air entrainment decreases it even further. The experiments were conducted by increasing the compression ratio of the free-piston device from ~60:1 up to ~100:1 and capturing images for each test. A sample image is shown below.

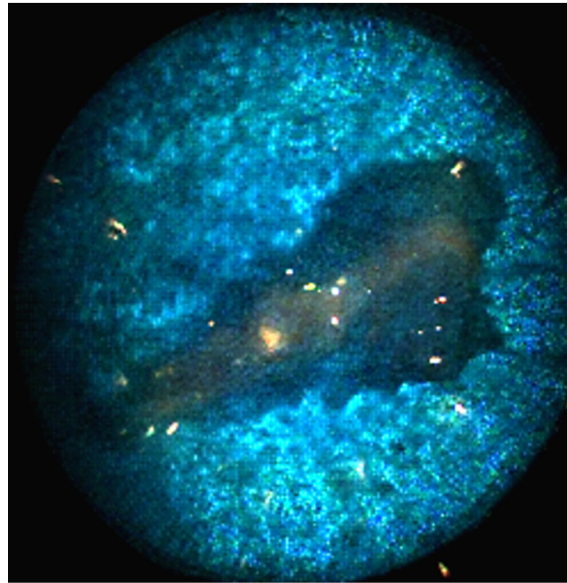


Figure 8: Image of equimolar ethanol/water direct injection combustion 1.36ms after start of injection, compression ratio is ~60:1.

The image in Figure 8 is shown during the quasi-steady-state period. The small bright white spots are due to graphite bits from the piston rings getting into the combustion chamber and oxidizing. Within the jet there is some yellow luminosity from radiating soot particles. This luminosity is not ubiquitous throughout the flame, as would be the case for a diesel fuel injection. It is possible that the exposure time and laser light intensity overwhelm additional soot luminosity. The initial temperature of the air at SOI is ~1350 K, although the gaseous fuel/water/air mixture region within the jet is less than this due to the latent heat of vaporization of the liquid.

By increasing the compression ratio of the piston cylinder device up to ~100:1, there are no major findings in terms of amount and location of observed soot luminosity. It is noted that water is a relatively difficult molecule to dissociate. It is thought that the temperature within the premixed vapor region for these conditions is not high enough to break apart enough of the water to initiate participation in the fuel reformation process. The next step is to pre-heat the air before compression and drive up the temperature.

Progress

Presently this research is still within a preliminary phase. Much of the progress thus far has been in understanding the context with which this problem stands and how the tools available, both numerical and experimental, can be used to move forward. If we are successful in promoting a fuel reformation process within the jet and reaching equilibrium, thereby eliminating soot formation within the jet core, then the impact on engine-out emissions could be very significant. Provided that transients before and after the steady-state mixing controlled combustion phase can be managed appropriately, this work will pave the way towards increasing engine load up to the maximum possible, by moving towards an overall stoichiometric mixture. This would ultimately have a drastic impact on the transportation sector by both increasing load and fuel efficiency of the Diesel engine.

Future Plans

The immediate plan is composed of two fronts: continue to build combustion models and analysis tools, and continue to run experiments. Numerically, we are in the process of building a chemical mechanism that can predict the propensity for ethanol to form soot, through the formation of significant PAH species (i.e. all within the gas phase). This will allow for a systematic investigation of the change of chemical pathways with temperature and moderator species, and will be necessary in both predicting and explaining experimental results. Experimentally, the next step is to begin pre-heating the air before compression, still injecting ethanol/water mixtures. Once the range of ethanol/water mixture ratios and SOI air temperatures has been investigated, the plan is to move onto the use of higher alcohols, such as propanol and butanol. Beyond the use of alcohols, diesel fuel or a diesel fuel surrogate (such as n-heptane) would likely require an emulsifier to create homogenous fuel/moderator mixtures.

Further in the future, there are plans to make investigations with use of a gaseous hydrocarbon fuel, namely methane. In this case, CO₂ may be an appropriate moderator species. We currently have a gas booster that is capable of producing gas pressures sufficient for actuating the diesel injectors. It will be similarly important to model this combustion process in order to interpret and predict experimental results.

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