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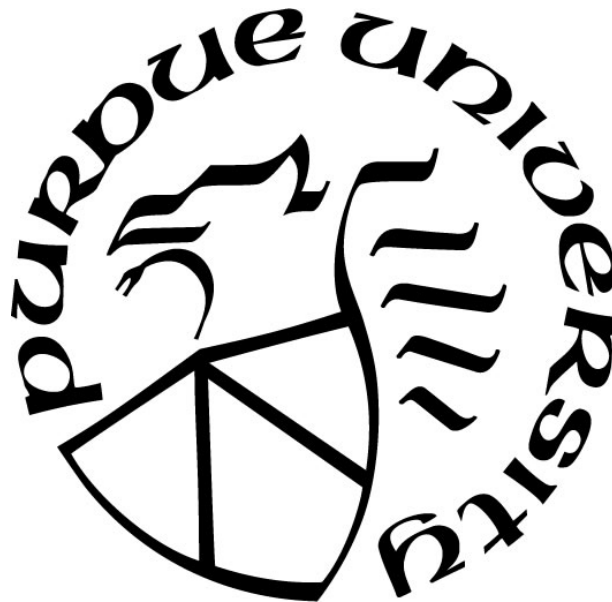
CHARACTERIZATION OF CARBON DEPOSITION IN FUEL-FILM COOLED ROCKET COMBUSTORS

by
Philip Piper

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To my family, for their never-ending support.

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ABSTRACT

Carbonaceous deposits can reduce heat flux in fuel-film cooled oxygen-rich staged combustion engines, but the deposition process at these conditions is poorly understood. Modeling requires a better understanding of the mechanisms for deposition and the deposits' insulating effect on the chamber wall, the latter of which depends on deposit depth and thermophysical properties. A fuel-film cooled combustor, creatively named the Task 1 combustor, was designed and tested to produce carbonaceous deposit samples which were analyzed for deposit depth, physical/chemical characteristics, and thermophysical properties. Additionally, heat flux was measured via an inverse method that took advantage of the heat sink cooled combustor design.

An optical profilometer and scanning electron microscope were used to distinguish between two different deposit layers: a smooth, lacquer-like "dense" layer and a fluffy, soot-like "porous" layer. Images of the sample indicated that the porous layer is likely formed via thermophoretic diffusion of soot formed in the fuel-rich gaseous boundary layer. Deposit layer depths were measured as a function of axial distance from the fuel-film injector at varying conditions, including fuel-film mass flow rate, bipropellant run time, chamber liner material (thus changing wall temperature), fuel composition, and metal surface roughness.

Gas chromatography mass spectrometry, Raman spectroscopy, and x-ray photoelectron spectroscopy were used to characterize the chemical structure of the two deposit layers. All three analysis methods revealed evidence that the dense layer is likely formed by heterogeneous condensation of heavy polycyclic aromatic hydrocarbons (PAHs) on the cool chamber wall.

Density varied considerably between the dense and porous layers. Average porous apparent density was measured at 1910 kg/m^3 , while porous and dense layer envelope densities were 216 and 1460 kg/m^3 respectively. A thermal conductivity of $0.2\text{-}1.1 \text{ W/m-K}$ was measured for deposits generated in a gas generator with similar conditions as the Task 1 combustor with relative uncertainties of approximately 10%. Emissivity was found to increase from 0.2 to 0.65 in the first 6 mm (0.24 inch) of the film injector, after which it remained constant.

A higher pressure combustor was designed to solve the Task 1 combustor shortcomings and operate at conditions closer to those expected in oxygen-rich staged combustion. Qualification testing was largely completed, with minor main injector adjustments required before carbonaceous deposits can be collected and analyzed.

1. BACKGROUND

Staged combustion rocket engines often operate at temperatures over 3500 K and pressures over 10 MPa to increase performance at the cost of higher cooling requirements. Several methods of cooling, such as regenerative, radiative, and internal (film, transpiration, and sweat) cooling, have been used alone and in tandem to meet the demands of modern high-pressure combustion devices.

The Soviet Union had considerable success in designing and operating a variety of staged combustion engines starting as early as the late 1950s, whereas the United States avoided staged combustion flight engines until the Space Shuttle Main Engine (SSME/RS-25) which was developed in the 1970s, and didn't fly until 1981 [1]. The Soviet Union flew at least 30 different staged combustion engines, which is still, to this day, more than all other countries combined [1]. Based on Soviet/Russian successes with the NK-33 and RD-180 lines of oxygen-rich staged combustion (ORSC) engines, the United States has expended considerable effort to better understand the cooling technologies and materials required to operate a kerosene-oxygen engine at pressures up to 25 MPa through the Air Force Hydrocarbon Boost program [2]. A high thrust engine of this type would typically use regenerative and internal film cooling in parallel to meet the elevated heat fluxes inherent to increased chamber pressure. For instance, the RD-170 family of engines injected fuel-films from three annular slots to cool the combustion chamber and nozzle throat in conjunction with regenerative cooling [3].

One useful aspect of kerosene-oxygen combustion is the formation and deposition of an insulating carbon layer between the hot combustion gases and the cool chamber wall. This carbon deposition phenomenon occurs in fuel-rich combustion conditions, such as the boundary layer formed from fuel-film cooling. As an example of the cooling benefits obtained from carbon deposits, Cook and Quentmeyer [4] found that a kerosene engine system-level design depended on the insulating properties of carbonaceous deposits to match the performance of a transpiration cooled methane-based design. The thermal resistance provided by an insulating carbon layer on the interior of the RP-1 engine chamber made up for the limited regenerative cooling jacket temperature of RP-1 due to pyrolysis. Cook and Quentmeyer [4] accounted for the insulating effects of the carbon layer with low pressure engine-specific empirical correlations, which they noted may not extend to higher pressure devices.

Despite the potential benefits associated with carbonaceous deposits in kerosene engines, the available film cooling literature often ignores deposits' thermal resistance to simplify modeling and correlations. Initiation and growth of carbonaceous deposits at ORSC conditions are not fully understood because they are strongly coupled with turbulence, mixing, heat transfer, and multiphase reaction kinetics. Additionally, the differences between deposits from low mixture ratio combustion in a fuel-rich gas generator or preburner versus those formed due to fuel-film coolant are not well understood. A better understanding of carbonaceous deposits' physical and chemical properties is required to model the reaction mechanisms that could be useful for modeling future ORSC engine cooling designs.

Research into hydrocarbon-oxygen high pressure combustion started with the inception of modern rocketry due to the availability of gasoline as a fuel, as can be seen with Robert H. Goddard's early work using liquid propellants. Carbon-based fuel use continued through World War II with the Germans using alcohol (ethanol) to fuel their V-2 missile, and through the Cold War with both the Americans and Soviets using kerosene for their F-1 and NK-33 moonshot boost engines respectively. U.S. boost engine propulsion research turned to hydrogen for the RS-25 in the 1970s and 1980s, then switched back to kerosene when the Soviet Union dissolved and American scientists discovered the startling Soviet advances in ORSC. In more recent years, kerosene fuels have fallen out of favor in the United States for cryogenics such as methane and hydrogen when concerning boost engines due to the direction of private industry. The significance of this brief history is that a large portion of U.S. kerosene fuel rocket research was completed in the 1950s and 1960s to develop the F-1, and in the 1990s and 2000s to catch up with the Soviet advances in ORSC. Kerosene research funding has ebbed and flowed just like other propulsion topics, such as hypersonics, depending on the current U.S. political climate and technical leaders. Additionally, some quantity of research related to carbon deposits in engines may have been lost to the security requirements imposed by the Cold War. Most of the literature referenced herein comes from the decades in which kerosene propulsion interest was at its peak, namely the years of F-1 development and after the fall of the Iron Curtain.

1.1 Liquid Film Cooling

Carbon deposition in fuel-film coolant flows occurs at different conditions than soot deposited from strictly fuel-rich combustion, the latter being expected in a gas generator or preburner. Figure 1.1, as copied from a variety of Air Force Research Laboratory (AFRL) papers [5,6], shows the mass, momentum, and heat transfer processes that occur when a liquid annular film interacts with high momentum gas flows typical of low contraction ratio (flight-weight) rocket combustors. Several early studies, such as Kinney in 1952 [7], showed that the liquid film acts as a thermal barrier preventing the chamber wall from exceeding the liquid's saturation temperature at the given chamber pressure. A hot-gas-to-liquid-film heat transfer coefficient can be defined to determine the length of the liquid film before it fully evaporates. As the liquid film vaporizes, a coolant-vapor-rich boundary layer grows over the liquid coolant, further reducing heat transfer to the wall. Once the film fully vaporizes, the coolant-rich boundary layer continues to reduce heat fluxes further downstream, although to a significantly lesser extent than when the liquid film was present due to increased mixing with the core flow. When heavier hydrocarbons are used as film coolants, they form carbonaceous deposits as the fuel-film heats and mixes through a combination of pyrolysis, dehydrogenation, and condensation reactions with the, typically near-stoichiometric, core flow. To fully understand the process of carbon deposition due to fuel-films, it is useful to understand the processes that occur in liquid films when no carbonaceous deposits are present. Shine et al. [8] recently wrote a review paper on film cooling in rocket engines; several of the references in the upcoming paragraphs are summarized in their work.

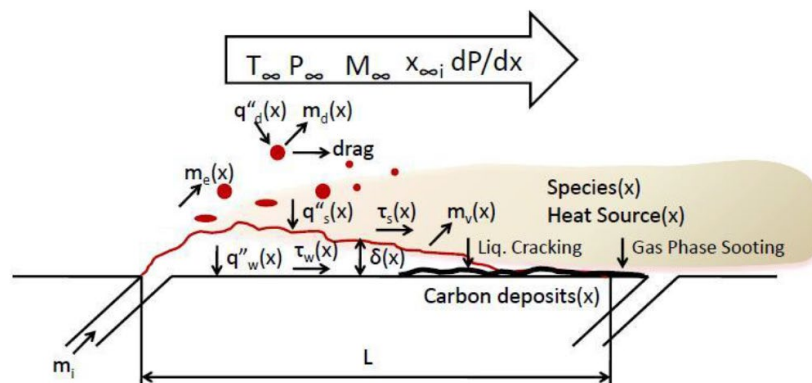


Figure 1.1. Liquid kerosene film cooling mass, momentum, and heat transfer processes [5].

One interesting phenomenon that occurs in liquid annular film cooling is the entrainment of liquid droplets when the coolant mass flow rate is increased beyond a critical value. Small waves form at the gas-liquid boundary due to the momentum mismatch between the two layers and grow in amplitude as the coolant mass flux is increased. This process limits the liquid cooled area/length and “wastes” excess liquid coolant by mixing it with the core flow. Kinney et al. [7] in 1952 used a vitiated air heater with a water film coolant to find that the coolant critical mass flow rate depended on the gas core flow conditions, concluding that the liquid coolant could be injected at multiple locations to cool more area with less coolant mass flow. The RD-170 engine family did just that, introducing a fuel-film in three annular rings at different axial locations between the injector head and the nozzle throat [3]. Morrell [9] in 1951 confirmed Kinney’s entrainment conclusions in a more representative 1000 lbf liquid oxygen, anhydrous ammonia combustor, specifically avoiding carbon species in the fuel to prevent the formation of deposits that could skew his data. Knuth published a two part paper in 1954 [10] and 1955 [11] along with his Ph.D. thesis in 1954 [12] concluding that the film stability only depends on the coolant flow properties, specifically a viscosity ratio of the liquid and vapor states at the saturation temperature. He also noted that entrainment was observed to be independent of core flow properties such as Reynolds number and momentum flux, which directly conflicts with the conclusions of Kinney and Morrell. Since the early 1950s, a number of researchers including Graham [13] [14], Gater and L’Ecuyer [15], and Sawant et al. [16] have shown that the liquid entrainment rate is dependent on the core flow Reynolds number, momentum flux, and various other parameters such as liquid coolant surface tension. The takeaway from this research is that flight-weight combustors with lower contraction ratios, and therefore higher gas core flow mass fluxes, require more film coolant injection stations to cool the same axial length in order to prevent liquid entrainment.

Liquid films can be injected through discrete holes/slots or a continuous lip at varying radial-to-axial and circumferential angles. Morrell [9] found that 45° axially-angled injectors with tangentially angled holes did not improve cooling effectiveness compared to rectangular slots that were perpendicular to the inner gas flow. More recently, Yu et al. [17] described an experiment to investigate subcritical and transcritical liquid films with a swirl film injector. Further studies both supporting and refuting the use of tangential injection in liquid film cooling at a variety of conditions can be found in the Shine et al. [8] review paper, which concluded that there is a lack of consensus on this topic.

Many liquid coolants, including kerosene, are often injected at subcritical temperatures and supercritical pressures resulting in a transcritical transition of the liquid film. In the case of kerosene, pyrolysis begins to occur at around the “pseudo-critical” temperature cited by most of literature [18] further complicating the process. On the other hand, fuels like hydrogen and methane remain stable through their critical point, with the transition often occurring before injection. Most literature from the late 1900s ignores the transcritical transition of the film, treats the supercritical phase as a gas, or experimentally uses water to ignore criticality concerns entirely. Yu et al. [17] and Haberlan et al. [19] investigated transcritical kerosene films in high pressure kerosene-oxygen combustors. Haberlan et al. [19] adapted a liquid film model by Grisson [20] to predict heat fluxes measured via coaxial thermocouples to within 33% accuracy. Although computational fluid dynamics (CFD) can account for supercritical properties with real gas equations of state, further work is required to incorporate transcritical transition in film cooling empirical models, as noted by Shine et al. [8].

Modeling liquid film cooling has been largely empirical due to several complexities including: convective heat transfer from the gas to the liquid, radiative heat transfer from the gas to the liquid, convective heat transfer from the liquid to the wall, entrainment of the liquid coolant, recovery temperature reduction due to the formation of a coolant-rich gaseous boundary layer, free stream turbulence effects on heat transfer coefficients, film injection geometrical characteristics, transcritical film transition, endothermic reactions of the coolant, carbonaceous deposits due to hydrocarbon coolants, and others. Models since the early 1950s have captured varying portions of these complexities in 1D and 2D formats, culminating in CFD models such as those published by Ananda et al. [6] which solve the conservation equations directly, typically with reduced chemical kinetics models. Despite our increased capability to model the physical and chemical processes occurring in film cooling, we still lack the fundamental knowledge of carbon deposition chemical and physical processes in these high pressure, temperature, and momentum flows.

1.2 Carbonaceous Deposits

Pure carbon exists as two well-known allotropes (and a few rarer allotropes such as fullerenes): graphite that is sp^2 hybridized and diamond that is sp^3 hybridized. Graphite has a delocalized pi-bond-forming electron that connects planar layers of hexagonally structured carbon atoms whereas diamond forms a face centered cubic (FCC) structure. Graphitic-like carbon is of

the most interest to solid carbons formed and deposited from propulsion-related flames because diamond is typically formed at extreme pressures, well above even the highest feasible rocket combustor pressures. Although these two allotropes are most well-known, carbon exists in a variety of other forms distinguished by structure and manufacturing process, as discussed in the IUPAC “Recommended terminology for the description of carbon as a solid” [21]. The ideal graphite crystal contains flat, hexagonally stacked sp^2 carbon atoms in sheets with 120° bond angles as shown in Figure 1.2. Strength and thermal/electrical conductivity are high in the flat plane direction, but are low in the plane-normal direction due to the weak van der Waal’s bonding force of the delocalized pi-bond-forming electron between sheets. Ideal graphite does not exist at the bulk scale due to crystallite imperfections including vacancies, stacking faults, and disclination structures, although pyrolytic graphite can have crystallites with dimensions on the order of microns [22]. The imperfections can become so numerous that single planes exist in a disoriented manner without long-range crystalline order, resulting in “turbostratic” carbon. An allotrope of carbon often denoted as “amorphous” has the distinguishing feature of dangling pi bonds terminated by hydrogen. Carbon deposited in propulsion-related applications can be more amorphous or graphitic in structure depending on the conditions of its formation. [23]

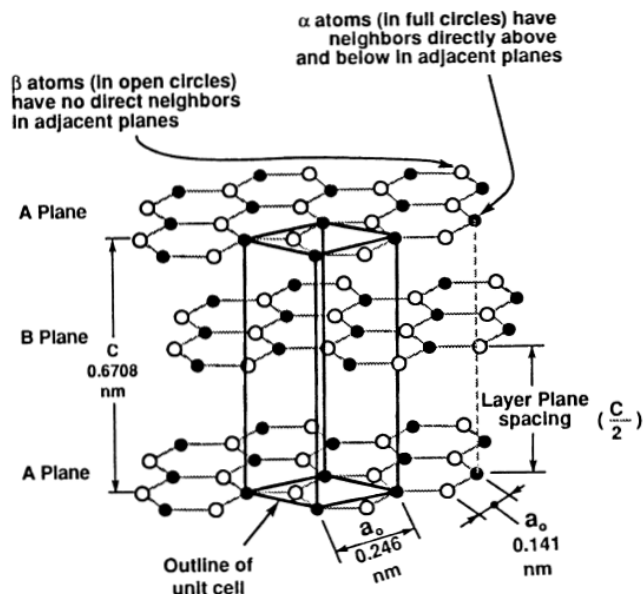


Figure 1.2. Hexagonal structure of graphite with thermodynamically-stable ABAB stacking [23].

graphite. Organic precursors are carbonized into volatile components and solid carbon residue by simultaneous dehydrogenation, condensation, and isomerization reactions. Carbonization is normally a slow process, in which the carbon content of the residue depends on the diffusion of volatile molecules and the preservation of a solid carbon network. Solids formed from carbonization are often deemed amorphous carbon: high in carbon content (up to 99% elevated temperatures above 1600 K) and highly disordered. The mechanism for carbonization involves PAHs condensing into higher molecular weight, higher carbon content aromatics while producing hydrogen-containing gas-phase volatile species. Moldoveanu [24] gives an overview of pyrolysis literature for various hydrocarbons, including n-dodecane which is often used as a surrogate for propulsion kerosenes such as JP-8 and RP-2. While dodecane represents kerosene's physical properties to a certain extent, it significantly misrepresents propulsion kerosenes chemically due to their numerous, and varied, hydrocarbon constituents [18]. Graphitization is the transformation of turbostratic carbon solids at high temperatures and pressures into well-ordered graphite crystallites. Graphitization occurs at temperatures often exceeding 2800 K, and results in a decrease of property isotropy and an increase in bulk density. [23]

Heterogeneous condensation of heavy PAHs can occur directly on cooled walls which are significantly lower than the flame temperature. Saito et al. [25] sampled a methane-air diffusion flame with a fine quartz needle to collect carbon deposits, which were then examined with scanning electron microscopy (SEM) and x-ray photoelectron spectroscopy (XPS). They noted that deposits occurring earlier in the flame (closer to the burner) were shiny and smooth, "almost as if they had been formed in a liquid." Smedley et al. [26] also noted a shiny deposit structure from the regions of their fuel-rich ethene-air flame closest to the flat burner face, especially when using a cooled probe. They used Fourier transform infrared (FTIR) spectroscopy to determine that the cooled probe deposits had higher concentrations of PAHs when compared with the uncooled probe deposits. Preciado et al. [27] carried out a similar experiment to Smedley et al. [26], confirming their results using gas chromatography mass spectrometry (GCMS), while also noting that the condensed PAH deposits had significantly higher density and thermal conductivity compared to the uncooled soot deposits. Shim and Shin [28] examined morphology of deposits from a propane-air laminar diffusion flame by collecting them on 15 μm silicon carbide fibers. They noted liquid-like smooth surfaces along the entire fiber, which bisected the flame's center radially, despite the fiber heating to the flame temperature. However, the smooth deposits were often

covered by soot agglomerates. Condensation of PAHs must be considered as a carbon deposition mechanism for a wide range of fuels, even at higher wall temperatures.

Research concerning carbon deposition on solid surfaces has spanned numerous processes at varying conditions from petroleum refinement to diesel engines and rocket combustors. Several variables affect the physical and chemical processes involving deposition, including but not limited to fuel composition, presence of oxidizing species, catalytic materials, and thermodynamic state. Within propulsion systems, a distinction can be made between three main types of carbon deposition:

1. Pyrolysis (carbonization) of fuels due to heating, such as in supersonic aircraft fuel tanks or regeneratively-cooled rocket combustors. Fuel is heated in a mostly non-oxidizing environment, typically with considerable residence times up to tens of seconds, at relatively low temperatures of 450 to 650 K. Carbon formed catalytically from pyrolysis is filamentous in structure. Carbon formed at temperatures higher than 650 K non-catalytically is typically amorphous or partially-graphitic in structure.
2. Thermophoretic diffusion of carbon agglomerates (soot) that were formed in fuel-rich combustion reactions, such as in fuel-rich gas generators, preburners, or zoned combustion. Soot particles formed in fuel-rich combustion conditions accelerate towards cooled surfaces due to the temperature gradient between the hotter soot-forming conditions and the cooler wall. The particles stick to the wall and can chemically bind to the growing carbon surface. Carbon formed as soot is often considered amorphous in structure, but some graphitization can occur to form graphitic carbon.
3. Condensation of polycyclic aromatic hydrocarbons (PAHs) directly on the wall, which can occur in either fuel-film cooled flows or fuel-rich combustion devices. Wall temperatures must be kept low (compared to adiabatic flame temperatures) for engineering materials to survive. Heavy PAHs can condense directly on the wall due to the lower temperature, resulting in the growth of a graphitic carbon layer. This deposition mechanism has not been considered in propulsion literature concerning carbonaceous deposits, although it is more common in fundamental combustion research.

Bozzano et al. [29] outline the similarities and differences between mechanisms for furnace pyrolysis, steam cracking, and soot formation. Important parallels can be drawn between the processes, such as chain radical mechanisms, polymerization reactions, and thermal

degradation of intermediates, but important distinctions concerning conditions such as residence time, temperature, and oxidizing species complicate the formation of a global fouling phenomenon model. Carbon deposition in fuel-film cooling likely has contributions from liquid pyrolysis, soot formation, and PAH condensation mechanisms. The liquid fuel-film is heated until vaporization, which is intertwined with pyrolysis to more volatile species and carbon deposits in a mostly non-oxidizing flow. Additionally, a fuel-rich gaseous boundary layer develops as the liquid film vaporizes (see Figure 1.1), resulting in soot formation near the wall. The large thermal gradients associated with film cooling generate a thermophoretic force to push soot particles into the chamber wall. As dehydrogenation and condensation chemical reactions occur in the fuel-rich boundary layer, heavier PAH molecules can physically condense directly on the wall. While these mechanisms are physically and chemically different, they act in concert to varying degrees resulting in the carbon deposition seen in kerosene-film cooled combustors.

1.3 Carbon Deposition in Cooling Jackets

Several researchers have studied fouling phenomena of various propulsion-related kerosenes using heated tube tests, where liquid flowing through a tube is heated to measure wall temperatures, heat fluxes, and carbon deposit masses. Edwards and Liberio [30] found that slower auto-oxidative reactions with pre-dissolved air dominated up to a critical temperature that varied based on fuel, after which faster pyrolysis reactions resulted in rapid thermal cracking of hydrocarbon fuels. The former is more applicable to aircraft engine design, whereas the latter applies more to regenerative cooling jackets in rocket propulsion. An interesting conclusion from their work was that higher temperature (800 K) pyrolysis reactions were suppressed by dissolved oxygen, likely due to oxygen-suppressing radicals formed from breaking carbon bonds. On the contrary, auto-oxidative reactions at lower temperatures required dissolved air to occur. Though auto-oxidative carbon deposition mechanisms are important for jet fuel tanks and engines with high residence times, they are typically less important in the rocket propulsion field due to their relatively long time scales.

Hydrocarbon pyrolysis at rocket conditions involves lower residence times, higher heat fluxes, higher wall temperatures, and narrower-cut fuels than auto-oxidative deposition. Roback et al. [31] studied RP-1, JP-7, and propane at pressures up to 34.5 MPa (5000 psia), bulk velocities up to 30 m/s, and wall temperatures up to 811 K (1000°F). They noted a carbon structure

with discrete particles packed over a fused substrate, with spherical (amorphous) particles for the kerosenes and dendritic (filamentous) particles for propane. Deoxygenation of the fuel made little difference at these conditions, but nickel as a wall material showed significantly less carbon deposition when compared with copper. Stiegemeier et al. [32] compared heat transfer, pressure drop, and carbon deposition of JP-7, JP-8, JP-8+100, JP-10, and RP-1 in C10100 and S30400 tubes at flow velocities up to 23 m/s, wall temperatures up to 811 K (1000°F), and pressures of 6.9 MPa (1000 psia). They found that the higher sulfur content in JP-8 and JP-8+100 resulted in over an order of magnitude higher carbon deposition rates in the copper tube when compared with a stainless steel tube at the same flow conditions. Irvine et al. [33] gave an overview of sulfur's deleterious effect on deposition of pyrolysis products at regenerative cooling jacket conditions, culminating in the definition of the RP-2 military specification for a low sulfur kerosene rocket propellant [34] to supersede the 1967 specification for RP-1.

Research regarding heat fluxes, pressure drops, and carbon deposits in RP-2 began with the definition of a new military specification for rocket grade kerosene [34]. Billingsley et al. [35] designed an asymmetric heater for high heat flux analysis of heat transfer coefficients and carbon deposition in copper tubes. Billingsley et al. have yet to publicly report significant results related to carbon deposition, but their experimental setup closely matches the conditions expected in flight-weight copper chamber liners, especially due to the asymmetric heat flux application. Van Noord and Stiegemeier [36] used axisymmetrically heated tubes, similar to Roback's study from 1981 [31], but with RP-2 as the coolant. They noticed a carbon deposition and shedding phenomenon at average wall temperatures greater than 728 K (850°F), specifically near thermocouple attachment points. Novel research in regenerative cooling kerosene cracking has mostly focused on applying old measurement techniques to new fuels (RP-2 in this case). Future work could investigate the carbonaceous deposit physical and chemical structures with modern spectroscopy and imaging techniques to further inform chemistry-based modeling.

1.4 Carbon Deposition in Fuel-Rich Combustion Chambers

Deposition of carbon in combustion chambers can occur due to thermophoretic diffusion of soot from hot combusted gases to the cooler chamber wall. Soot requires a certain set of conditions to form, meaning that carbon deposition can be avoided with careful mixture ratio control. However, mixing patterns resulting from injector design often lead to fuel-rich regions

where soot is unavoidable. Fuel-rich regions result in soot deposition streaks on the chamber walls of smaller single-element engines. This can be less of an issue for larger multi-element combustors where most of the soot remains entrained in the core flow and can oxidize/combust with further mixing, assuming a high enough residence time. An example of deposition-injector patterning is demonstrated by Soller et al. [37], who showed an image of carbon deposition streaks linked with the kerosene injector orifice pattern. When Soller et al. [38] added a swirl component to the oxygen side of the injector, the carbon deposits were reduced and the flame color changed from yellow to blue, indicating better mixing. Additionally, some combustors do not have the option of operating at stoichiometric or oxygen-rich conditions, such as with fuel-rich gas generators or preburners

Kerosene fuel-rich gas generator and preburner studies have found that soot deposition can prevent reusability, and even impact performance for firing times typical of boost stage engines. Schoenman [39] developed a simple soot deposition model based on C_2H_2 concentration for fuel-rich preburner design. Makel [40] made further progress on fuel-rich gas generators and preburners by investigating methane, propane, and RP-1 as fuels. He found that methane had no carbon deposits, propane could be operated up to 1090 K (1500°F) without incurring significant deposits, and RP-1 could not be operated in the desired temperature range without significant carbon deposition. Suggestions for reducing carbon deposition included rapidly mixing fuel and oxidizer to prevent soot particle nucleation, using fuel additives to suppress soot surface growth reactions, and tailoring the wall temperature profile to capture soot in non-critical regions and reject soot in critical regions. For typical soot particle sizes of 10 to 200 nm, Makel found that soot thermophoretic forces were orders of magnitude larger than diffusion and inertial impaction forces. Additionally, he stated that pyrolysis of fuel droplets from the injector could be a source of carbon deposition, but is likely dwarfed by soot-forming mechanisms. His 1D empirical model formulation for soot deposition would account for soot thermomphoresis and reentrainment (shedding), but required significant experimental data that was not available at the time. As a secondary source on thermophoresis in propulsion literature, Soller et al. [41] noticed higher carbon deposition rates in a water-cooled main combustion chamber with lower wall temperatures compared to a heat sink cooled chamber with higher wall temperatures.

A wide array of fundamental research focuses on experimenting with and modeling of soot, but typically at conditions far from those expected in rocket combustors. The goal is to isolate soot

formation and growth mechanisms from mixing, turbulence, deposition, oxidation, and other difficult to control physical/chemical phenomena. The left side of Figure 1.3 outlines the major processes that occur in soot formation. Polyenes are highly reactive, and play a major role in soot formation [42]. Acetylene (C_2H_2) can be formed from pyrolysis in fuel-rich regions. PAHs form via the hydrogen abstraction, C_2H_2 addition (HACA) mechanism into large structures, at which point particle nucleation occurs. Surface growth of the nearly-spherical particles continues, after which agglomeration and coagulation occurs to form larger particles.

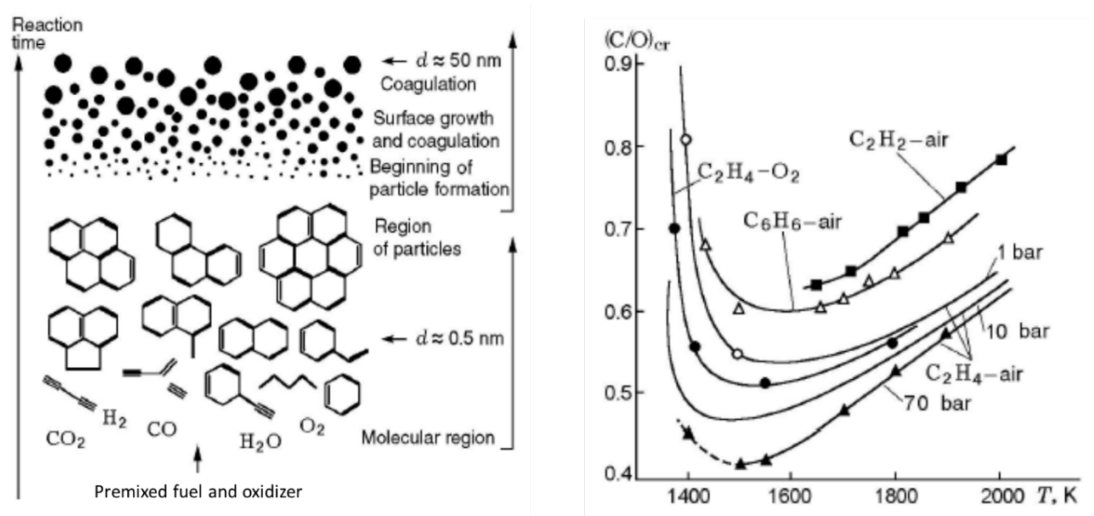


Figure 1.3. Soot formation chronology including PAH formation, particle nucleation, surface growth, and agglomeration [43] (left). Critical carbon-to-oxygen atom ratio for various fuels, pressures, and oxidizers showing a minimum at 1400-1600 K due to a balance of pyrolysis and oxidation reactions [42,44] (right).

Mansurov gives an overview of soot in combustion research that covers a wide range of conditions. A threshold value for the carbon-to-oxygen atom ratio above which soot begins to form, called the critical carbon-to-oxygen ratio $(C/O)_{cr}$, is often determined in premixed flat flame burner systems, with typical results shown on the right of Figure 1.3. Note that C/O is another metric for quantifying mixture ratio, or O/F , where the latter is typically used in propulsion nomenclature. A C/O ratio of one corresponds to hydrocarbon combustion directly to CO and H_2 , above which soot formation is favorable due to the lack of oxygen. Critical C/O ratios are typically lower than one even in these premixed systems due to the slow reaction kinetics of CO_2 and H_2O reduction reactions, both of which have high activation energies [45]. Too low of a flame temperature, typically less than 1400 K, results in a sudden increase in $(C/O)_{cr}$ because pyrolysis cannot occur. A minimum $(C/O)_{cr}$ of around 0.4 to 0.6 occurs at around 1400 to 1600 K depending on the fuel.

Increasing flame temperature past 1600 K results in a monotonically increasing $(C/O)_{cr}$ because oxidation reactions begin overtaking pyrolysis at the higher oxygen-content mixture ratios. Increasing pressure up to 7 MPa decreases $(C/O)_{cr}$ while using pure oxygen as the oxidizer increases the critical ratio with C_2H_4 as the fuel. Higher pressure weakly reduces the critical C/O ratio in a premixed system (right of Figure 1.3) and it strongly increases the soot volume fraction produced. High C/O ratio also exponentially increases soot volume fraction just above the critical C/O, as shown in Figure 1.4. The flame temperature, concentration of hydrocarbons subject to pyrolysis (pressure), and residence time are the main factors affecting soot formation. [42]

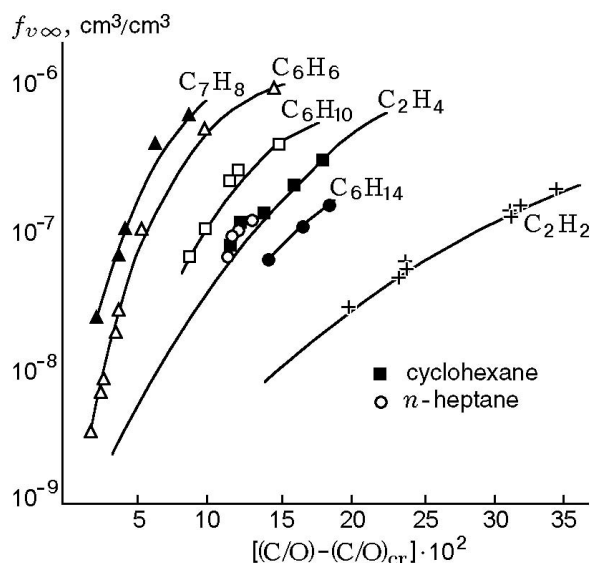


Figure 1.4. Soot volume fraction as a function of premixed fuel-air composition above the critical C/O ratio. [42,44]

Thermophoresis causes particles to follow temperature gradients due to uneven heating on either side of the particle. In soot literature, it is widely accepted that thermophoresis is the dominant force (aside from convection) that determines how soot particles formed in an interior flame deposit on cooler surrounding walls (see Chapter 2.1 of [46]). Diffusion, turbophoretic, electrostatic, and gravitational forces are orders of magnitude lower than thermophoretic forces for typical soot particle sizes in typical flame thermal gradients. In the free molecular region, for Knudsen numbers much greater than one, the thermophoretic steady-state velocity is independent of particle size. The validity of this assumption is highly dependent on the pressure of the soot-producing flame, and somewhat less dependent on the soot particle size which typically doesn't vary by more than an order of magnitude. Waldmann [47] derived Equation 1.1 for

thermophoretic velocity U_T in the $Kn \gg 1$ range, where μ is gas dynamic viscosity, ρ is gas density, α_m is the accommodation factor, ∇T is the gas temperature gradient and T is the particle temperature.

$$U_T = -\frac{3\mu}{4\rho(1+\frac{\pi}{8}\alpha_m)} \frac{\nabla T}{T} \quad (1.1)$$

The thermophoretic velocity is in the opposite direction as the temperature gradient, meaning that particles are pushed towards cooler surfaces since more gas molecules impact the particle on its hot side. Multiplying thermophoretic velocity U_T by soot volume fraction f_V results in the soot volume flux Φ_V in the direction of the thermal gradient, which is typically towards the wall (Equation 1.2). Assuming all soot particles stick to the wall and no shedding occurs, the deposition growth rate is proportional to the soot volume flux. While the thermophoretic velocity is fairly insensitive to chamber conditions which can be predicted fairly accurately, the soot volume fraction can vary by multiple orders of magnitude for small changes in local C/O ratio as shown in Figure 1.4.

$$\Phi_V = f_V U_T \quad (1.2)$$

1.5 Carbon Deposition in Fuel-Film Coolant Flows

The carbon deposition mechanism in fuel-film coolant flows likely has liquid pyrolysis, thermophoretic diffusion of soot, and PAH condensation components. Liquid fuel-films have lower residence times and higher temperatures when compared with regenerative cooling jackets; but liquid fuel-films have higher residence times and lower temperatures when compared with the bulk soot formation conditions in combustion chambers. The fuel-film cooling deposition problem can be thought of as a hybrid between these two, already studied problems.

Several older experimental studies investigated kerosene-film cooling and noticed advantageous performance due to carbon deposition thermal resistance downstream of the fuel-film injector. Graham [14] compared kerosene as a film coolant with water and white fuming nitric acid (WFNA) in a kerosene-WFNA combustor with a chamber pressure of 3.5 MPa (500 psia). He determined a cooling efficiency factor that was specific to his combustor which measured liquid film coolant length increase due to the carbonaceous deposits. Volkmann et al. [48] investigated kerosene film cooling at chamber pressures up to 14 MPa

(2000 psia) and concluded that film cooling could be an effective way to reduce nozzle throat heat flux without compromising specific impulse significantly.

A set of experiments tested at Technische Universität München (TUM) looked at film cooling in small-scale, single element, kerosene-oxygen combustors at chamber pressures up to 14 MPa (2000 psia). Soller et al. [41] noticed intermittent burning of carbon deposition from the liquid fuel-film in videos of the plume, in addition to the wall temperature effect on thermophoresis mentioned previously. Höglauer et al. [49] varied the film coolant between kerosene, water, and inert gases at similar mass flow rates to isolate the effects of carbon deposition. Water was expected to cool more effectively than kerosene or inert gases based on empirical liquid film cooling correlations, but kerosene had better performance. The researchers postulated that carbon deposition may have been the cause for increased cooling compared to water. The TUM team has published numerous papers on film cooling that call for future work on carbon deposition characterization based on results from these single-element experiments.

AFRL rectangular duct combustor data was tabulated in a database to aid kerosene-film cooling modeling efforts. Himansu et al. [6] ran 2D CFD models in rectangular coordinates for the fuel-film injector with convective, radiative, and conjugate heat transfer. Predicted heat fluxes were within an order of magnitude of those measured at AFRL. One of the key improvements identified in the future work section was the incorporation of soot formation/oxidation and carbon deposition mechanisms. Follow-on CFD work by Bills et al. [50] improved the radiative heat transfer model, but still noted that the inclusion of a carbonaceous deposit model was intended for future numerical modeling.

Gokulakrishnan et al. [51] fired a propane/air burner over n-dodecane and RP-2 film-cooled copper coupons while sampling gas composition above the fuel-film with a gas chromatogram. They concluded that the primary mechanism for carbon deposition in film cooling was pyrolysis because most of the measured species were olefins with an absence of acetylene, the latter of which would be expected for soot formation via the HACA mechanism. However, firing at atmospheric pressure may have resulted in reduced soot formation compared with the conditions expected in rocket combustors, potentially invalidating the extension of this conclusion to higher pressures.

The key factor missing in these fuel-film combustor experiments was a focus on identifying and measuring the properties of carbonaceous deposits. Measuring heat flux is useful for CFD

validation, but physically acceptable models depend on a better understanding of how the deposits form.

2. OBJECTIVES

Three different regimes of solid carbon formation have been identified in the literature review: pyrolysis at regenerative cooling conditions, sooting in fuel-rich combustion, and PAH condensation on cool combustor walls. A variety of experimental and modeling literature covers these regimes, especially when concerning soot formation. However, fuel-film carbon deposition is at a middle-ground between the conditions of these regimes, meaning that experiments and models may have to account for all three mechanisms. Investigating carbon deposit properties with modern imaging and spectroscopy is key to better understanding the conditions at which the deposits are formed. Additionally, the development of an axisymmetric set of temperature, heat flux, and carbon deposit thickness data at various fuel-film conditions would provide validation cases for CFD deposition models. The proposed research attempts to answer the three main questions below, in order from applied to fundamental:

1. How do ORSC conditions affect fuel-film carbon deposition thermal resistance?
2. What are the carbonaceous deposits' physical and chemical structure?
3. What mechanisms contribute to carbon deposition?

The following work is an attempt at determining an answer to the third question in tandem with the first two via a combination of in-situ heat flux, thermophysical property, and carbon depth measurements, along with spectroscopic analysis.

3. TASK 1 COMBUSTOR

The following work was a collaboration between CFD Research Corporation (CFDRC) and Purdue University under a Phase II STTR project sponsored by the U.S. Air Force to develop and validate chemical kinetics models for the prediction of carbon deposition in fuel-film cooled rocket engines.

3.1 Requirements

The experimental hardware consisted of a kerosene-H₂O₂ bipropellant fuel-film cooled rocket combustor operating at pressures up to 4.8 MPa (700 psia) and run times up to 15 s. The oxidizer was 90 wt.% hydrogen peroxide, which was chosen due to Purdue University's extensive experience with the propellant despite its lower adiabatic flame temperature and hydrogen-rich combustion conditions when compared with the kerosene-oxygen propellant combination. The combustor design, as shown in Figure 3.1, focused on preserving axisymmetry where possible, and sample symmetry elsewhere to reduce computational time for validation of CFD carbon deposition models. The experiment was designed to satisfy the following goals:

- Axisymmetry maintained throughout the combustor where possible to enable rapid 2D model development.
- Chamber pressures and temperatures up to 4.8 MPa (700 psia) and 2800 K (6600°F) were a first step towards achieving oxygen-rich staged combustion conditions of approximately 26 MPa (3800 psia) and 3900 K (6600°F). The Task 4 combustor described in Section 5 more closely approaches the conditions expected in ORSC engines.
- Post-test analysis required access to the surface of a removable sample tube, which can be difficult in an axisymmetric combustor. The Purdue team developed a sectioning method for sample preparation that preserved the carbonaceous deposits while exposing them for analysis.
- Easily-removable samples and interchangeable mass flow rate limiting cavitating venturis allowed for rapid testing at different conditions.

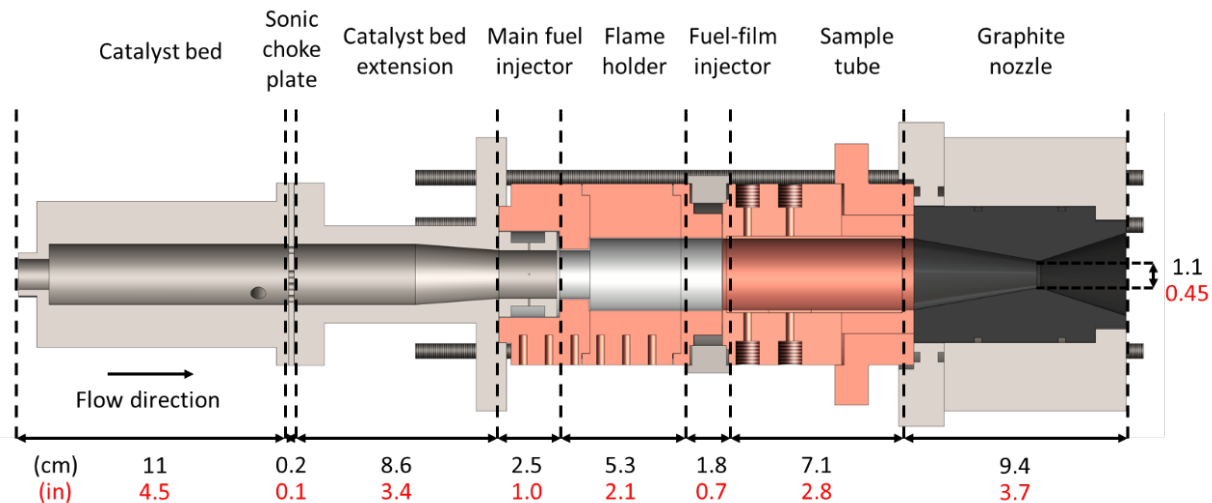


Figure 3.1. CAD cross section of the Task 1 heat-sink and fuel-film cooled combustor for carbon deposition analysis.

Figure 3.1 shows the fuel-film combustor used for all of the tests outlined in the present experimental effort. Flow through the combustor started with 90 wt.% hydrogen peroxide injected through a 25 mm (1 inch) inner diameter catalyst bed packed with silver-coated stainless steel screens to decompose H_2O_2 to approximately 1000 K (1340°F) hot oxygen and steam. A sonic choke plate with holes in a 1, 5, 10 pattern prevented back-flow of carbon combustion products should bipropellant over-pressurization occur. The catalyst bed extension part between the catalyst bed choke plate and main fuel injector allowed for boundary layer development such that the flow could more closely approach axisymmetry. At the main injector, fuel radially injected through four 0.64 mm (0.025 inch) holes penetrated the hot oxygen and steam flow at a mixture ratio ranging from 4 to 7.5 (stoichiometric) depending on the target test conditions. A rearward-facing axisymmetric step further promoted mixing while acting as a flame holder, increasing the internal diameter from 20 mm (0.8 inch) to 30 mm (1.2 inch). The design criterion used to determine the dimensions of this step is described by Sisco [52]. Downstream of the step, a fuel-film injector introduced a low velocity kerosene flow through a 0.25 mm (0.01 inch) gap to cool the inner wall of a tubular sample. The fuel-film flow rate and sample length were set such that liquid-gas transition of the fuel-film occurred on the sample. A graphite converging-diverging nozzle choked the flow to achieve elevated chamber pressures up to 4.8 MPa (700 psia).

3.2 Test Operation

The combustor was operated on a liquid bipropellant test stand using a SCXI-based National Instruments data acquisition system with measurement frequencies between 500 and 1000 Hz depending on the number of thermocouples used in each test. A hardware timed cDAQ-based National Instruments system was used to control run valves with an auto-sequence. Three choked cavitating venturis were used to set H_2O_2 , main fuel, and fuel-film mass flows with upstream pressure measurements to determine mass flow rate to within 1% relative uncertainty. Hydrogen peroxide concentration, and therefore density, was measured using a Fisher Scientific model 334620 bench-top refractometer with an uncertainty of 0.1%. RP-2 [53] and JP-8 [54] fuel densities were determined using the Tait equation of state for mass flow rate calculations. H_2O_2 density was calculated by an experimental fit against concentration and temperature from Rocketdyne's "Hydrogen Peroxide Handbook" [55]. The venturi discharge coefficients were calibrated in place using a water discharge method with an atmospheric exit condition. Other key pressure transducers were located upstream of the catalyst bed orifice plate, main fuel injector orifices, and graphite nozzle to measure the catalyst bed outlet, main fuel injector manifold, and combustion chamber pressures respectively. Each pressure transducer was calibrated with a NIST-traceable high accuracy pressure transducer at room temperature. Omega GKMQSS-062E-6 1.6 mm (1/16 inch) diameter exposed tip thermocouples placed at 50 locations within the copper main sample chamber were used to measure heat flux via an inverse method which will be discussed in Section 3.5.

Remotely controlled pneumatic valves and electronically controlled pressure regulators were operated by auto-sequences capable of automated red line abort sequences. The catalyst bed was typically pulsed three times for approximately 0.5 seconds each to heat the silver screens and fill H_2O_2 dead volume before running the main auto-sequence. In most tests the auto-sequence involved a monopropellant mode without main fuel or fuel-film injection for 2 seconds, followed by a bipropellant burn. An approximately 0.5 second long, 0.7 MPa (100 psia) nitrogen purge through the oxidizer and fuel lines reduced post-test contamination of the carbonaceous deposits by excess hydrogen peroxide or fuel. The nitrogen purge was pressurized behind a check valve during the last second of bipropellant test firing, such that the purge started immediately after the chamber pressure reduced below 0.7 MPa (100 psia). Purging with this method reduced liquid propellant dribble and shutdown transient times. Purges through the main fuel and fuel-film

injectors were shut down before the H₂O₂ catalyst bed purge to prevent backflow of fuel contaminants. Red line abort sequences checked for under/over-pressure during monopropellant and bipropellant modes to return the stand to a safe state when the red line conditions were satisfied. After firing, propellant tanks were vented to atmospheric pressure and any remaining propellant was dumped into separate oxidizer and fuel containers, each of which was disposed in an appropriate manner. The combustor was allowed to cool by natural convection before removal of the sample with carbonaceous deposits. An auto-sequence for the baseline test conditions, such as those used in tests 53 and 54, is shown in Table 3.1. Valves were commanded at the indicated entries, where empty entries retained their previous states. All valves started in the closed state before $t = 0$ seconds. Propellant tank ullages were pressurized prior to starting the auto-sequence.

Table 3.1. Auto-sequence timing table for the H₂O₂, fuel, and purge valves of the Task 1 combustor.

Time (s)	H₂O₂ Valve	Fuel Valves	H₂O₂ Purge Valve	Fuel Purge Valves
0	open			
2		open		
7.5			open	open
8	close	close		
8.5				close
8.6			close	

3.3 Test Conditions

Several combustor parameters were varied to determine their effect on carbon deposition in the fuel-film cooled combustor. The main fuel and fuel-film could be either RP-2 POSF5433 or JP-8 POSF10264 to determine the effect of fuel sulfur, olefin, and aromatic content on carbon deposition. Fuel-film mass flow rate could be adjusted by changing the fuel-film cavitating venturi and upstream set pressure. Bipropellant run time was varied between 1 and 15 seconds, where the baseline run time was 6 seconds.

The tubular sample surface roughness was varied to determine the effect of surface finish on carbon deposition. Each sample was machined on a lathe from tube stock, leaving a nearly polished surface finish. The surface roughness was increased by sandblasting the inner diameter

of the sample tube with Black Blast™ [56] abrasive (1.5 - 2.0 mil anchor profile) after masking the outer, heat transfer surface, as shown in Figure 3.2.

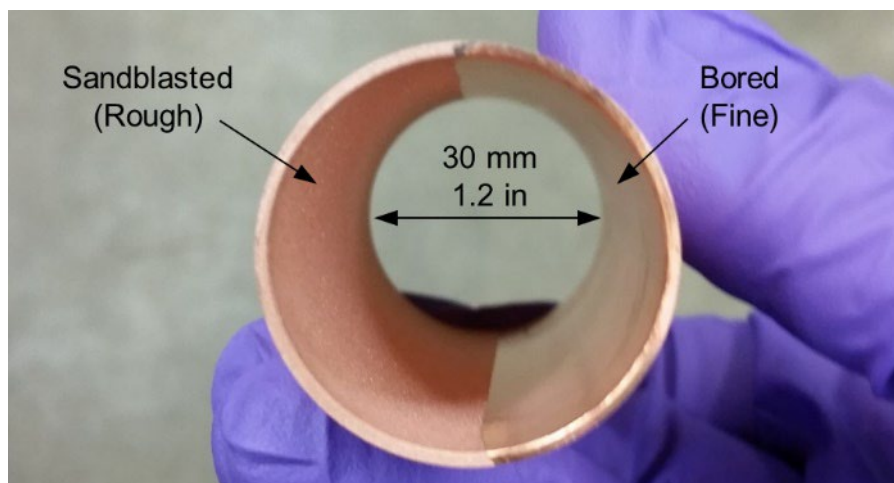


Figure 3.2. Sample tube surface roughness was varied by approximately an order of magnitude via sandblasting.

Chamber liner materials of oxygen-free high thermal conductivity copper UNS C10100 (C101), stainless steel UNS S30400 (S304), and Inconel 600 UNS N06600 (N066) were tested to determine if catalytic carbon deposition occurred at fuel-film combustion conditions, where the baseline material was C101. Changes in sample material were accompanied by changes in chamber/liner temperature profiles due to the differences in metal thermal properties. A baseline condition was chosen for each parameter, where variations from the baseline could be used to identify tests from one another. Most of the baseline feed system and combustor conditions are shown in Table 3.2 and Table 3.3 respectively, which list the conditions of test 53. The bipropellant core flow entries only include fuel from the main injector, whereas the bipropellant total entries include fuel from the main and film injectors. All values are measured except for stagnation temperature, which was calculated from NASA's chemical equilibrium analysis (CEA) code [57] based on measured chamber pressures and mixture ratios. Note that the fuel-film mass flow rate seems high compared to the main fuel mass flow rate because of the higher stoichiometric mixture ratio of kerosene-H₂O₂ when compared with kerosene-oxygen. The fuel-film mass flow rate was 12% of the total propellant mass flow, despite being over half of the total fuel mass flow. Additionally, smaller combustors have higher surface area to volume ratios, requiring more film coolant than equivalent larger combustors. A full test matrix of completed tests can be found in Appendix A.

Table 3.2. Example feed system conditions from test 53 of the fuel-film combustor.

Feed System Property	Oxidizer	Main Fuel	Fuel-Film
Propellant	90.8 wt.% H ₂ O ₂	RP-2 POSF5433	RP-2 POSF5433
Ullage Pressure MPa (psia)	13.1 (1900)	8.0 (1160)	8.0 (1160)
Venturi Throat			
Diameter mm (inch)	1.3 (0.052)	0.61 (0.024)	0.71 (0.028)
Mass Flow Rate g/s (lb _m /s)	252 (0.556)	33.6 (0.074)	37.8 (0.083)

Table 3.3. Example combustor conditions from test 53 of the fuel-film combustor. Stagnation temperatures calculated from NASA CEA [57].

Combustor Property	Monopropellant	Bipropellant (core flow)	Bipropellant (total)
Mixture Ratio	N/A	7.51	3.53
Stagnation Temperature K (°F)	1030 (1390)	2780 (4540)	1990 (3120)
Chamber Pressure MPa (psia)	2.14 (311)	4.57 (663)	4.57 (663)

Figure 3.3 shows a typical chamber pressure curve, specifically for the baseline conditions of test 53. Monopropellant mode ran from 0 to 2 seconds while bipropellant mode ran from 2 to 8 seconds, with an ignition delay of approximately 0.5 seconds mostly due to the main fuel dead volume. An approximately 2% chamber pressure instability typically occurred during bipropellant mode operation at a fundamental frequency of 80 Hz. Previous testing with a converging-only nozzle showed that the instability was likely coupled with acoustics from the exhaust diverter. This conclusion is further supported by the first longitudinal mode frequency being an order of magnitude larger than the measured instability. Chamber pressure slightly increased from 2.5 to 4 seconds as the combustor approached a quasi-steady-state of carbon deposition and shedding in the nozzle throat. Throat deposit thickness was approximately 0.12 mm (0.005 inch) based on chamber pressure measurements, which seemed plausible based on post-test pin gaging of the throat and the chamber liner deposit thickness measurements described in Sections 4.2. This chamber pressure quasi-steady state was reached at approximately 4 seconds of every test because the 2 second monopropellant mode cleared carbonaceous deposits from previous tests, and the initial bipropellant burn from 2 to 4 seconds built them back up again.

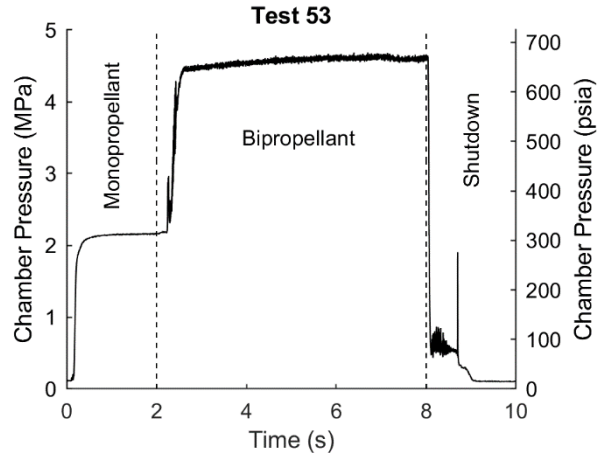


Figure 3.3. Test 53 chamber pressure curve showing a 2 second H_2O_2 monopropellant mode and a 6 second kerosene- H_2O_2 bipropellant mode.

Several combustor conditions were different from those expected in typical ORSC engines to simplify the design and operation of the Task 1 combustor. Hydrogen peroxide was used as the oxidizer due to Purdue's significant experience with the propellant and the availability of a H_2O_2 catalyst bed. Bipropellant flame temperatures were reduced by approximately 1000 K (1800 R) and combustion gas hydrogen content was increased compared to typical ORSC conditions due to this oxidizer choice. The oxidizer and catalyst bed selection placed a limitation on chamber pressure of approximately 4.8 MPa (700 psia). The reduced pressure affected the thermodynamic state of the combustion gases, specifically water (supercritical in high pressure engines), and likely changed the soot formation chemistry towards being more kinetics-limited as opposed to diffusion-limited when compared with soot formation at higher pressures. Additionally, a lower chamber pressure pushes the mixture ratio for optimal specific impulse towards lower values due to recombination kinetics in the nozzle, further affecting the combustion and carbon formation chemistry in the chamber. The propellant temperatures at injection were chosen to simplify the combustor's operation. Both the oxidizer and fuel-films injected in ORSC engines would be preheated due to the preburner and regenerative cooling jacket respectively. For instance, the RD-180 injected oxygen-rich turbine effluent into the main chamber at approximately 550 K [58]. The Task 1 combustor injected approximately room temperature kerosene, extending the length and cooling capacity of the fuel-film when compared to the ORSC case. Despite these shortcomings, the design of this combustor allowed for rapid design, build-up, and testing with simplified heat flux calculations, as will be described in Section 3.5. Section 5 describes an

18 MPa (2600 psia) kerosene-oxygen combustor that used lessons learned and post-test carbon analysis techniques developed from this combustor.

3.4 Heat Transfer Analysis

The Task 1 combustor was fairly safe from thermal hardware damage due to the long thermal transients inherent to heat sink cooled hardware. A 0D lumped capacitance model and 2D axisymmetric heat transfer model were used to verify combustor integrity for the up to 15 second bipropellant test fires.

3.4.1 Lumped Capacitance Model

A 0D lumped capacitance model was used to compare with experimental data from qualification test 29, which had no fuel-film and occurred at a reduced pressure of approximately 14 bar (200 psia). Appendix A further describes the conditions of test 29. Three K type thermocouples clamped to the outside of the sample chamber measured the outer wall temperature. The Dittus-Boelter correlation [59] for turbulent flow was used to calculate a convective heat transfer coefficient of $1400 \text{ W/m}^2\text{-K}$ for the hot combustion gas flow with a recovery temperature of 1690 K from NASA's chemical equilibrium analysis (CEA) code [57]. A constant copper specific heat of 386 J/kg-K and thermal conductivity of 400 W/m-K were assumed due to the small change in temperature of the sample chamber. An inherent model error of approximately 5% is expected because the Biot number was calculated to be 0.14. This error is evident from the measured data on the left plot of Figure 3.4 where the peak temperature occurs 12 seconds after the combustor shuts down. A lower Biot number would reduce thermal soak-back because the sample chamber would have a smaller temperature gradient across its thickness. Additionally, the following heat fluxes and thermal resistances were neglected and are listed in order of decreasing importance:

1. Carbon layer thermal resistance between the hot gas flow and the copper inner tube wall.
2. Thermal contact resistance between the copper inner tube and the copper sample chamber.
3. Increased convective heat flux due to the boundary layer formed after the flame holding step.
4. Radiation heat flux from soot in the flow to the copper chamber wall.

5. Axial heat flux from the copper sample chamber through the graphite gaskets to nearby parts.
6. Natural convection from the outer chamber wall to ambient conditions.

The left plot of Figure 3.4 shows the measured and lumped capacitance model temperatures vs. time. The temperatures at the autosequence start time of $t = 0$ seconds are 340 K due to the H_2O_2 pulses used to heat up the catalyst bed before firing in bipropellant mode. The slope of the two lines when multiplied by the total copper mass and specific heat constants is equal to the heat power input in watts from the combustion gas convective heat flux. Slopes corresponding to 7.3 and 8.4 kW were measured and calculated for the experiment and model respectively when fit with a linear regression. The over approximation of the model heat flux by about 15% is highly encouraging and can likely be mostly explained by the first assumption in the list above. The slopes are nearly constant due to the high recovery temperature compared to the copper chamber temperature. As the copper sample chamber temperature increases, the heat input and temperature vs. time slope would decline due to the decreasing temperature gradient. Additionally, as carbonaceous deposits increase in thickness, the temperature profile will similarly decrease in slope.

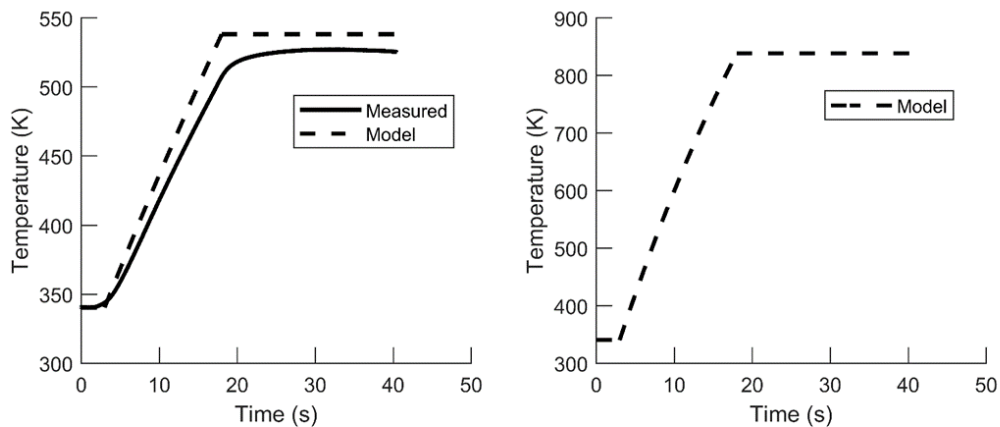


Figure 3.4. Test 29 low pressure combustor heat sink temperature vs. model (left) and predicted temperatures for the nominal higher pressure Task 1 combustor (right).

3.4.2 2D Axisymmetric Transient Model

A 2D axisymmetric transient COMSOL heat transfer model was used to predict temperatures and heat fluxes for the Task 1 combustor. The domain of the model shown in

Figure 3.5 encompasses the entire combustor from the catalyst bed inlet to the converging nozzle exhaust. The default COMSOL triangular mesh was used with 3649 domain elements and 652 boundary elements. This mesh size was considered appropriate because refining the mesh with more elements consistently resulted in the same solution. Many mesh elements were concentrated around the thin TBC to resolve the temperature gradient across it.

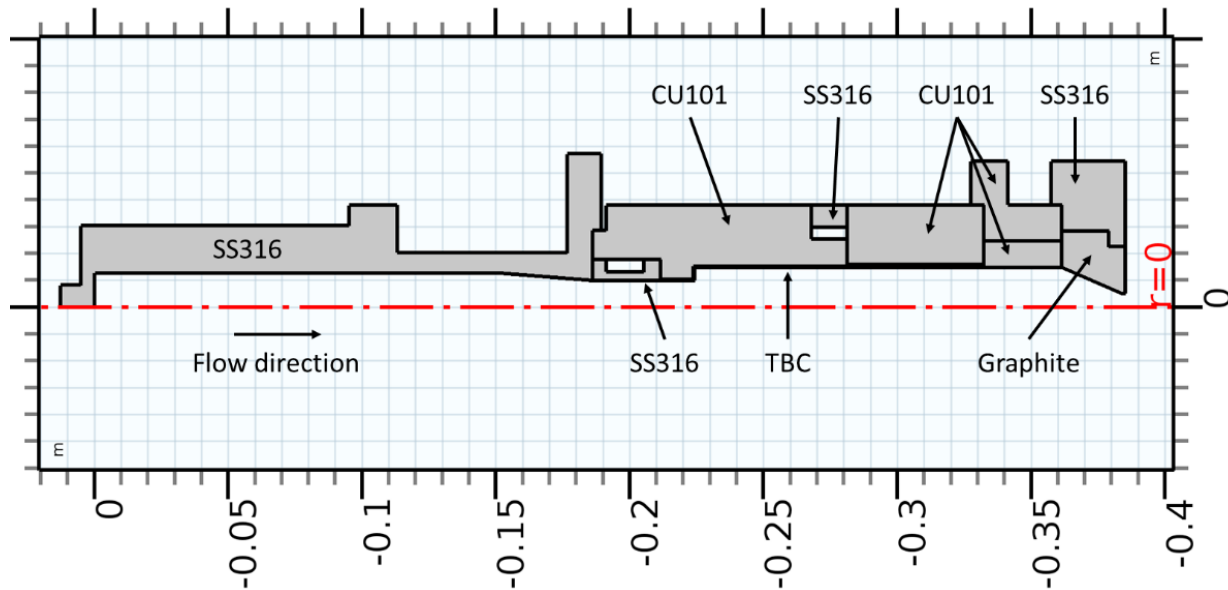


Figure 3.5. High pressure combustor COMSOL heat transfer model domain with materials.

The Bartz correlation [60] for turbulent heat transfer coefficients was used on the gas side in the catalyst bed, core flow, and fuel-film regions of the combustor. The fuel-film was assumed to be perfectly mixed with the core flow when injected, which would cause the boundary condition to over predict gas side heat flux.

It was assumed that the radiative heat transfer above the fuel-film injection point would be negligible due to the stoichiometric mixture ratio of the core flow. However, a Stefan-Boltzmann radiation boundary condition was combined with the convective boundary condition downstream of the fuel-film injector as a conservative measure. A more accurate radiative heat transfer model would account for soot particle formation and radiation as the fuel-film vaporizes and mixes with the core flow. A natural convection heat transfer coefficient of $5 \text{ W/m}^2\text{-K}$ and a radiation boundary condition with an emissivity of 0.1 was used on the outside of the combustor.

Graphite gaskets were not included in the COMSOL heat transfer model. The thermal resistance of these axial 1 mm (when compressed) thick gaskets is small, and likely negligible

since most of the heat flows radially through the combustor. All parts were considered to be in perfect thermal contact with each other due to the axial compressive preload provided by six mild steel 6.35 mm rods.

As mentioned previously, a thermal contact resistance model for the sample inner tube contact with the outer sample chamber would require a contact pressure, which is not known in this particular application. A Cooper-Mikic-Yovanovich correlation [61] was used with contact pressures ranging from close to 0 bar, essentially an insulating boundary condition, up to the chamber pressure of 52 bar. The results presented below assume perfect contact between the sample and chamber for lack of a method for determining the correct contact pressure.

The fuel manifolds were modeled as an insulating boundary condition because a thermal barrier coating was applied to most copper surfaces in the main fuel and fuel-film manifolds. The stainless steel surfaces had a low enough thermal conductivity such that the fuel manifold could be modeled as insulating without significant loss of accuracy. The temperature dependent thermal properties of thermal conductivity and heat capacity for pure copper [62,63], stainless steel 316 [64,65], yttria-stabilized zirconia TBC [66], and graphite [67] were used to improve the model's accuracy at high temperatures. An initial condition of 300 K was used, which does not account for the monopropellant mode firing to heat the catalyst bed that typically raises the combustor temperature by around 50 K.

The upper part of Figure 3.6 shows the temperature contours of the combustor calculated by the COMSOL heat transfer model. Upstream of the main fuel injector, the recovery temperature of the hot oxygen and steam was low enough that the SS316 parts could be run continuously without failing. The hottest, and most likely to fail, area of the combustor was just upstream of fuel-film injection due to the location of the fuel-film manifold. As mentioned previously, the model likely overpredicts the heat flux in this area because of the fuel-film perfect mixing assumption. The lower part of Figure 3.6 zooms into the fuel-film injection point to take a closer look at the hottest area of the combustor. The thermal gradient across the TBC is established within the first few seconds of firing, however the copper around the TBC prevents it from heating past 1900 K. Based on this model, run times past 15 seconds would be infeasible as the copper would begin yielding at temperatures above 850 K.

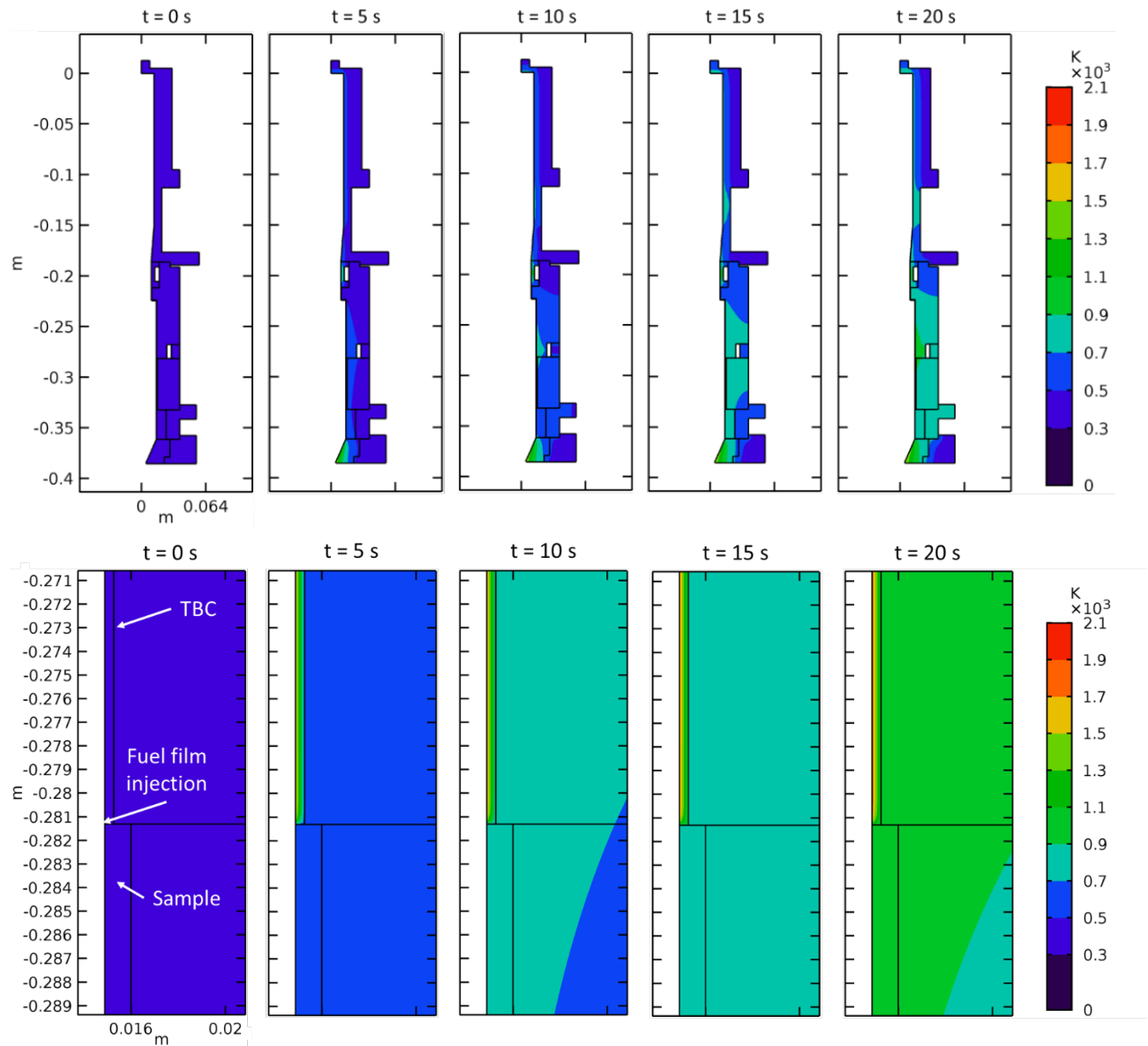


Figure 3.6. Combustor temperature contours predicted by a 2D axisymmetric, transient heat transfer model for bipropellant run times up to 20 seconds.

3.5 Heat Flux Measurements

Heat flux measurements were used to determine the effectiveness of the fuel-film as a function of different combustor operating conditions, like many of the experiments referenced in Section 1. Several authors have described heat flux measurement techniques for high enthalpy flows [68,69]. The null point calorimeter style heat flux measurement was chosen because it pairs well with the copper heat-sink cooled chamber. Small temperature gradients with both distance

and time can be accurately measured for large distances and times. The C101 chamber was used as the thermally conducting element, similar to the small copper cylinders typically used in null point calorimeters, and thermocouples were embedded into the chamber at various depths to measure temperature as a function of radial and azimuthal position. Temperature at multiple discrete radial and azimuthal positions could then be used to calculate heat flux on the inner sample tube surface since the copper chamber had known thermal properties.

Large portions of this section are identical to those to be published in the journal paper by Piper et al. [70]

3.5.1 Thermocouple Installation

Type K 1.6 mm (0.063 inch) sheath diameter exposed tip thermocouples were adhered into 50 blind holes within the copper chamber to measure temperature at combinations of 14 azimuthal and four axial positions, as shown in Figure 3.7. Exposed tip thermocouples were chosen because the approximately 0.5 mm (0.02 inch) diameter of the nickel-chromel/nickel-alumel junction fit well into the 118° point angle pocket left behind by the sample chamber drilling operation with a #51 drill bit. The thermocouples were grouped into clusters of two and three, with each thermocouple in a group located at a different radial depth (top left inset of Figure 3.7). Three radial depths from the outer wall of 8.9, 12.1, and 15.2 mm (0.35, 0.475, and 0.6 inch) were used such that radial temperature differences could be measured at each azimuthal grouping location. The axial distances of thermocouple levels A, B, C, and D pictured on the right side of Figure 3.7 were 7.6, 19.1, 30.5, and 41.9 mm (0.3, 0.75, 1.2, and 1.65 inch) from the fuel-film injector respectively. A number and capital letter indicating azimuthal and axial location respectively determined each thermocouple location for data collection and analysis purposes. For example, TC-7B had the largest radial depth of 15.2 mm (0.6 inch) and was in the second axial position, 19.1 mm (0.75 inch) from the fuel-film injector.

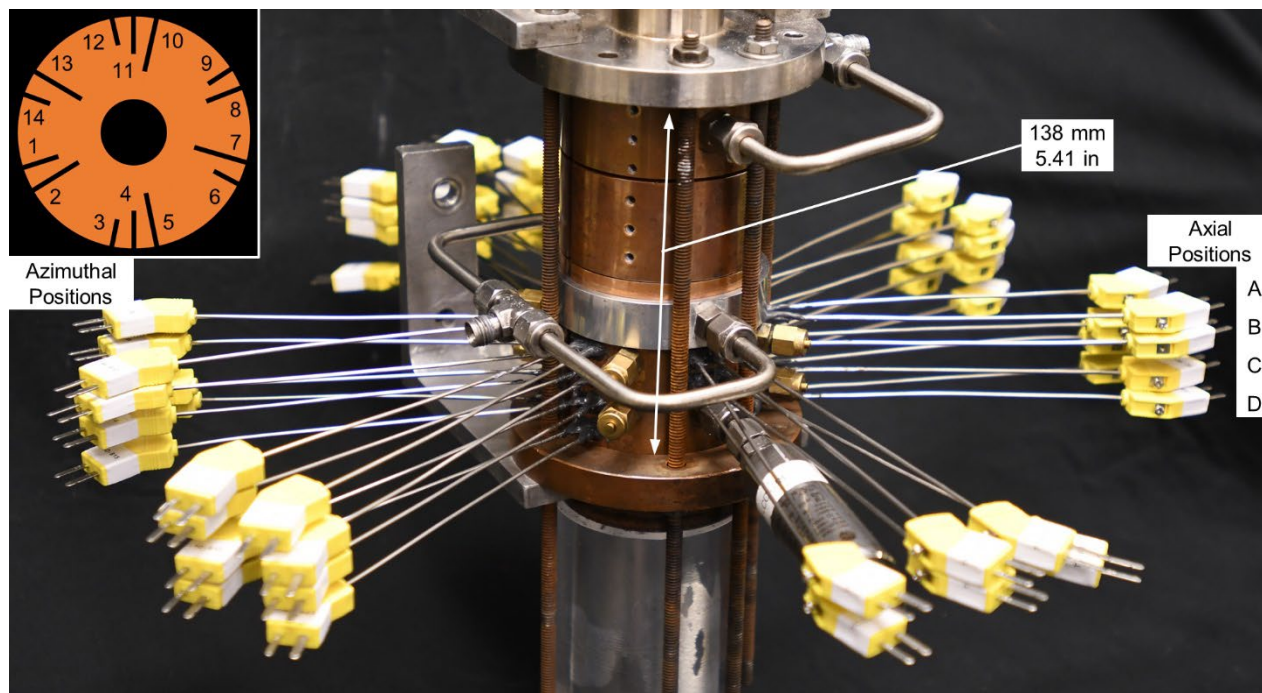


Figure 3.7. Fifty thermocouples were installed in the fuel-film cooled combustor sample chamber (main image). An axial cross-section of the combustor is overlaid (top left) to show the thermocouple azimuthal location number labels (1-14). Axial location capital letter labels (A-D) are shown on the right.

Thermocouples were attached to the sample chamber with a well-defined procedure to reproduce a consistent thermal contact resistance across different probes. First, the thermocouple and its corresponding hole were cleaned and degreased. A droplet-sized amount of OMEGABOND® 700 (OB-700) high temperature thermal cement was then applied to the exposed tip of the thermocouple, after which it was inserted into the sample chamber hole. OB-700 was chosen as the thermal contact cement because it most closely matched the thermal expansion coefficient of copper while maintaining an acceptable thermal conductivity of 0.65 to 0.85 W/m-K (4.5 to 5.9 Btu-in/ft²-hr-°F). Thermocouples were installed incrementally such that each installed probe maintained a 30° or less angle with the gravity vector to prevent disturbance of the OB-700 bond during the cure time. As many thermocouples were installed as could be while following the previously stated angle guideline, after which a liberal amount of J-B weld contact cement was applied between the sample chamber hole exterior and the thermocouple probe sheathe. Care was taken to maximize the J-B weld contact area while reducing its interconnectedness between adjacent thermocouples, in case one thermocouple needed to be replaced without affecting others.

This two-part adhesive method favored a relatively low thermal contact resistance at the thermocouple tip with a high mechanical pullout and shear strength at the hole base. Thermocouples could be replaced by chipping the J-B weld connection with hard plastic (softer than C101) and dissolving the OB-700 residue using a 10% NaOH solution applied with a syringe and 22 gauge needle. The test matrix in Appendix A indicates the tests before which all thermocouples were reinstalled. Individual thermocouples were occasionally replaced between tests due to anomalous data.

Thermocouple data from test 54 are shown in Figure 3.8 and are representative of typical raw temperature data collected for tests 53 to 64. Note that test 54 is a repeat of the baseline conditions used in test 53. Data from test 54 is plotted because it had more thermocouples installed than test 53, which was used as an evaluation test for the heat flux measurement method. In Figure 3.8, the temperature rapidly increased while firing in monopropellant mode after a delay of 0.3 seconds from the main oxidizer propellant valve open command at 0 seconds. The main fuel and fuel-film valves were opened at 2 seconds, after which the slope of the temperature increased at approximately 2.5 seconds. After ignition transients, the temperature slope gradually decreased with time in each respective combustion mode due to wall heating and carbonaceous deposits, where the latter only occurred in bipropellant mode. The temperature rapidly decreased at combustor shutdown with a 0.6 second nitrogen purge that started at 8 seconds. The temperature traces from thermocouples 10D, 11D, and 12D in Figure 3.8 were measured at radial distances of 6.6, 9.8, and 12.9 mm (0.26, 0.38, and 0.51 inch) respectively from the sample chamber-liner interface, and at an axial distance of 41.9 mm (1.65 inch) from the fuel-film injector. Note that, as expected, the thermocouples closer to the hot gas wall experienced higher temperatures and sharper gradients than thermocouples farther away from the hot gas wall. Increased thermal resistance at the exposed probe tip was often easy to identify, as shown by the solid black line of thermocouple 10D in Figure 3.8. The rapid drop in temperature at 4.5 seconds likely occurred due to a debonded thermocouple tip, potentially because of cracks in the OB-700 thermal contact cement. Inspection of thermocouple tip bond status could only be inferred from temperature data due to the design of the small diameter blind holes in the sample chamber. Occasionally the hardened JB-weld mechanical bond would crack while handling the sample chamber, usually due to the large moment arm of the thermocouple combined with forces from the thermocouple extension grade cable. In these cases, the thermocouple was removed, cleaned, and reinstalled

according to the procedures outlined in the previous paragraph. The thermocouple manufacturer-stated uncertainty of 2.2 K (4.0 R) was used because calibrating 50 thermocouples per test was deemed unnecessary given that temperature rises of over 15 K/s (27 R/s) were expected. Figure 3.8 shows uncertainty as transparent, shaded bounds around the data line which are nearly imperceptible for the raw temperature data.

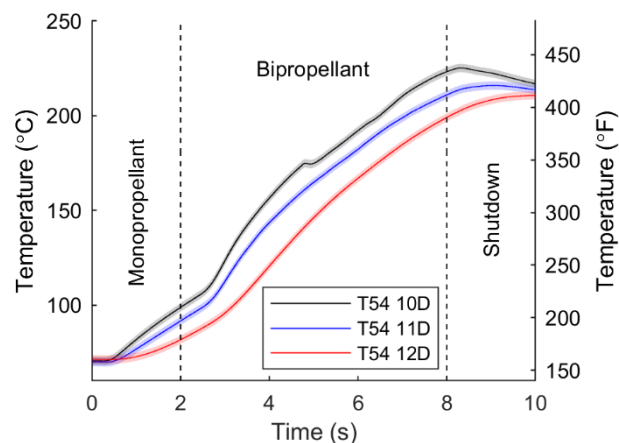


Figure 3.8. Raw temperature data and uncertainty from baseline test 54 (T54) thermocouples 10D, 11D, and 12D.

3.5.2 Methods

Determining heat flux from temperature data is an inverse problem because the temperature function is known from empirical data while the heat flux boundary condition is not known, often resulting in an ill-posed problem. A lumped capacitance-based method modeled the fuel-film combustor, significantly simplifying the inverse problem solution. The close proximity of the thermocouple tips to the inner wall and the relatively long test times also increased solution accuracy and stability. A two-step approach was used to first determine an initial heat flux guess, then iteratively improve the heat flux using a Gauss-Newton algorithm with a constant Jacobian matrix, as adapted from more common inverse heat transfer solutions outlined in heat transfer textbooks [71].

The Direct Problem

The inverse problem solution starts with a solution to the direct problem, where heat flux is known and the temperature function is unknown. The transient 1D radial heat diffusion

equation (HDE) used in the direct problem assumed that the radial heat flux was significantly larger than the axial and azimuthal heat fluxes. The radial domain ended at the copper sample chamber outer diameter and started at the boundary between the sample chamber and the chamber liner such that their thermal contact resistance was not modeled. Copper thermal properties of specific heat [63] and thermal conductivity [72] varied with temperature, while the density was taken as a constant 8960 kg/m³ (559 lb_m/ft³). The HDE, with all assumptions applied, reduced to Equation 3.1 where ρ is density, C_p is specific heat, k is thermal conductivity, T is temperature, r is radius, and t is time.

$$\rho C_p(T) \frac{\partial T(r,t)}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left[r k(T) \frac{\partial T(r,t)}{\partial r} \right] \quad (3.1)$$

The high thermal diffusivity of copper enabled a constant temperature initial condition. Averaged temperature data from the first 0.15 seconds of a given test, before any thermocouples measured an appreciable temperature rise, were used to calculate the constant initial temperature T_0 . The initial condition can be expressed mathematically per Equation 3.2.

$$T(r, t = 0) = T_0 \quad (3.2)$$

The inner radial Neumann boundary condition introduced the unknown heat flux function $\dot{q}''$, as in Equation 3.3, where r_i was the inner domain radius of 16 mm (0.63 inch).

$$\dot{q}''(t) = -k(T) \frac{\partial T(r=r_i, t)}{\partial r} \quad (3.3)$$

The outer radial Neumann boundary condition (Equation 3.4) was adiabatic because the convective heat transfer coefficient at the copper sample chamber outer radius r_o of 37.8 mm (1.49 inch) was multiple orders of magnitude lower than the interior forced convection heat transfer coefficient.

$$\frac{\partial T(r=r_o, t)}{\partial r} = 0 \quad (3.4)$$

A numerical solution was used for the direct problem, although it did not add significant computational cost to the inverse problem solution because of the constant Jacobian matrix method described in the next subsection. Numerically solving the HDE allowed for individual heat flux parameters to be determined at each temperature measurement data point such that a functional model for heat flux with respect to time was unnecessary. The *pdepe* function in the MATLAB® R2017b partial differential equation toolbox was used to solve the given HDE using a finite element approach. A grid sensitivity analysis using representative temperature data

indicated that ten points for radial discretization were sufficient. The temporal domain was discretized dynamically by MATLAB's variable-step, variable-order ordinary differential equation solver *ode15s*.

The Inverse Problem

Solving the inverse problem started with the determination of a heat flux initial guess near the expected solution to mitigate Gauss-Newton algorithm instability problems. As an initial guess, the HDE was simplified by the lumped capacitance method such that heat flux was proportional to the temperature derivative with time. A 100 point window moving mean filter smoothed the temperature data. Then, a forward differencing method computed the derivative using an adiabatic guard point at $t = 0$ s. The computed time derivative of temperature was then proportionally scaled by a single constant while minimizing the sum of the square errors between the temperature model and raw data. This procedure produced a heat flux guess in less than five iterations of approximately the correct line shape from the derivative, and order of magnitude from the iterative scaling. The initial heat flux guess $\dot{q}_0''$ for each temperature measured at radius r_m was calculated using Equation 3.5 where sample chamber volume V and sample chamber-liner interface area A have been simplified in the right-most form.

$$\dot{q}_0'' = \frac{V}{A} \rho C_p(T) \frac{dT(r=r_m, t)}{dt} = \frac{r_o^2 - r_i^2}{2r_i} \rho C_p(T) \frac{dT(r=r_m, t)}{dt} \quad (3.5)$$

After iterative proportional scaling, the initial heat flux guess was improved using the Gauss-Newton algorithm with a reduced step size. The Jacobian of this method was the derivative of temperature with respect to the heat flux at each measured temperature data point. The lumped capacitance approximation from Equation 3.5 can be rearranged and integrated to determine an approximation of the temperature (Equation 3.6) as a function of heat flux such that the Jacobian can be calculated.

$$T(r = r_m, t) = \frac{2r_i}{r_o^2 - r_i^2} \frac{1}{\rho} \int_0^t \frac{\dot{q}''(t)}{C_p(T)} dt \quad (3.6)$$

Reducing the integral to a summation using temperature data point index j resulted in a relationship between the measured temperature T_j at time t_j and the heat flux parameters with index k . Each index spanned from 1 to N , where N was the number of data points collected. Note that the specific heat was simplified to its constant value at 400 K such that the temperature only

depended on constants multiplied by a sum of the heat flux parameters, as shown in the explicit Equation 3.7.

$$T_j = \frac{2r_i}{r_o^2 - r_i^2} \frac{1}{\rho C_p(T=400K)} \sum_{k=1}^j \dot{q}_k'' \quad (3.7)$$

Taking the derivative of T_j with respect to $\dot{q}_k''$, where k is the heat flux parameter index, resulted in the constant Jacobian J_{jk} described in Equation 3.8 and used with the Gauss-Newton algorithm.

$$J_{jk} = \frac{dT_j}{d\dot{q}_k''} = \begin{cases} \frac{2r_i}{r_o^2 - r_i^2} \frac{1}{\rho C_p(T=400K)} & \text{if } k \leq j \\ 0 & \text{otherwise} \end{cases} \quad (3.8)$$

Note that J_{jk} is a lower triangular square matrix where all non-zero values are constant and equal. The Jacobian can be determined before iterating such that it does not need to be recomputed during each iteration, which is often the most expensive step of the Gauss-Newton algorithm when finite difference derivatives are involved. The step size was reduced using a constant value of 0.5 to increase stability. A line search method for this parameter could be used to decrease computation time, but was considered an unnecessary programming expense due to the computational time savings provided by the constant Jacobian matrix. A 200 point moving mean filter was used to smooth the residuals and heat flux parameters to prevent thermocouple data noise from affecting the calculated heat fluxes in each iteration. These filter windows were set high enough to reduce noise, yet low enough to capture the initial temperature spike of the monopropellant mode. The Gauss-Newton algorithm iterated for 50 steps after which the solution with the lowest residuals was selected. Appendix B contains the MATLAB code used to calculate heat fluxes from raw temperature test data.

3.5.3 Results

Figure 3.9 shows a typical heat flux solution for test 54 thermocouple 11D. The model temperatures were nearly imperceptible from the raw data due to the high number of degrees of freedom in the model, falling well within the manufacturer-stated thermocouple temperature uncertainty. Typical inverse problem solutions matched the thermocouple data to within 0.25 K (0.45 R) at every data point except for startup transients, which were typically matched to within 0.5 K (0.9 R). Heat flux uncertainty of approximately 0.05 MW/m² (0.03 Btu/s-in²) was

propagated from temperature uncertainty via a Monte Carlo method with 1000 points, as shown by the transparent, shaded bounds on the heat flux in Figure 3.9.

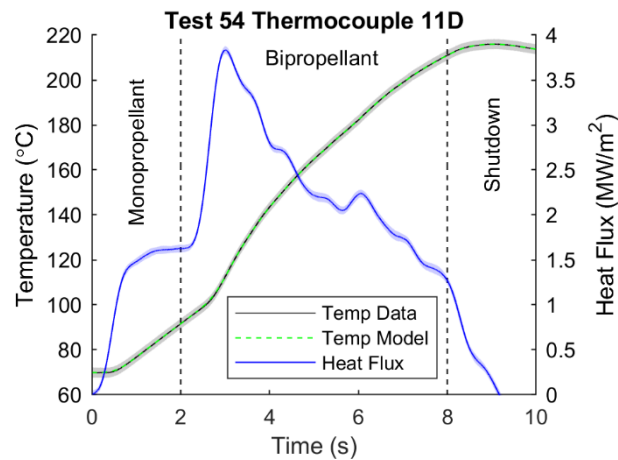


Figure 3.9. Temperatures calculated from the heat flux model typically matched raw data to within 0.25 K (0.45 R), as illustrated for test 54 thermocouple 11D.

Azimuthal Variation

1D radial heat flux estimates were calculated for up to 50 temperature traces per test depending on the number of thermocouples installed. Figure 3.10 shows representative heat flux profiles from axial positions A and D of test 54, where each line of the same type is from a different azimuthal location. The approximately 0.3 seconds delay after the main oxidizer valve opening at 0 seconds was reflected in the heat flux curves. Additionally, the bipropellant ignition heat flux peak occurred at 2.5 seconds, similarly reflecting the trends seen in the raw temperature data of Figure 3.8. Note that lines of the same type vary by up to 2 MW/m² during the monopropellant and bipropellant startup transients, but converge to within 0.1 MW/m² of the mean once the startup transients pass. Non-axisymmetric startup transients follow from the non-axisymmetric manifold inlet design of the main fuel and fuel-film injectors. The manifold was designed to distribute fuel axisymmetrically once steady flow was achieved, the results of which can be seen in the heat fluxes from 4 to 8 seconds in Figure 3.10. Heat fluxes have been averaged across azimuthal thermocouples of the same axial level to simplify data analysis from this point onwards.

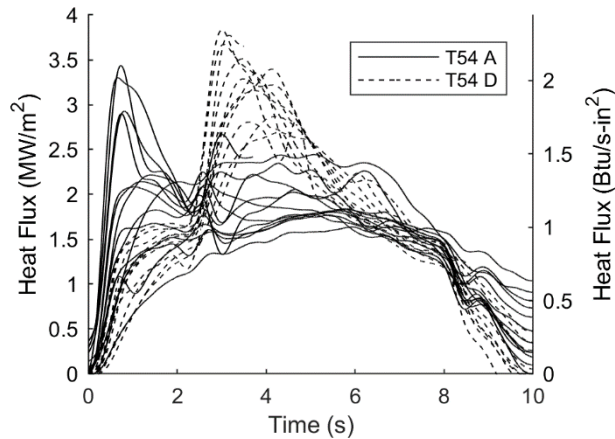


Figure 3.10. Calculated heat flux profiles of test 54 (T54) from levels A and D at various azimuthal positions.

The result of averaging all heat fluxes for each axial level of the baseline test 54 can be seen in Figure 3.11. Note the significantly higher uncertainty, as represented by shaded bounds, in Figure 3.11 when compared with Figure 3.9 due to the azimuthal variation in measured heat flux which was shown in Figure 3.10. Jump discontinuities in the average heat flux data occurred when heat flux calculations were artificially limited temporally due to obviously non-physical behavior, as demonstrated in Figure 3.8. The highest monopropellant heat flux was recorded at axial level A, which was closest to the fuel-film injector. During monopropellant mode, the axisymmetric fuel-film injector acted as an insulating axial boundary condition when compared to the copper flange in direct contact with the bottom of the sample chamber (see Figure 3.1). Axial positions closer to the fuel-film injector seemed to have higher heat fluxes during monopropellant mode due to the 1D radial HDE not accounting for this axially insulating gap. Physically, the heat fluxes may have been slightly higher at level A due to the sharp fuel-film injector corner disrupting the developing boundary layer, however most of the discrepancy is likely a result of the model used. After bipropellant ignition, the heat flux trend with axial position reversed because of the cooling effects of the fuel-film flow. As expected, the heat flux was lowest closer to the fuel-film injector and highest further away. However, by the end of bipropellant mode the heat flux trend with axial position reversed once again, such that levels A and B had the highest heat flux despite being closest to the fuel-film injector. Higher carbon deposition at levels C and D compared to A and B can explain this phenomenon, as opposed to axial differences in wall temperature which were within 50 K (90 R) due to the high thermal conductivity of the chamber. Heat flux uncertainty

calculated from averaging data across the azimuthal domain was significantly higher than the uncertainty propagated from temperature data, especially during startup transients. Non-axisymmetric manifold inlets likely contributed to this increase in uncertainty during startup and shutdown.

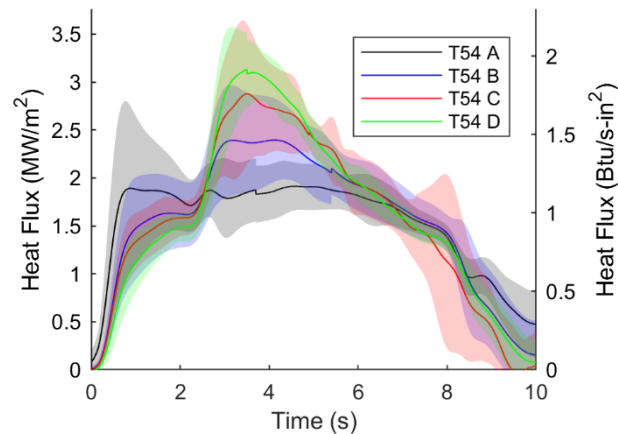


Figure 3.11. Test 54 (T54) heat flux profiles averaged across azimuthal positions in axial levels A, B, C, and D.

Repeatability

Tests 53 and 54 were operated over one week apart at the same baseline conditions with different thermocouple installations. Figure 3.12 shows repeatability between axial levels A and D of tests 53 and 54. The monopropellant and bipropellant startup transients match most closely, while bipropellant operation from 5 to 8 seconds seemed to have lower heat fluxes for test 53. Part of this difference can be explained by test 53 having only 25 thermocouples installed as the heat flux measurement methodology was being initially tested. Another source of error could have been differences in thermocouple installation technique as the procedures were being developed. The sudden drop in test 53 axial position D uncertainty at approximately 4 seconds was also due to the limited number of thermocouples installed. Only two temperature traces were usable at position D by the 4 seconds mark, and when those two traces crossed one another they resulted in an uncertainty close to zero.

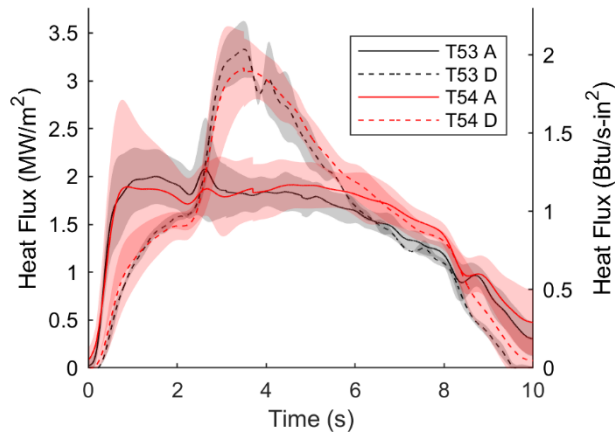


Figure 3.12. Tests 53 and 54 (T53 and T54) were operated at the same conditions, demonstrating repeatable heat flux measurements in tests taking place over a week apart.

Chamber Liner Material

The chamber liner material was varied from the baseline, C101, to S304 and N066 in tests 57 and 58 respectively, with results shown in Figure 3.13. Lower thermal conductivities for the stainless steel and Inconel liners resulted in monopropellant and bipropellant startup transient heat fluxes of approximately half that of the baseline copper tests. Differences between the stainless steel and Inconel tests were minimal, which follows from the two metals having similar thermal conductivities, densities, and specific heats. The C101 heat flux approached that of the S304 and N066 tests by the end of the bipropellant test duration, especially for axial position D. The carbon deposits' thermal resistance likely increased enough that it became the primary term in limiting the heat flux when compared to the chamber liner thermal properties. The slower convergence of the C101 axial position A heat flux with those of the lower thermal conductivity metals can be explained by lower carbon deposition rates at axial positions closer to the fuel-film injector. Differences in carbon deposit rates due to wall material are addressed in Sections 4.2.

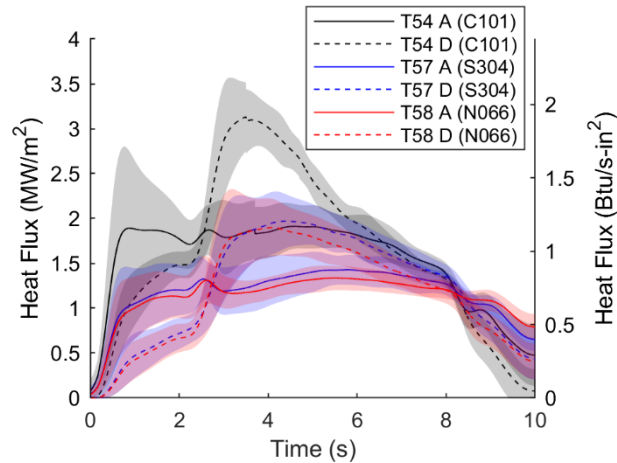


Figure 3.13. Comparison of heat flux profiles for tests with chamber liners machined from C101 (T54), S304 (T57), and N066 (T58).

A first estimate at steady-state gas/carbon-side metal wall temperature can be made by assuming a negligible thermal contact resistance between the chamber liner and the C101 sample chamber. The 2.21 mm (0.087 inch) thick metal chamber liner had a length-specific thermal resistance of 28, 790, and 760 m-K/MW for C101, S304, and N066 respectively, assuming room temperature thermal conductivities. Note that S304 and N066 have similar thermal conductivities, resulting in nearly identical thermal resistances. All heat flux curves, irrespective of material, converge to approximately 1.3 MW/m² (0.80 Btu/s-in²) in Figure 3.13, which can be converted to a length-specific heating power of 0.13 MW/m (3.2 Btu/s-in) by accounting for the circumferential distance associated with the liner-chamber interface diameter of 32.0 mm (1.26 in). The expected temperature drop through the chamber liner can then be calculated by multiplying the length-specific thermal resistance with the length-specific heating power to get 4, 103, and 99 K (7, 185, 178 °F) for C101, S304, and N066 respectively. The peak temperature of approximately 470 K (386°F) in Figure 3.9 would then correspond to metal wall temperatures of 474, 573, and 569 K (393, 571, 564°F) for C101, S304, and N066. Note that there will be some appreciable contact resistance, and corresponding additional temperature drop, that maintains equilibrium through the contact pressure formed by the thermal expansion of the hotter chamber liner. Furthermore, significant temperature resistances and therefore temperature drops across the carbon deposit layer would be expected. Future work would develop a more thorough heat transfer model, considering factors such as thermal contact resistance, carbon layer resistance, and axial heat flow.

Surface Roughness

Every test that measured heat flux used a chamber liner with different surface finishes on either half, as mentioned in the combustor section. Surface roughness's effect on heat flux was visualized with a ratio of heat flux measured by thermocouples on the rough half of the chamber liner, divided by those on the fine half at each axial level. These surface roughness heat flux ratios were averaged across tests 53 to 59 and test 63 to identify the effect of surface roughness on heat flux, as shown in Figure 3.14. Heat flux ratio during the monopropellant and bipropellant startup transients, up to about 4 seconds, likely reflected the injector geometry characteristics more than the surface roughness effects, as demonstrated by axial levels A, B, C, and D not following any coherent trends. However, the heat flux ratio of levels C and D were on average higher than A and B at 4 s, and all four ratios converged to approximately 0.95 by 7 seconds. Sample surface roughness should not affect heat flux once a large enough carbon deposit layer adheres to the surface, explaining the convergence of the axial level heat fluxes and their trend towards a value of one near the end of the bipropellant burn. Additionally, levels C and D had higher carbon deposition rates for all tests, which could explain their heat flux ratio maintaining a value close to unity for the entire bipropellant burn. Heat flux ratios for levels A and B, on the other hand, were lower at the beginning of the bipropellant burn with a value of approximately 0.9, indicating that the fine surface finish had a higher heat flux than that of the rough surface finish. A potential explanation for this is that carbon particles more easily adhered to the rougher surface finish. Overall, the heat flux ratios were close enough to unity that it is hard to definitively stand by any of these conclusions without further analysis of the carbon deposits' depth, physical/chemical structure, and thermal properties.

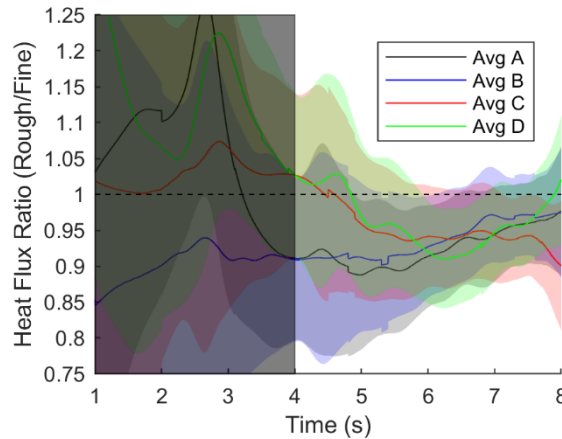


Figure 3.14. Average ratio of heat flux as measured behind a rough surface finish, divided by that behind a fine surface finish, at four axial distances from the fuel-film injector. Data at times before 4 seconds are grayed out because they occur during the startup transient, and therefore cannot be trusted.

3.5.4 Future Work

The radial, azimuthal, and axial spacing of thermocouples in the Task 1 sample chamber would allow for a 2D axisymmetric or 3D direct model to more accurately predict heat flux in the chamber, at the cost of significantly higher computation time. The constant Jacobian sensitivity parameter assumption from Equation 3.8 would not hold in these cases. A 2D axisymmetric model would give heat losses through the axial ends of the sample chamber while the 3D model would also elucidate asymmetries in the azimuthal direction.

A further step would be to empirically or semi-empirically model the carbon deposition's effect on heat flux using deposit depth, layer structure, and thermophysical properties from Sections 4.2, 4.3, and 4.4 respectively. This work could build upon previous liquid film models developed without carbonaceous deposits in mind.

3.6 Lessons Learned

The data collected from the Task 1 combustor was a good first step towards better understanding carbon deposition in fuel-film cooled combustors, but it has several shortcomings in terms of operating conditions, data integrity, and combustor operation:

- **H₂O₂ oxidizer:** Combustion of kerosene with hydrogen peroxide does not match the conditions expected in ORSC. The adiabatic flame temperatures are up to 1000 K lower

and the combustion gases have excess hydrogen. Both temperature and hydrogen concentration can significantly affect soot formation and thermophoresis in the fuel-rich boundary layer. More representative tests should use gaseous oxygen at room temperature or in a preburner to more closely match ORSC conditions.

- **Low chamber pressure:** A chamber pressure of 4.8 MPa (700 psia) is much lower than expected ORSC chamber pressures which can be as high as 25 MPa (3600 psia). Pressure has been shown to affect both pyrolysis and soot mechanisms, as described in Section 1.
- **Large contraction ratio:** Most flight-weight engines have low contraction ratios to reduce weight at a small cost to performance. The Task 1 contraction ratio of 6.8 is approximately three times larger than the contraction ratios expected in ORSC engines, resulting in lower combustion chamber velocities and core flow to film coolant momentum ratios. Residence time, and therefore contraction ratio, is one of the major factors in soot formation, therefore it needs to be both representative and well-controlled in future experiments.
- **Thermal transients:** The Task 1 combustor is heat-sink cooled, therefore the wall temperatures steadily rise with burn time. More useful carbon deposition data would be produced in a thermally-steady combustor because liquid pyrolysis, soot thermophoresis, and PAH condensation have strong dependencies on temperature.
- **Operation requires fuel-film:** The current Task 1 combustor requires a significant fuel-film flow to prevent ablation of its graphite nozzle for even modest run times of a few seconds. Future experimental efforts should be able to operate without a fuel-film as a baseline case for comparison of pyrolysis and soot thermophoresis deposition mechanisms.
- **Short run times:** The Task 1 combustor is limited to a 10 second bipropellant run time with the baseline fuel-film flow rate. Longer run times are required to establish pseudo-steady-state carbon layer thicknesses to study the balance of deposition and shedding.
- **Oxidizer inlet boundary condition:** The hydrogen peroxide catalyst bed outlet exhausts into a sonic choke plate, after which a stainless steel part transitions to a smaller inner diameter. The length to diameter ratio before the sonic choke plate is less than 0.1, meaning that there will be circumferential inconsistencies that cannot be measured for CFD boundary conditions. Increasing the distance from the silver catalyst packing and adding a

flow straightener would solve this problem. Additionally, the sonic choke plate contains multiple discrete orifices, breaking axisymmetry at the boundary condition.

- **Main fuel inlet boundary condition:** The main fuel flow is radially injected through four discrete orifices into the hot oxygen and steam flow. Future injector designs should maximize axisymmetry such that axisymmetric CFD more accurately models the experiment.
- **Wall thermal boundary condition:** A sample tube with tight outer diameter tolerancing is inserted into the copper heat-sink cooled sample chamber that has tight inner diameter tolerancing. The thermal contact resistance between the two parts prevents accurate determination of the inner tube wall temperature based on outer sample chamber temperature measurements. Future experimental designs should have a more direct way of measuring wall temperature.
- **Fuel-film injector tolerancing:** The fuel-film is injected through a 0.0100 ± 0.0014 inch axisymmetric gap with no pressure drop device to prevent combustor coupling with the fuel-film manifolds. The kerosene film coolant is incompressible, therefore a cavitating venturi upstream of the manifold prevents backflow from the chamber to the manifold. However, future designs should implement a pressure drop device between the manifold and the axisymmetric injection point to prevent pressure coupling of the chamber and the film manifold.
- **Graphite gasket seals:** The selected gaskets and flanges resulted in difficulties with thin gasket manufacturing, numerous gasket blowouts at nominal chamber pressures, imprecise combustor assembly, and graphite gasket material contamination in the combustor flow. Future combustors should avoid graphite gaskets, specifically for the latter two reasons, with the caveat that the gaskets in the Task 1 combustor acted as a thermal expansion relief in the longitudinal direction.

Improvements upon the Task 1 combustor design will be discussed in Section 5, which describes a higher pressure kerosene-oxygen combustor based on these lessons learned.

4. CHARACTERIZATION OF CARBONACEOUS DEPOSITS

Figure 4.1 shows the top (left) and bottom (right) of the sample tube from test 40, directly after it was removed from the combustor. The operating conditions for test 40 can be found in Appendix A. Two forms of carbon deposition were identified: lighter gray, denser deposits that adhered more tenaciously to the metal substrate and darker black, porous, soot-like carbon that could be rubbed off by hand. The lighter gray “dense” deposits were always present underneath the darker black “porous” deposits when wiped off by hand. The deposits within 5 mm (0.20 inch) of the fuel-film injector were thin enough that discoloration from the base metal could be seen. A surface transition from dense to porous deposits typically occurred between 5 and 15 mm (0.20 and 0.59 inch) of the fuel-film injector. The carbon deposit thickness seemed to monotonically increase in thickness from the fuel-film injector to the end of the tube for most tests, except when shedding occurred. Shedding of the soot layer was sometimes evident near the end of the sample tube, where millimeter-sized sections of the porous layer were missing. Soot shedding seemed to occur in axial streaks (see right image of Figure 4.1) for some tests, potentially caused by high velocity gases during steady-state operation or cold nitrogen during the shutdown transient (thermal shock). The deposition seemed mostly axisymmetric to visual inspection, however there were subtle indications of the injector pattern in the porous carbon deposits, which would suggest that porous carbon deposition is affected by the core flow structure. For instance, the transition to porous carbon seemed to start closer to the fuel-film injector, aligned with the discrete main fuel injection orifices, although this was more evident for some tests than others.

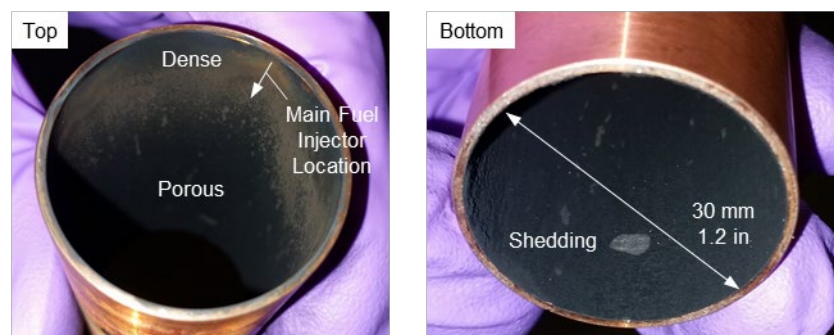


Figure 4.1. Post-test images of the top (left) and bottom (right) of a sample tube chamber liner removed from the combustor directly after test 40.

Each subsection in this section can be related directly back to the objectives stated in Section 2. Deposit depth is proportional to thermal resistance and can be used for CFD validation. Chemical characterization of deposits can reveal relevant mechanisms for deposition. Thermophysical property measurements are direct inputs to models for carbon deposition.

4.1 Sectioning Method

Most of the post-test analysis techniques considered needed a sample that was as flat as possible, requiring the annular sample tube to be sectioned into at least eight octants azimuthally. The sample length of 74 mm (2.9 inch) was too long for certain analysis techniques, notably the scanning electron microscopy presented in Section 4.2.2, therefore the octants were cut in half for a total of 16 octant halves, each approximately 35 mm (1.4 inch) long.

A sample sectioning procedure was developed to avoid contamination and minimize vibrational disturbance of the carbonaceous deposits. Octant lines were scored on the sample outer surface using a razor blade and printed paper template. Clear packing tape was adhered to both open ends of the sample tube and folded over the edges, effectively sealing the interior of the sample. A standard bench vise lightly clamped both axial ends of the taped tube, exposing the scored surface for cutting operations using a Dremel[®] tool with a 1.14 mm (0.045 inch) thick fiberglass reinforced aluminum oxide abrasive cutting wheel. The crucial aspect of this operation was to deepen the scored lines without cutting all the way through the sample. The sample tube was then repositioned between cuts and allowed to cool back to room temperature. After every score had been deepened, the clear packing tape was removed and checked for metal dust. The vice was then used to incrementally crush the sample tube radially until the metal yielded along the deepened score lines, resulting in 16 sample octant halves as shown in Figure 4.2. Deposits near the cut edges were affected by the metal bending and yielding process, especially for larger porous carbon thicknesses. However, deposits on the octant half centerline were visually identical to pictures taken prior to sample sectioning.

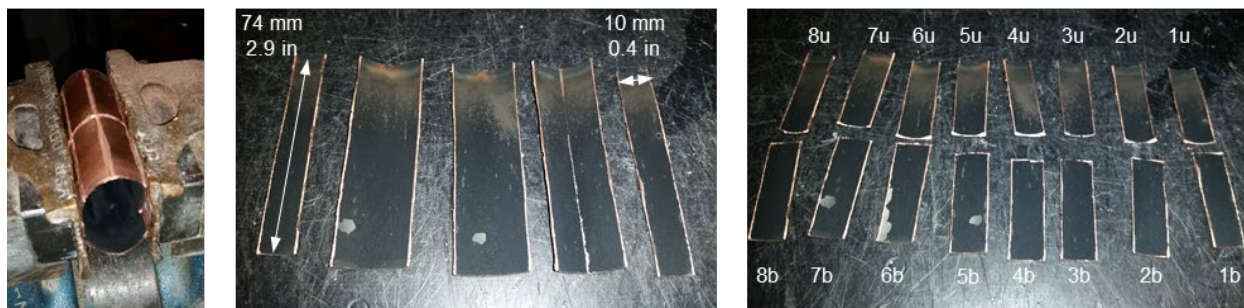


Figure 4.2. Copper sample tube chamber liner from test 40 while being radially crushed (left), after separation into octants (middle), and completely separated into 16 octant halves (right).

Azimuthal positions were numbered one through eight to keep track of the sample octant location. The letters “u” and “b” represented upper/top and lower/bottom samples respectively, where upper samples were closer to the fuel-film injector. A secondary azimuthal naming scheme used letters “A” through “H” to indicate an alternative sample cutting template which was azimuthally half an octant out of phase with the one through eight numbering scheme. The key difference between these two azimuthal naming schemes was that locations two, four, six, and eight were aligned with the main fuel injectors in the one through eight naming scheme, while location boundaries between B-C, D-E, F-G, and H-A were aligned with the main fuel injectors in the “A” through “H” naming scheme. An example of a sample octant half name is “T54_B_u”, which corresponds to the upper (closest to fuel-film injector) half of octant B from test 54.

High resolution images of each sample octant were taken as a locational reference for the various post-test analysis techniques. Octants were fixed to microscopy sample stubs and stored in unsealed plastic containers. Exposure to air was not considered an issue due to the stability of the solid carbon combustion products near room temperature. The plastic containers, however, were stored in a humidity-controlled room to prevent undue exposure to moisture.

4.2 Deposit Depth

The steady-state thermal resistance through carbonaceous deposits depends primarily on thermal conductivity and thickness, the latter of which can be as small as microns to as large as millimeters depending on the run conditions and burn time of a given combustor. Measurement and modeling of deposition rates at representative oxygen-rich staged combustion (ORSC) conditions is crucial to optimizing combustion chamber thermal management design to enable

higher engine performance. Validation of CFD codes for carbonaceous deposits at relevant conditions will depend heavily on comparisons with deposit depth measurements.

Several methods have been used to measure carbonaceous deposit thickness, typically after test completion as opposed to during test firings. The measurement methods vary depending on expected deposit thickness. Carbon burn-off methods and microscopy cross-sections have been used for carbon layers as thin as microns [31]. Gravimetric analysis and direct measurement with a tool such as calipers can measure deposits on the order of millimeters thick. Kerosene fuel-film cooling literature often focuses on heat flux measurement as opposed to carbonaceous deposit analysis, however kerosene regenerative cooling jacket literature has thoroughly addressed post-test deposit measurements. Roback et al. [31] attempted to apply several measurement methods to deposits formed in kerosene heated tube tests at a wide variety of conditions. Low deposition rates precluded gravimetric analysis and direct measurement of the deposits. Photomicrograph cross-sections resulted in inconsistent data due to the high carbon deposit variance with position. As with most cooling jacket literature [30,32,35], Roback et al. [31] found that carbon burn-off methods offered the most useful quantification of carbon deposition rates.

Carbon burn-off methods combust carbonaceous material with a steady flow of air or oxygen, then measure CO₂ effluent by infrared spectroscopy to determine carbon mass of the unburned sample. Certain burn-off instruments also have the capability of measuring hydrogen and sulfur content from H₂O and SO₂ respectively. While this method destroys the sample during the measurement process, it can be used to determine carbon mass across a large surface area, effectively averaging the deposition rate such that local variations are inconsequential. Averaging across local variations can be useful for certain regenerative cooling studies where deposition rates vary over the axial length of tens of centimeters, but it is less useful for fuel-film deposit measurements where the fuel-film conditions vary over the axial length of millimeters, and fuel-films fully vaporize after a few centimeters. Additionally, regenerative cooling studies were primarily concerned with the binary presence or lack of carbon deposits. Measuring the deposit thermal properties and thickness was unimportant because their mere presence presented a danger of clogging and insulating coolant jackets, then inevitable combustor failure. For this reason, carbon burn-off methods were sufficient to quantify deposition rates, despite measuring carbon mass as opposed to deposit thickness. In contrast, the deposit thermal resistance and therefore thickness is crucial to quantifying fuel-film deposition effectiveness as a reducer of heat flux. The

measurement of carbon deposition rate in terms of mass is therefore less useful than a direct measurement of deposit thickness for fuel-film combustor studies.

Figure 4.3 shows the two-layer structure that was typical of carbonaceous deposits measured in this dissertation. A tenacious, graphitic-like “dense” layer stuck to the metal substrate, and a “porous” soot-like layer rested on top of it. A two-layer structure for carbon deposition has been noted in diesel engine EGR cooler literature, albeit at significantly lower temperatures (~ 600 K) and higher residence times (100s of hours). Abarham [46] described a dense, lower layer primarily formed from heavy hydrocarbon condensates, with a fluffy upper layer. He attributed most deposition in EGR coolers to thermophoretic diffusion of soot particles in the gaseous core flow, with a competing shedding mechanism that may be explained by the kinetic theory balance between kinetic energy (thermal forces) and Van der Waals potential energy.

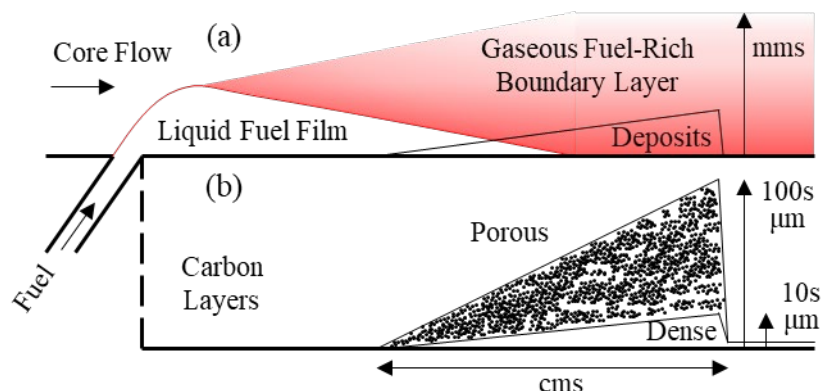


Figure 4.3. Typical fuel-film injection geometry, liquid vaporization, and gaseous boundary layer development is shown in the upper image (a). The lower image (b) shows the dual carbon layer development with typical order of magnitude lengths and depths from the Task 1 combustor.

Carbonaceous deposit depth was measured by optical profilometry and scanning electron microscopy to determine total and dense layer depths, where the former was typically on the order of 10s-100s μm thick while the latter was approximately 1s-10s μm thick.

4.2.1 Optical Profilometry

Optical profilometers measure surface roughness non-destructively using interferometry of light reflected from the sample surface and a reference mirror. The major benefit of optical profilometry was low acquisition time of 2D surface roughness maps without sacrificing high resolution in the depth direction. Profilometers are typically a non-destructive measurement

technique, however, parts of the sample base metal needed to be exposed for proper depth measurement, therefore sections of sample were destroyed when measuring depth.

Large portions of this section are identical to those to be published in a journal paper by Piper and Pourpoint [73].

Methods

Sample octants were circumferentially scored with 0.5 mm (0.020 inch) thick plastic razor blades to expose the metal surface beneath the carbonaceous deposits. Plastic razor blades were used, as opposed to metal, to prevent damaging of the metal substrate which would affect the depth measurements. Analysis of a sample both before and after the deposit scoring procedure showed that measurable sample contamination never occurred outside of a 0.25 mm (0.01 inch) region axially above and below the score mark. Samples with larger deposit depths had larger regions of contamination, which were avoided by only using data from outside of the contaminated region. Each sample was aligned with the profilometer's XY stage by using the lowest point of each exposed metal strip, as measured by the profilometer. Data was typically taken at five sites per octant half. Distance was measured from the top of the sample for upper octant halves and from the bottom of the sample for lower octant halves.

A Zygo ZeGageTM optical profiler with a 2.75X objective was used to measure 2D surface roughness profiles of the octant half samples. The carbonaceous deposits reflected the profilometer's visible light significantly less than the sample tube metal. Collecting data from both the exposed metal and carbonaceous deposits presented an issue since higher light levels and exposure were required for the deposits compared to the metal. A dual-level light scan was used to stitch together two scans per site, each at differing light settings, resulting in acceptable data from both the metal and the deposits. Typical light level/exposure levels were 0.9/0.03 for the metal and 1/0.06 for the carbon deposits, as reported by the ZeGageTM optical profiler software. Scan depth varied from 150 to 400 μm (5.9 to 15.7 thou) based on the expected carbonaceous deposit depth and sample tilt angle with respect to the XY stage normal axis. Detector signal threshold was set between 0.5% and 0.8% to maximize signal-to-noise ratio while maintaining enough data points, especially for regions with porous carbonaceous deposits, which were highly absorbing.

Raw data from baseline test 39 (see Appendix A) is shown on the left of Figure 4.4 along with an image of the octant half and sample site on the right. The sample tube axial, azimuthal, and radial positions varied along the X, Y, and Z axes of the contour plot respectively. Absolute Y distance was measured with respect to the fuel-film injection point using an XY translating stage. The profilometer recorded more data points in the exposed metal region because of its high reflectivity in the visible light wavelengths. Denser carbon reflected light more than the porous soot-like deposits, resulting in more data points for denser carbon. The sample's circular curvature is seen as regions of increasing Z position towards the left and right edges of the images. Sample pitch with respect to the XY stage is seen as nearly vertical lines of constant Z position narrowing or broadening in the X dimension. Turning witness marks from the sample tube lathe boring operation were present as small sinusoidal variations in the vertical lines of constant Z position, and were most visible for sites closest to the fuel-film injector. These boring marks were present in all metal surface data, but only showed in carbonaceous deposit data closest to the fuel-film injector where the deposition rate was lowest.

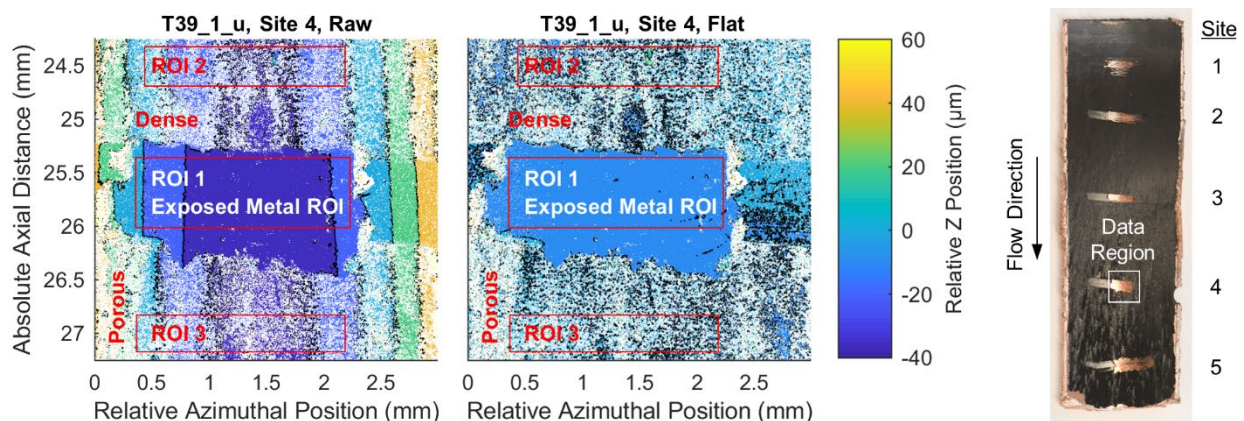


Figure 4.4. Raw (left) and flattened (middle) optical profilometer data from baseline test 39, octant 1, upper half, site 4 with red region of interest (ROI) rectangles for the exposed metal and sample sites. The region of data collection is outlined by a white rectangle overlaid on an image of the sectioned octant half (right).

Three rectangular regions of interest (ROIs) were selected at each sample site, as shown in the left and middle contour plots of Figure 4.4. Absolute Y distance was measured from the fuel-film injection point. Dense and porous carbon can be distinguished by the density of data points, where more points occur in denser carbon. The first ROI covered the exposed metal surface, which was used for cylinder and tilt correction. It also served as a depth reference point for

comparison with the second and third ROIs. The X width and Y height of the first ROI typically needed to cover at least 400 and 50 data points respectively for accurate fitting, however these dimensions were made larger where possible. The second and third ROIs captured data axially above and below the exposed metal strip. The selection criteria for these two ROIs were uniformity of deposits to avoid shedding, X indices within the first ROI calibration region, and minimal Y height to avoid variations due to axial Y position. The last criterion conflicted with maximizing the number of data points and was sometimes compromised to insure a statistically relevant population of at least 1,000 points, especially in porous regions where data points were scarcer. Typical dense and porous deposit ROIs had approximately 50,000 and 10,000 data points respectively.

Post-processing of the profilometry depth data occurred after all three ROIs were selected by the user. A circle model was used to fit Z height data versus the azimuthal X axis at each axial Y index in the exposed metal ROI. The *fitnlm* function in MATLAB R2017b used the Levenberg-Marquardt algorithm to fit the data resulting in a list of circle position and radius fit parameters equal in length to the number of Y points in the first ROI. The X circle center position and radius fit parameters were averaged across the first ROI, and the fit radius typically matched the expected radius of 14.9 mm (0.59 inch) to within 0.5 mm (0.020 inch). The *robustfit* function in MATLAB R2017b used an iteratively reweighted least squares method with a bisquare weighting function to linearly fit the circle's lowest point, equivalent to Z circle position minus the mean circle radius, to account for the sample tilt in the axial Y direction. Circles using the average X center position, average radius, and linear model for Z lowest point were subtracted from the raw data to produce flattened profilometer data such that corrected depth comparisons could be made between the three ROIs. An example of flattened profilometer data is shown in the middle image of Figure 4.4. The exposed metal ROI mean Z height was subtracted from the two deposit ROI mean Z heights to determine carbonaceous deposit depth at two axial locations per site. Standard deviation was measured across the entire ROI to determine the surface roughness R_a pattern. Appendix C documents the MATLAB® code used to process profilometer data.

Figure 4.5 shows example data from two octant halves of test 39 at azimuthal location 1. Carbonaceous deposit depth increased linearly from the fuel-film injection point as the kerosene vaporized and pyrolyzed. An increase in deposit depth slope correlated with an increase in surface roughness (standard deviation) due to the presence of porous carbon. A sudden transition back to

the denser deposits occurred after 60 mm (2.4 inch) from the fuel-film injector, which was typical for tests with the baseline fuel-film flow rate. The baseline test conditions were described in Section 3.3. Depth data mostly followed monotonic trends with small variations of less than 5 μm , often due to a combination of shedding, metal ROIs thin in the Y direction, and fitting procedure inadequacies. These variations often manifested in a larger spread between the two data points of a single site, which when averaged, closely followed the data from axially neighboring sites. Averaging the depth values for the two data ROIs of the same site solved this problem. However, the data ROIs had to be the same distance from the exposed metal ROI centerline due to the linear inaccuracy of the robust fit to the sample's lowest point. All data presented after Figure 4.5 have averaged ROI data points resulting in one depth measurement per site. The long-dashed line in Figure 4.5 represents the physical cut between octant halves, each of which was processed separately using the optical profilometer. The upper and lower octant half distances from the fuel-film injector were measured from the axial top and bottom of the sample respectively to avoid the uncertainty of measuring distance with the rough edges of the sectioning cut. Smaller dashed lines on the X axis of Figure 4.5 represent thermocouple axial positions A, B, C, and D where heat flux was measured with null point calorimeters, as described in Section 3.5.

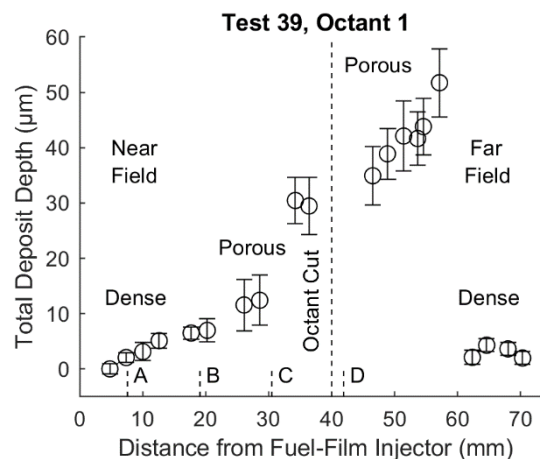


Figure 4.5. Typical total carbon deposit depth data from test 39, octant 1. Error bars represent the R_a surface roughness parameter, which was always higher for the porous deposits when compared with the denser deposits.

Results

Repeatability and Effect of Film Mass Flow Rate

Figure 4.6 shows the repeatability of total carbon deposit depth between tests operated at the same conditions, but on dates up to a year apart. Tests with the baseline fuel-film flow rate of 37.8 g/s (0.083 lb_m/s) are on the left while those on the right have a higher fuel-film flow rate of 52.6 g/s (0.116 lb_m/s) with all other conditions held constant. The 40% higher fuel-film flow rate of tests 36 and 43 resulted in a longer axial region of porous carbonaceous deposits of approximately the same thickness as the deposits from tests 39, 53, and 54 which operated at the baseline fuel-film flow rate. Fuel-film flow rate may not have a significant effect on deposit depth within the near field region since the deposits up to 60 mm (2.36 inch) matched quite well between all tests shown in Figure 4.6. The liquid coolant surface temperature reaches saturation conditions quickly after injection due to high heat flux from the gaseous core flow. Once the liquid reaches this saturated state, the coolant film's temperature does not increase further until it completely vaporizes, locking the wall temperature condition at a constant value with respect to axial position in the near field. Carbon deposition likely does not increase at higher fuel-film flow rates because these rates result in the same saturation temperature as the lower rates, albeit for longer axial distances. This result is similar to the common liquid film cooling result of increased film coolant mass flow rate resulting in the same heat flux reduction at the injector face, but increasing the total film cooled length, at least up to a certain critical mass flow rate as described in Section 1.1.

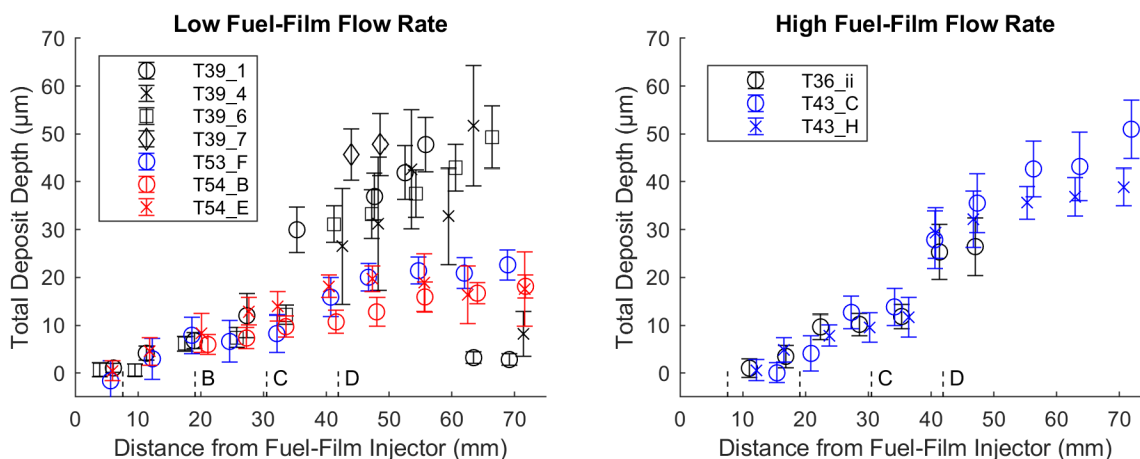


Figure 4.6. Repeatability of total deposit depth data for low (left) and high (right) fuel-film flow rates. Data are colored according to test number, and point markers differ for each octant of a given test.

Little to no deposits were observed up to 10 mm (0.39 inch) downstream of the fuel-film injector in all tests, likely because the fuel-film had not reached saturation conditions yet, where pyrolysis would be expected to occur. Total carbon deposit depth matched best in the dense deposit region closest to the fuel-film injector, which typically ended at around 35 mm (1.38 inch). Deposit depths matched well for octants from the same test, as demonstrated by test 39. However, test 39 and tests 53/54 operated at the same conditions, but showed differing depth trends past 35 mm (1.38 inch) downstream of the fuel-film injector. The only difference between test 39 and tests 53/54 was a small geometry change in the nozzle converging section, namely the removal of a post-combustion recirculation region that existed for hybrid rocket tests which used the same nozzle assembly. The differences in total deposit depth could have been a result of this nozzle change, which occurred 4.8 mm (0.19 inch) axially downstream of the discrepant region. Note that tests 53 and 54 match quite well in the porous region, having occurred back-to-back with the same nozzle after the change. Deposits from tests 36 and 43 with the higher fuel-film flow rates matched quite well, having both occurred before the nozzle change. All total deposit depth plots within the remainder of this dissertation compare tests using the same nozzle geometry. The nozzle geometry change occurred between tests 46 and 47, and persisted to the remaining tests after 47.

Another, albeit less likely, explanation for the discrepancy at distances further from the fuel-film injector could be the fragility of the porous carbon layer, as evidenced by it flaking off when touched by a finger. Manually exhausting high velocity, 0.7 MPa (100 psia) nitrogen on samples with porous carbon did not seem to have an effect post-test. However, the high temperature gradients occurring during the shutdown may have resulted in residual stresses high enough to allow for the shedding phenomenon, potentially explaining the discrepancy between tests 39 and 53/54.

Effect of Surface Roughness

Initial metal chamber liner surface roughness may have affected carbonaceous deposit surface roughness and total deposit depth. Test 54, octants B and E had initial surface finishes of $0.66 \pm 0.02 \mu\text{m}$ ($26.0 \pm 0.8 \mu\text{inch}$) and $5.32 \pm 0.68 \mu\text{m}$ ($209 \pm 27 \mu\text{inch}$) respectively, as measured by the ZeGageTM optical profiler. The rougher initial surface finish of octant E had, on average, two to three times higher carbonaceous deposit R_a values than the finer initial surface finish of octant B, as can be seen in the left plot of Figure 4.6. There were signs of dissimilar shedding

between octants E and B which may have been caused by axisymmetry deficiencies in the nitrogen purge during the shutdown transient, thus explaining this dissimilar carbonaceous deposit surface finish. Approximately 50% larger deposit depths were recorded for the rougher surface finish at axial positions up to 45 mm (1.77 inch). The mean deposit depth values were approximately the same past this initial region, despite dissimilar starting surface roughnesses. Surface finish seemed to affect deposition rate when the carbonaceous layer was smaller than the initial surface finish of the metal chamber liner, which occurred mostly at regions closest to the fuel-film injector for shorter bipropellant burn times. Test 53 operated at the same conditions as test 54 and octant F had a rough surface initial finish. The results from this test 53 octant F match well with test 54 octant E, demonstrating repeatability of initial surface finish effects on carbon deposition between tests and octant positions. These results agree with the surface finish heat flux results presented in Section 3.5, where initial surface finish had a larger effect on the near field region of the sample tube.

Effect of Run Time

Longer test times resulted in larger total carbon deposit depths. The left plot of Figure 4.7 shows total deposit depths for tests 40 and 43 with bipropellant run times of 15 and 6 seconds respectively at the higher fuel-film mass flow rate. The right plot of Figure 4.7 shows similar trends for tests 56, 58, and 63 which all had N066 sample tubes and the baseline fuel-film mass flow rate. All tests had total carbon deposit depths near zero for the first 10 mm (0.39 inch) downstream of the fuel-film injector. The fuel-film was likely liquid at a low temperature, resulting in little to no carbon deposits regardless of run time. After this initial region, the longer duration test 40 and 63 depths had considerably thicker deposits than those of the baseline tests 43, 56, and 58, with a nearly linear trend for deposit thickness with bipropellant run time. Carbon deposition on a carbon substrate was expected to be linear for a steady-state combustor, at least until the porous layer thickness becomes large enough to enhance shedding. The far field region past 30 mm showed signs of shedding both visually, and in the data of Figure 4.7. It was difficult to determine if the shedding occurred during quasi-steady-state operation of the combustor, or during the shutdown transient. Additionally, porous carbon was found closer to the fuel-film injector for the longer duration tests, as evidenced by higher standard deviations. Further depth measurements that can

distinguish the dense and porous layers are required to determine if the far field asymptotic behavior with time is caused by shedding, or some other phenomenon.

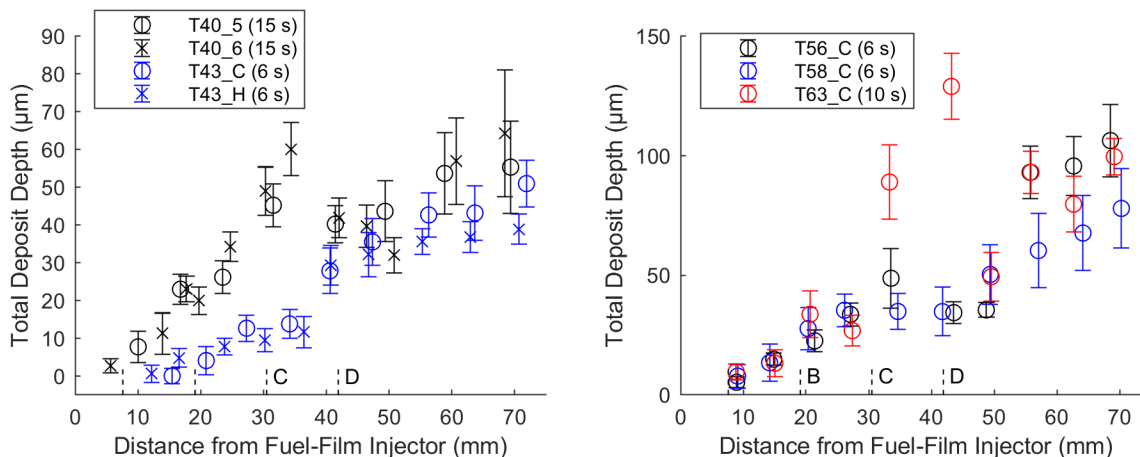


Figure 4.7. Tests 43 and 40 (left) operated at the higher fuel-film flow rate with bipropellant run times of 6 and 15 seconds respectively. Tests 56, 58, and 63 operated at the baseline fuel-film flow rate with a N066 sample tube material and bipropellant run times of 6, 6, and 10 seconds respectively.

Effect of Fuel Composition

Figure 4.8 shows carbon deposit depth for baseline test 39 compared to test 38, which used JP-8 POSF10264 as the main fuel and fuel-film as opposed to RP-2 POSF5433. RP-2 is a narrower cut fuel with lower olefin, aromatic, and sulfur content than JP-8. There were three primary differences between JP-8 test 38 and the baseline tests:

1. Porous carbon started appearing closer to the fuel-film injector, as evidenced by higher standard deviations.
2. Total carbon deposit depth increased more quickly with axial distance from the fuel-film injector.
3. Total carbon depth peaked at an earlier position of 40 mm (1.57 inch) compared to 55 mm (2.17 inch), before returning to lower depth, dense deposits.

Higher olefin/aromatic content in JP-8 (5%/25%) [74] compared to RP-2 (1%/5%) [34] may explain these differences due to shorter reaction pathways to polycyclic aromatic hydrocarbons (PAHs), where PAHs are generally accepted as the most important precursor to solid carbon deposits in both pyrolysis and soot formation mechanisms [75]. The data in Figure 4.8 suggests that less wall surface was protected by the fuel-film when using JP-8 compared to RP-2, as would be expected based on a logical extension of the high temperature results from

regenerative cooling jacket literature. Stiegemeier et al. [32] found that JP-8 and JP-8+100 could not be operated at similar temperature conditions to RP-1 due to excessive pressure drops from carbon deposit flow restrictions. Sulfur has also been shown to increase carbon deposition in rocket kerosenes, but typically due to catalytic effects in high residence time regenerative cooling applications [32,33]. Scanning electron microscopy images showed no signs of filamentous carbonaceous deposits, which are formed via catalytic mechanisms. Based on this evidence, it was assumed that the olefin/aromatic content difference between JP-8 and RP-2 caused the carbonaceous deposit discrepancy between tests 38 and 39.

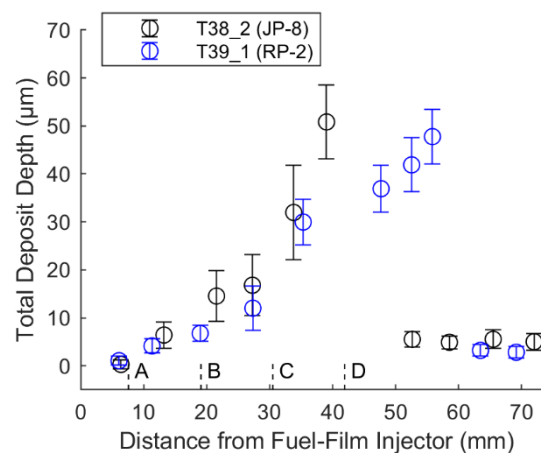


Figure 4.8. Tests 38 (baseline) and 39 used JP-8 and RP-2 respectively in the main fuel and fuel-film injectors. The higher olefin, aromatic, and sulfur content of JP-8 resulted in carbon deposit formation at axial positions closer to the fuel-film injector.

Effect of Chamber Liner Material

Chamber liner material mainly affected total carbon deposit depth through changes in material properties such as thermal conductivity, density, and specific heat. Figure 4.9 shows data from tests 54, 57, and 58 which had chamber liners of oxygen-free high thermal conductivity copper UNS C10100 (C101), stainless steel UNS S30400 (S304), and Inconel UNS N06600 (N066) respectively. Both S304 and N066 have similarly low thermal conductivities when compared with C101, resulting in higher wall temperatures. The similarity between total deposit depth results for S304 and N066 confirmed the nearly identical heat flux trends from Section 3.5.

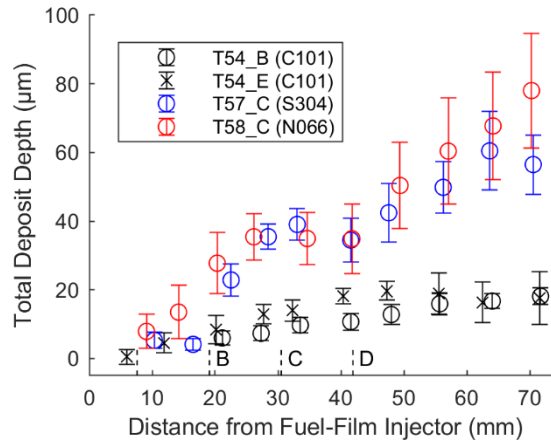


Figure 4.9. Tests 54, 57, and 58 were tested at the same baseline conditions apart from having chamber liner materials of C101, S304, and N066 respectively. Higher total deposit depths were observed for the lower thermal conductivity metals.

Higher wall temperatures would have resulted in a lower thermal gradient, and therefore a lower thermophoretic velocity of soot particles towards the wall. At first glance, this conflicts with the data, which shows higher soot deposits for the higher wall temperatures of the S304 and N066 chamber liners. However, we must remember that thermophoretic soot growth is proportional to soot volume flux, which is proportional to both thermophoretic velocity and soot volume fraction (given the assumptions of Section 1.2). The higher wall temperatures likely resulted in higher soot volume fractions occurring closer to the wall. In fact, soot volume fraction increases exponentially with temperature until around 1500 K, whereas thermophoretic velocity is only proportional to temperature gradient. The results shown in Figure 4.9 are consistent with the trends that would be expected for a thermophoretic soot deposition mechanism.

While the N066 total carbon deposit depths were slightly larger than those of the S304 test, the primary difference was the higher standard deviation, and therefore R_a surface roughness of the N066 deposits. The differing total deposit depths and surface roughnesses may have been caused by N066's thermal expansion coefficient, which is approximately 30% lower than that of S304. A lower thermal expansion coefficient would have caused a higher thermal contact resistance between the chamber liner and C101 heat sink cooled chamber, thus resulting in higher wall temperatures for the N066 test. Higher wall temperatures would cause a larger thermal shock upon shutdown, which would increase post-test shedding and therefore surface roughness.

Scanning electron microscopy revealed no signs of catalytically-formed filamentous deposits, which will be further explored in Section 4.2.2.

4.2.2 Scanning Electron Microscopy (SEM)

Several previous researchers have used SEM to characterize carbonaceous deposits from rocket propulsion environments. Roback et al. [31] imaged carbonaceous deposits formed in heated tube tests, with filamentous structures from propane and non-filamentous structures from RP-1 and JP-7. It is difficult to discern if the non-filamentous structures were more amorphous or graphitic in nature due to the poor quality of the scanned article. A similarly dated, but better-scanned article by Atria et al. [76] showed that heated tube tests with Norpar-13, a straight chain paraffinic solvent sold by ExxonMobil, resulted in filamentous carbon deposition while tests with Jet A resulted in deposition that was more amorphous in nature. Particle sizes from the Jet A tests seemed to be on the order of hundreds of nanometers based on SEM images reported in the paper. Altin and Eser [77] thermally stressed JP-8 on nickel, stainless steel, Silcosteel, and glass-lined metal substrates at pressures up to 3.4 MPa (500 psig) and wall temperatures up to 770 K (930°F). They used temperature-programmed oxidation (TPO) and SEM micrographs to distinguish between different types of carbon, where catalytically formed carbon typically had larger crystallites or filamentous structures. Catalytic activity of the metal substrate decreased in the following order: nickel > stainless 316 > stainless 304.

As for film cooling literature, Gokulakrishnan et al. [51] investigated fuel-film carbon deposition in an atmospheric pressure propane-air burner, finding that the carbonaceous deposits looked more like a smooth thermal barrier coating than individual particles on the SEM, indicating a more graphitic structure.

In this dissertation, a Thermo Fisher Scientific FEI Quanta dual-beam SEM was used to capture high resolution images and cross sections of the carbonaceous deposits. The SEM contained both an electron and gallium ion beam, where the former was used for imaging and the latter was used for site specific milling, machining, and deposition. The Quanta's 5-axis powered stage allowed for precise sample positioning with respect to the two beams. All SEM images shown in this paper were captured with an Everhart-Thornley detector at high vacuum. Figure 4.11 shows the SEM chamber with a sample octant-half loaded.

Figure 4.10 shows typical SEM macroscopic images at 200X (left) and 2500X (middle), with axial flow from top to bottom. The two-layer structure is immediately evident, with the porous layer typically tens to hundreds of microns taller than the dense layer. Cross sections of the layer structure (see Figure 4.13) revealed largely homogenous dense layers and soot-like porous layers. The porous layer likely provided considerably more thermal insulation than the dense layer due to lower particle densities and larger thicknesses. Circumferential peaks and valleys from lathe boring persisted through the dense layer deposits, but were masked by the thicker porous layer deposits. Energy-dispersive x-ray spectroscopy (EDS/EDX) scans for carbon (top right) and copper (bottom right) of the dense layer zoom region in Figure 4.10 (middle) show that the dense layer deposits conformed to the original metal surface structure, where whiter pixels indicate presence of each element. EDS has a penetration depth on the order of microns, confirming that the dense layer was significantly thinner than the porous layer. Additionally, macroscopic images for all samples were used to confirm the absence of contaminants, as related to the sample sectioning methodology described in Section 4.1.

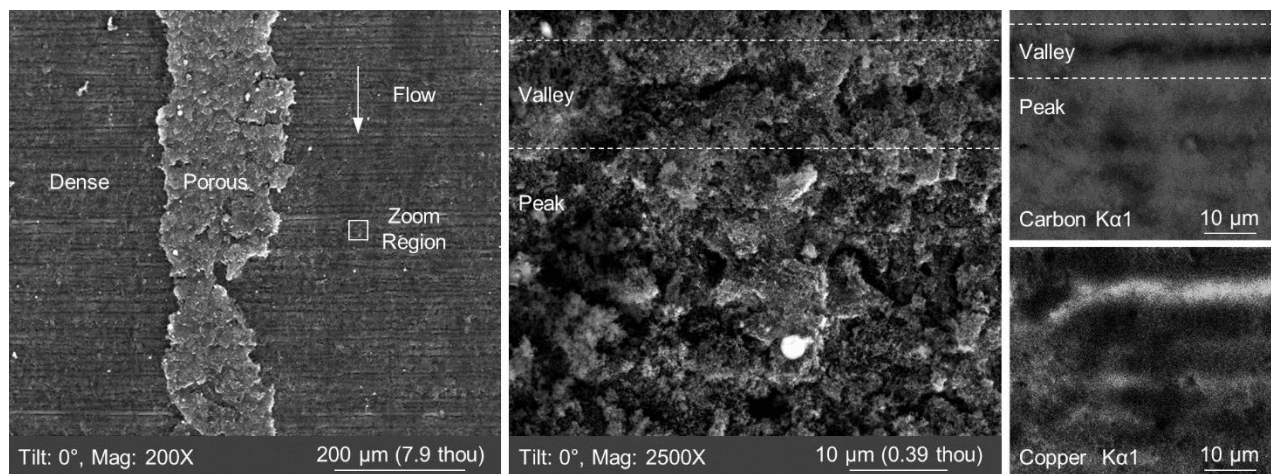


Figure 4.10. Typical macroscopic images of post-test sectioned samples showing the two-layer structure (left) and dense layer lathe boring marks (middle) as confirmed by energy-dispersive x-ray spectroscopy (right).

Large portions of this section are identical to those to be published in a journal paper by Piper and Pourpoint [78].

Methods

A gallium focused ion beam (FIB) angled at 52° to the main electron beam was used to mill cross sections such that the carbonaceous deposit morphology could be characterized and quantified as a function of depth. Figure 4.11 shows the main electron beam and gallium ion beam while defining the tilt angle between them. Sample sites were selected where porous layer shedding occurred because FIB milling time at a given accelerating voltage and probe current was proportional to milled volume. Typical cross section dimensions of width, length, and depth were 8, 10, and 20 μm (0.3, 0.4, and 0.8 thou), although these dimensions were varied based on expected deposition depths. Width had to be increased for larger depths to allow for sufficient secondary electrons to escape the bottom of the cross section, where the carbon-metal transition occurred. Length had to be increased for larger depths to obtain cross section imaging tilt angles of at least 25° , where smaller angles would have resulted in inaccurate depth measurements. Therefore, milling time increased with the cube of the depth. One downside of SEM cross sectioning was that statistical uncertainty could not be easily measured, since cross sections had micron-scale dimensions and could take up to an hour per site. Cross sections were compared between sample octant halves of a few baseline tests to estimate the expected uncertainty for all data. Additionally, optical profilometry in Section 4.2.1 showed that the dense layer had significantly lower surface roughness compared to the porous layer, which prompted the restriction of this SEM cross sectioning methodology to only measure dense layer depths.

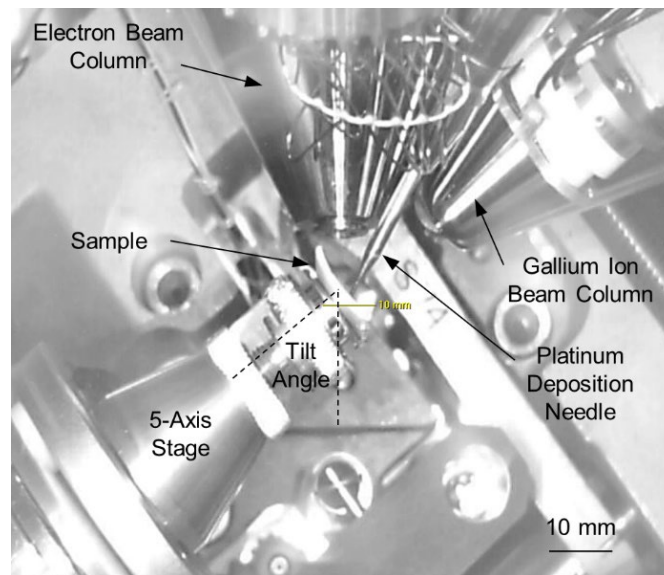


Figure 4.11. Scanning electron microscope vacuum chamber showing a sample during the platinum deposition process.

The SEM cross sectioning method required six main steps, as outlined in Figure 4.12: site selection, finding eucentric position, platinum deposition, rough cutting, finish cutting, and depth measurement. Typical cross sections took anywhere from 10 to 60 minutes depending on the deposit depth, and three to five cross sections were made per sample octant half.

1. Determine Sample Site

As previously mentioned, sites were selected to minimize expected milling time. The dense layer deposit depth and morphology were the primary outputs of this study; therefore, sites were selected where porous layer shedding occurred to reduce the total carbonaceous material between the surface and metal substrate.

2. Find Eucentric Position

The eucentric position of the sample is the axis where the electron and FIB columns intersect, assuming the sample surface is perfectly flat with respect to the microscope stage. Finding the eucentric position insures that the electron and FIB columns are looking at the same part of the sample irrespective of tilt angle. Samples were loaded and positioned such that the eucentric axis aligned with the axial direction of the combustor. All SEM images from this point onwards will have axial flow from right to left because of this axis alignment.

3. Deposit Platinum

The Quanta SEM is equipped with a platinum sputtering system, which was used to preserve the surface of the sample since platinum is milled significantly slower than the carbonaceous deposits. Typical platinum strips were 1.5 μm (0.06 thou) long, 1.5 μm (0.06 thou) deep, and the full width of each cross section. Deeper cross sections often required thicker platinum strips because more of the platinum would be eroded away during the longer cutting process. The FIB column was set to an accelerating voltage of 10 kV and beam current of 0.3 nA for optimal platinum deposition. Without this step, it would be difficult to determine depth because the top surface of the sample would be eroded by the FIB beam milling operation.

4. Rough Cut

A rough cut at a high beam current was used to remove carbonaceous material quickly at the cost of larger edge erosion and poorer cross section image quality. The “stair-case” shape of the rough cut only removed the material necessary for cross section imaging at the tilt angle defined by the length and depth of the milled volume, which was approximately half that of the entire rectangular prism volume. Typical rough cut FIB column parameters were 20 kV and 4.6 nA, although a higher beam current of 9.6 nA was used for particularly deep carbonaceous deposits.

5. Cleaning Cut

The cleaning cut only removed material directly next to the cross section imaging surface, but at a significantly lower beam current than the rough cut such that the sample morphology could be sharpened for imaging purposes. Higher rough cut beam currents required a longer cleaning cut dimension because more of the cross section imaging surface would be unevenly eroded. Typical cleaning cut length dimensions were approximately 1.5 μm (0.06 thou), which were cut with FIB column settings of 20 kV and 0.64 nA.

6. Measure Depths

Dense layer depth was determined manually from the cross section image by measuring the distance between the platinum-carbon transition and the carbon-metal transition. The carbon-metal transition could be identified by an axial line of slightly whiter pixels, which occurred due to the higher molecular weight of the base metal when compared with carbon. Dividing the measured depth by the sine of the tilt angle accounted for the sample stage tilt. Depth measurements were taken at multiple positions, then averaged, to determine a representative value for each cross section.

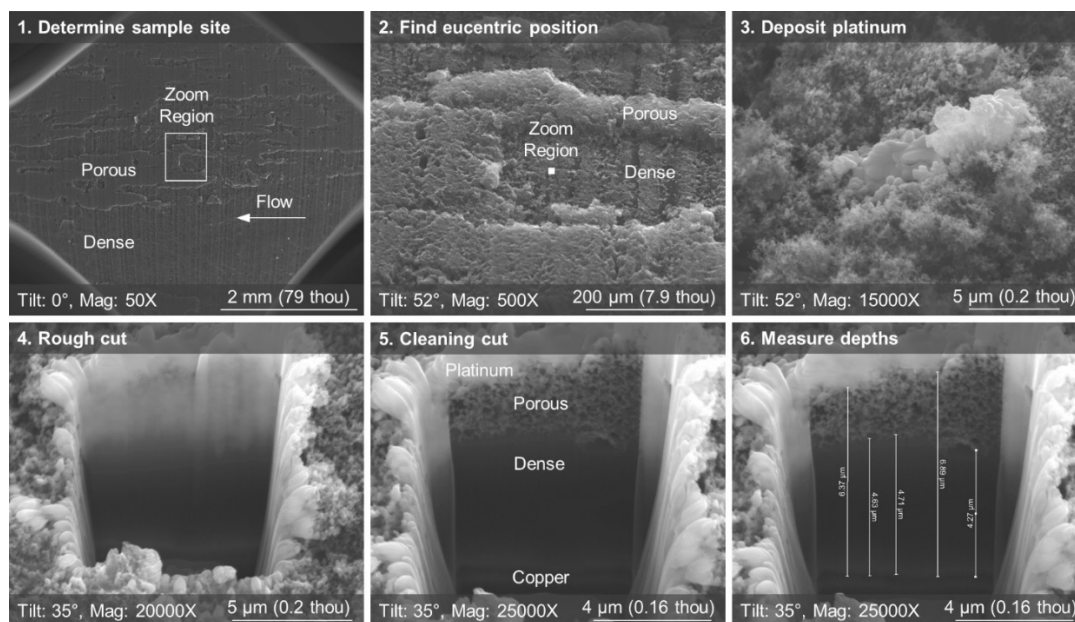


Figure 4.12. Annotated step-by-step procedure for cross sectioning a representative sample from test 40. Note that the depths shown in step 6 do not account for the indicated sample stage tilt of 35°, which was done after measurements were taken.

Not all sample cross sections had neatly defined boundaries between the platinum, porous layer, dense layer, and metal substrate as shown in Figure 4.13. The platinum deposits displayed as a whiter layer near the top of the image due to the higher molecular weight of platinum compared to carbon. A porous layer with particles on the order of tens to hundreds of nanometers in diameter would occur directly beneath the platinum layer, with a thickness dependent on the level of shedding at each given sample site. To reiterate previous paragraphs, measurement of the porous layer properties was not the primary goal of this paper because porous layer depth could be more accurately and quickly measured with optical profilometry, as demonstrated in Section 4.2.1. The porous to dense layer transition varied depending on the sample site position with respect to the fuel-film injector and the test conditions. Higher dense layer depths tended to have more ambiguous transitions, such as that shown in the right image of Figure 4.13. Multiple micron gaps occasionally occurred between consecutive porous or dense layers, potentially due to shedding of the porous layer during the bipropellant test. These gaps would display as brighter strips of material because gallium from the FIB column would deposit in the empty space, and gallium has a higher molecular weight than carbon. The carbon to metal transition was always well-defined as an axial white strip near the bottom of a properly-sized cross section, although it varied slightly more for metal sample tubes with higher pre-test surface roughnesses.

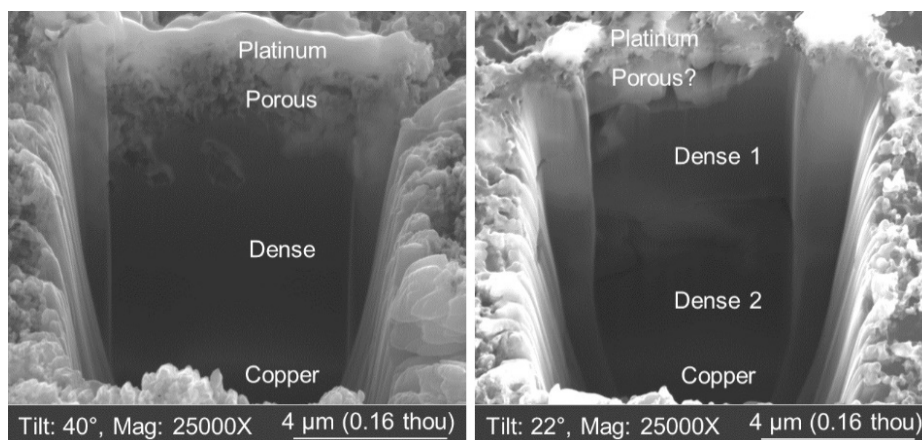


Figure 4.13. Representative well-defined (left) and ambiguous (right) porous-dense carbon transitions from two different axial positions of test 39.

Figure 4.14 was taken after performing a site cross section at an axial location far from the fuel-film injector, where carbonaceous deposit depths were highest and shedding was most prevalent. At this particular location shedding exposed two separate porous layers, the dense layer beneath them, and the metal substrate all within an imaged square of approximately 0.25 mm (10 thou) length. Depths of the second porous layer and dense layer matched between the cross section and the area exposed due to shedding. While shedding significantly affected the total carbonaceous deposit depth, it did not seem to affect the dense layer at all, which adhered more tightly to the metal substrate beneath it than the porous carbon layer above it.

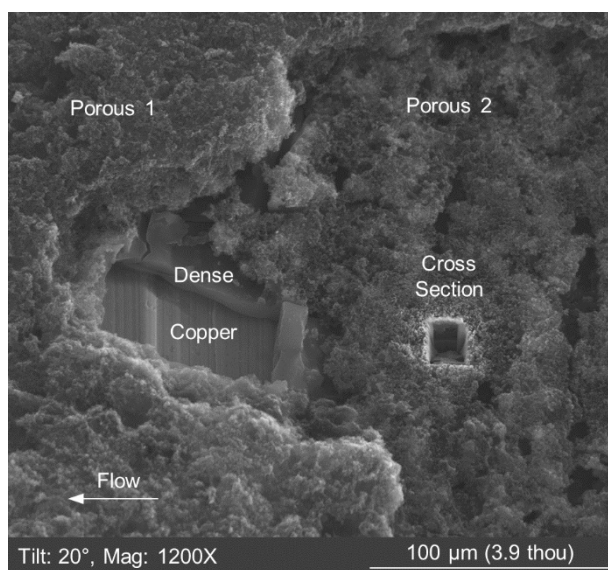


Figure 4.14. Shedding revealed two porous layers, a dense layer, and the copper substrate all within a small area of this SEM image. The feature on the right is a completed cross section.

Results

Repeatability and Effect of Film Mass Flow Rate

Multiple tests were conducted at baseline and high fuel-film flow rates of 37.8 g/s (0.083 lb_m/s) and 52.6 g/s (0.116 lb_m/s) respectively, with all other conditions held at the baseline values as shown in Appendix A and further described in Section 3.3. Figure 4.15 shows that dense layer deposit depth was nearly zero for the first 10 mm (0.4 inch) downstream of the fuel-film injector, after which depth monotonically increased with distance. The lower, baseline fuel-film flow rate had a significant drop in dense layer deposit depth at 60 mm (2.4 inch) downstream of the injector, which likely correlated with the end of liquid fuel-film vaporization and pyrolysis. Dense layer deposit depths were repeatable between tests of the same type; for instance, both tests 39 and 54 had the characteristic drop in depth at 60 mm (2.4 inch) axial distance. Fuel-film flow rate did not have any significant effect on the deposit depths up to 60 mm (2.4 inch) from the fuel-film injector. The main effect of increasing fuel-film flow rate seemed to be an increase in axial length of the dense deposit region, which follows from heat flux data of previous film cooling literature with other propellants [5,14]. All of these conclusions mirror those made about the total depth measured via optical profilometry in Section 4.2.1, with the primary difference being a lower depth magnitude when compared with total deposits. Similar dense deposit depths at varying fuel-film flow rates further verify the Section 4.2.1 hypothesis that the constant liquid saturation wall temperature results in similar deposition rates, even while varying film flow rate. Red data points in Figure 4.15 are from the no fuel-film flow rate qualification test briefly mentioned in Section 3.4.1. As expected, the dense deposits were much more constant for the no fuel-film flow rate test, compared to the baseline and high fuel-film flow rate tests. There were, however, still measurable depths of deposits for the no fuel-film flow rate test, which suggests that the mechanism for dense layer deposition is active even without a liquid fuel-film. This supports the hypothesis that PAH condensation may be occurring close to the cool wall, which will be further explored in the gas chromatography mass spectroscopy Section 4.3.1. The smaller dashed lines on the X axis of Figure 4.15 represent thermocouple axial positions A, B, C, and D where heat flux was measured, as described in Section 3.5.

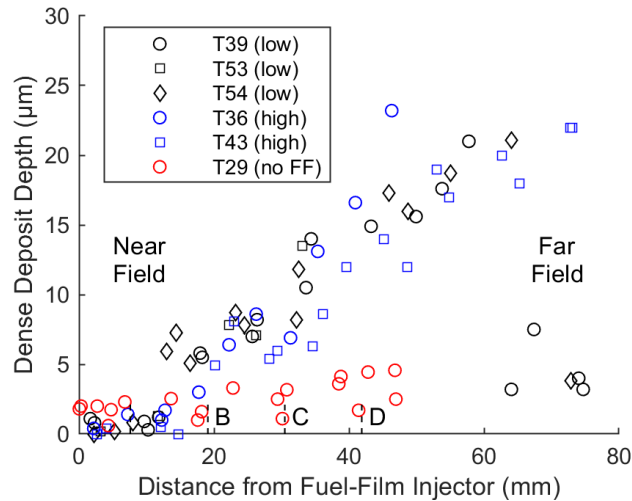


Figure 4.15. Dense layer carbonaceous deposit depths for baseline (black), high (blue), and zero (red) fuel-film flow rates from multiple tests and octants.

Effect of Run Time

Bipropellant run time affected dense layer deposit depth nearly linearly. Figure 4.16 shows dense deposit depth for varied bipropellant run times for high fuel-film flow rates on UNS C10100 samples (left) and baseline fuel-film flow rates on UNS N06600 samples (right). Since the dense deposit depth increases with bipropellant run time, we can conclude that the dense layer is formed at the same time as the porous layer, as opposed to the dense layer forming temporally first and the porous layer forming afterwards. The dense layer growth mechanism is likely related to condensation, where heavier PAHs diffuse through the porous layer to condense on the cool metal wall. Dense deposit depth increased approximately proportionally with run time in the near field between 0 and 40 mm (0 and 1.6 inch) from the fuel-film injector for both C101 and N066 samples. Deposits in the far field continued increasing approximately proportionally for the C101 long duration test T40, but leveled off in the N066 long duration test T63.

Note that these trends in dense deposit depth closely matched that for total deposit depth, as outlined in Section 4.2.1, where conclusions could not be drawn as to whether this phenomenon was driven by shedding or the shutdown nitrogen purge. Since dense layer deposits would be shielded from high velocity gases, we can conclude that the asymptotic behavior of the carbonaceous deposits is not caused by steady-state shedding or post-test purging. A decrease in the thermophoretic force on soot due to higher wall temperatures in the thick deposit regions may cause the leveling off of porous and dense deposit rates past 40 mm (1.6 inch) from the fuel-film

injector. Thicker porous deposits would cause higher carbon wall temperatures, reducing the temperature gradient between the gaseous film cooling boundary layer and the wall, thus reducing the diffusion of hot soot particles towards the wall. Section 4.2.1 concluded that pyrolysis may be the main deposition process in the near field based on higher deposition rates at higher wall temperatures. However, this should not be true in the far field, where the liquid film has fully evaporated and thermophoretic diffusion of soot should start becoming the primary deposition process, as indicated by the data in Figure 4.16.

Note the two low dense deposit depths in the far field region of T40, in the left plot of Figure 4.16. These points unexpectedly occurring at low dense deposit depths are a consequence of choosing sites near shedding to reduce total cross sectioning time. A second site was chosen on T40_5 to verify the low dense deposit depth of $\sim 5 \mu\text{m}$, only to find that the second site had a dense depth of over $30 \mu\text{m}$. Shedding of porous layer deposits may have removed dense deposits beneath them. The two outliers were kept in the left plot of Figure 4.16 to demonstrate the consequences of poor site selection, and remind the reader that shedding has the potential to invalidate portions of this research, despite all efforts being taken to prevent such a thing from happening. Transitioning the carbonaceous deposits from a hot combustion state to ambient conditions without damaging them is difficult, which is one reason why in-situ measurements for heat flux have been the primary focus of previous research.

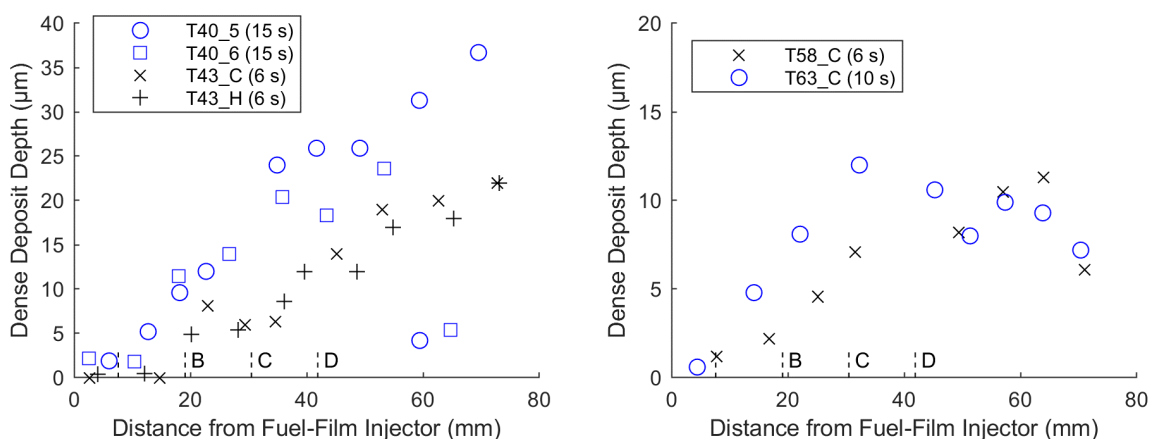


Figure 4.16. Dense layer deposit depths for high fuel-film flow rate copper base metal tests (left) and baseline fuel-film flow rate Inconel base metal tests (right) at varying bipropellant run times.

Effect of Fuel Composition

Changes in fuel formulation affected the dense layer deposit depths in a similar manner to the results seen for total deposit depths in Section 4.2.1, as shown in Figure 4.17. Tests 38 and 39 were tested with JP-8 POSF10264 and RP-2 POSF5433 respectively with all other conditions held at baseline values, as shown in Appendix A and further described in Section 3.3. The JP-8 test had thicker dense layer deposits near the fuel-film injector, a similar dense layer deposit peak depth of approximately 20 μm (0.79 thou), and an axially earlier drop in deposit depth at 40 μm (1.57 thou) as opposed to 60 μm (2.36 thou) as seen for baseline tests. All three of these conclusions directly corresponded with conclusions made in Section 4.2.1 about the total deposit depth as measured by optical profilometry. The extended region of approximately 5 μm (0.2 thou) dense layer deposit depths from 40 to 80 mm (1.57 to 3.15 inch) downstream of the fuel-film injector had less than 100 nm (3.9 μinch) of porous layer deposits above it. This region was likely the result of the fuel-rich gaseous boundary layer meeting the wall after the liquid fuel-film had fully vaporized and pyrolyzed.

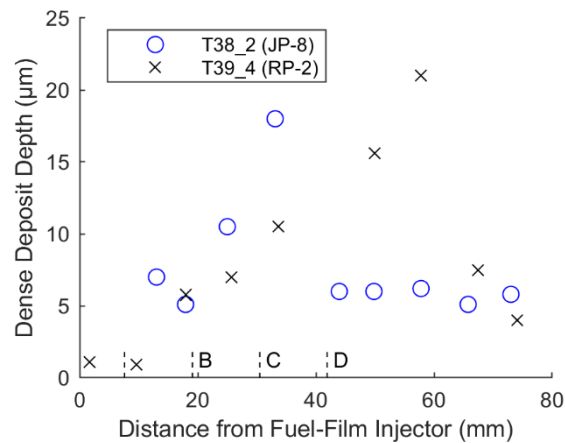


Figure 4.17. Tests 38 and 39 tested using JP-8 and RP-2 respectively, holding all other conditions to baseline values as described in Section 3.3.

Effect of Chamber Liner Material

Sample base metals of oxygen-free high thermal conductivity copper UNS C10100 (C101), stainless steel UNS S30400 (S304), and Inconel UNS N06600 (N066) were used to investigate catalysis and varying thermal properties on the carbon deposition process. Trends for dense layer deposit depth with varying base metal, and therefore varying thermal conductivity and wall temperature, were inverted when compared with those for total deposit depth as presented in

Section 4.2.1. Aside from a few outlying points, dense deposit depths for C101 walls were approximately two times higher than for S304 and N066 walls, as shown in Figure 4.18. S304 and N066 dense deposit depths matched well, likely due to their similar thermal properties. Catalytic effects between the mostly iron and nickel alloys respectively were similar based on the depth data, and likely absent entirely as indicated by the lack of filamentous carbon deposits in all SEM cross section images. A likely cause for the higher dense deposit depths for copper when compared with lower thermal conductivity metals is likely the lower wall temperature, which would result in more PAH condensation on the wall. Additionally, the thinner porous layer for the C101 samples when compared with S304 and N066 (as shown in Section 4.2.1) likely allowed for more diffusion of PAHs to the wall. Note that all tests in Figure 4.18 had the characteristic decrease in deposit thickness after 60 mm (2.4 inch), indicating that film cooled length was primarily a function of fuel-film flow rate as opposed to base metal type.

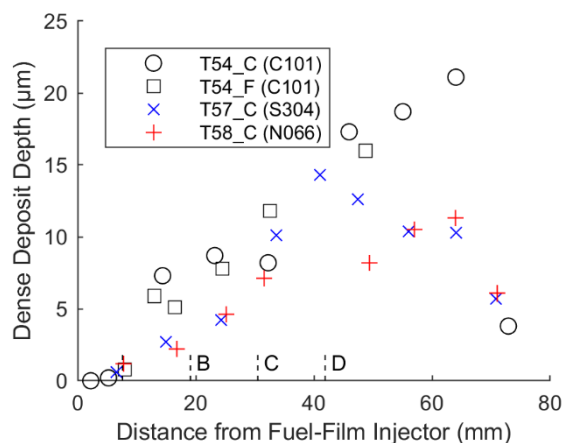


Figure 4.18. Dense layer deposit thickness variations for tests 54, 57 and 58 which had base metals of C101, S304, and N066 respectively.

Effect of Surface Roughness

Section 4.2.1 investigated initial base metal surface roughness' effect on total carbon deposition, which was enabled by statistically relevant data collected by the optical profilometer. Unfortunately, the low throughput and micron-scale site size of the SEM cross-sectioning method precluded any quantitative conclusions on initial metal surface roughness' effect on dense layer deposition.

The rougher surface finish is recognizable in SEM cross sections at the dense-copper transition, as shown in Figure 4.19. At the beginning of the bipropellant run time, surface finish

may have made a difference in the carbon deposition initiation on the bare metal surface. For instance, heat flux data in Figure 3.14 suggests that there were different deposition rates during the Task 1 combustor bipropellant startup transient. However, once a carbon layer begins forming on the surface, it seems to preferentially fill in or cover gaps in the surface, thus flattening the surface. The original rough surface finish of the metal tube likely had no effect on deposition rates past the startup transient.

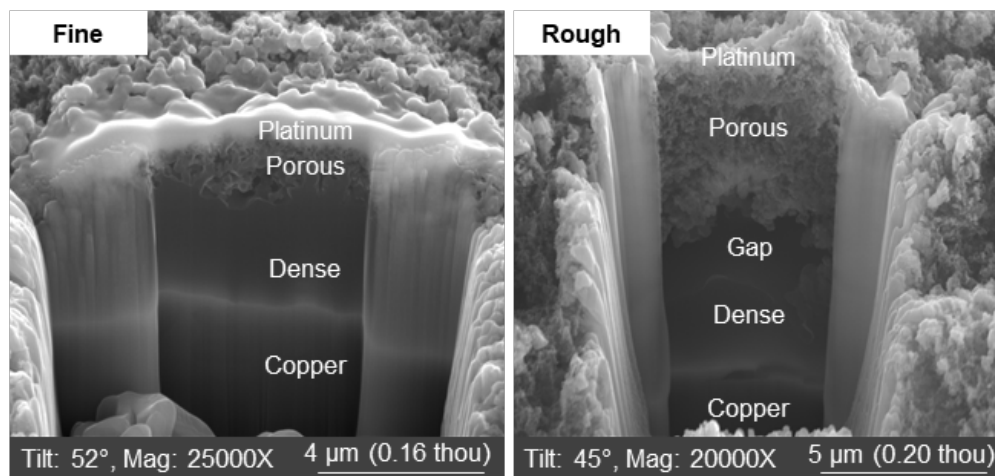


Figure 4.19. Sample tube surface finish affected the copper to dense layer transition, as revealed in SEM cross sections of test 49 carbonaceous deposits.

4.3 Chemical Characterization

I used spectroscopy to investigate the microscopic chemical and physical structure of the post-test carbonaceous deposits in an as-deposited state. Gas chromatography (GC) mass spectrometry (MS) was used to determine condensable PAH concentrations in the dense and porous deposits. Raman spectroscopy measured planar coherence length and other indicators of structural order while x-ray photoelectron spectroscopy (XPS) determined carbon hybridization, surface oxidation, and deposit impurities. All three of these spectroscopy techniques indicated independent signs of the dense layer PAH condensation mechanism. X-ray diffraction (XRD) measured crystallographic structure of the carbonaceous deposits, albeit with limited success. Where possible, spectra were measured as a function of axial distance from the fuel-film injector to identify changes in deposit structure as the fuel-film boundary layer vaporized and mixed with the core flow.

4.3.1 Gas Chromatography (GC) Mass Spectrometry (MS)

GCMS can be used to identify trace quantities of compounds by determining mass-to-charge ratios (m/z) as a function of gas chromatograph retention time. The gas chromatograph portion of the instrument separates the molecules by selectively retaining heavier molecules longer. Compound elution order, which is the order that the molecules leave the GC column, is a function of compound size and polarity, with heavier compounds eluting later. An electron beam is used to ionize the compounds emitted by the gas chromatograph before they enter the mass spectrometer detector, resulting in m/z fragmentation patterns that can be compared to known standards.

Preciado et al. [27] used a gas chromatograph to analyze carbonaceous deposits collected on a plate probe which could be water-cooled or uncooled. Their combustor was a premixed fuel-rich ethylene-air flat flame burner with a nitrogen shroud. The independent variables were probe height in the flame and probe temperature (300 K for cooled vs. 800 K for uncooled), with the goal of evaluating carbon deposit chemical and physical properties at different deposition temperatures. They used dichloromethane (CH_2Cl_2) to separate the extractable phase from the solid and unreactive soot particles such that the deposits could be analyzed in a GC. The uncooled, high probe temperature experiments had essentially 0% extractable material, whereas the cooled probe experiments had anywhere from 20 to 80% extractable material depending on the location in the flame. GC analysis of the extracted material revealed PAHs and PAH precursors for the cooled tests, which they proposed condensed on the soot particles and probe surface due to the lower temperature of the cooled probe. The uncooled extractable material did not show PAH peaks from GC analysis.

GCMS analysis of the Task 1 combustor carbonaceous deposits followed the Preciado et al. [27] methodology as closely as possible with the goal of determining if the porous and dense deposits could be distinguished by their percent extractable material and PAH concentrations in a similar manner to Preciado's uncooled and cooled probe experiments.

Methods

Dense and porous deposits from test 56 were carefully collected such that each sample contained as little of the other layer as possible. Porous deposits were lightly scraped from the

sample surface with a plastic razor blade. The sample was then lightly cleaned with a Chemwipe™ to remove as much porous deposits as possible while leaving the lower dense layer behind. The dense deposits were then scraped from the sample surface with a metal spatula. In this manner, the layers were separately removed from the sample surface without significant cross contamination. GCMS analysis occurred approximately a year after test 56, and the samples were stored in a temperature and humidity-controlled room during that time. However, any volatile deposits, such as smaller PAHs, would have evaporated off by the time of GCMS analysis.

GCMS samples were prepared by extraction with approximately 100 μL of dichloromethane (CH_2Cl_2) and filtering to remove the remaining solid soot particulates. Figure 4.20 shows the extracted and filtered samples after the CH_2Cl_2 evaporated off, multiple months after the GCMS samples were run. Note the yellow discoloration of the dense samples on the left, which qualitatively confirmed a difference in extraction compared to the clear porous samples on the right. When CH_2Cl_2 was present, it remained clear in the porous sample and was discolored yellow in the dense samples in a similar manner to the discoloration evident after it evaporated.

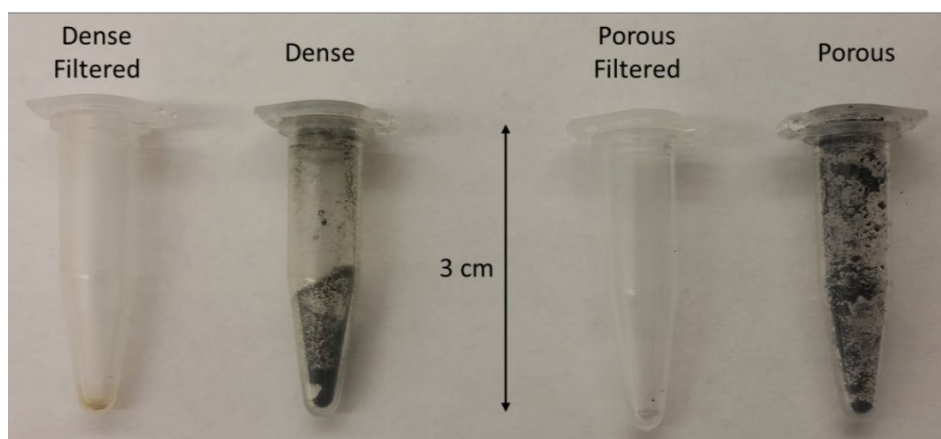


Figure 4.20. GCMS samples of dense and porous carbon from test 56, where the former had a yellow discoloration when extracted with dichloromethane.

Spectra were obtained on an Agilent 5975C mass spectrometer equipped with a HP 7890A gas chromatogram system. An Agilent DB-5MS separation column was used, which had the following dimensions: 30 m length, 0.25 mm inner diameter, and 0.25 μm film thickness. 1 μL of extracted and filtered liquid was injected for both the dense and porous samples. The temperature program was 80°C for 6 seconds, followed by a 10°C/min ramp to 320°C, then a 320°C hold for 15 minutes. The injector and transfer lines were maintained at 290°C.

Results

Figure 4.21 shows the chromatograms for the dense and porous sample. Table 4.1 describes significant peaks as determined by mass spectrometry. Mass spectra were compared to fragmentation patterns of standards from the NIST library [79], which conveniently tabulates previous literature, to determine likely compounds for each labeled peak. The lighter hydrocarbons in the 12-17 min range had similar spectra, and were not individually identified since aliphatic hydrocarbons have similar fragmentation patterns. However, PAH peaks in the 20-40 min range were more easily identified because they fragment much less. There were significant differences between the dense and porous sample 20-40 min spectra as related to PAHs, with some differences only evident in the mass spectra. Fluoranthenes, pyrenes, and chrysenes were all identified in the dense sample chromatogram, similar to those found by Preciado et al. [27] on their water cooled probe in a fuel-rich flat flame burner.

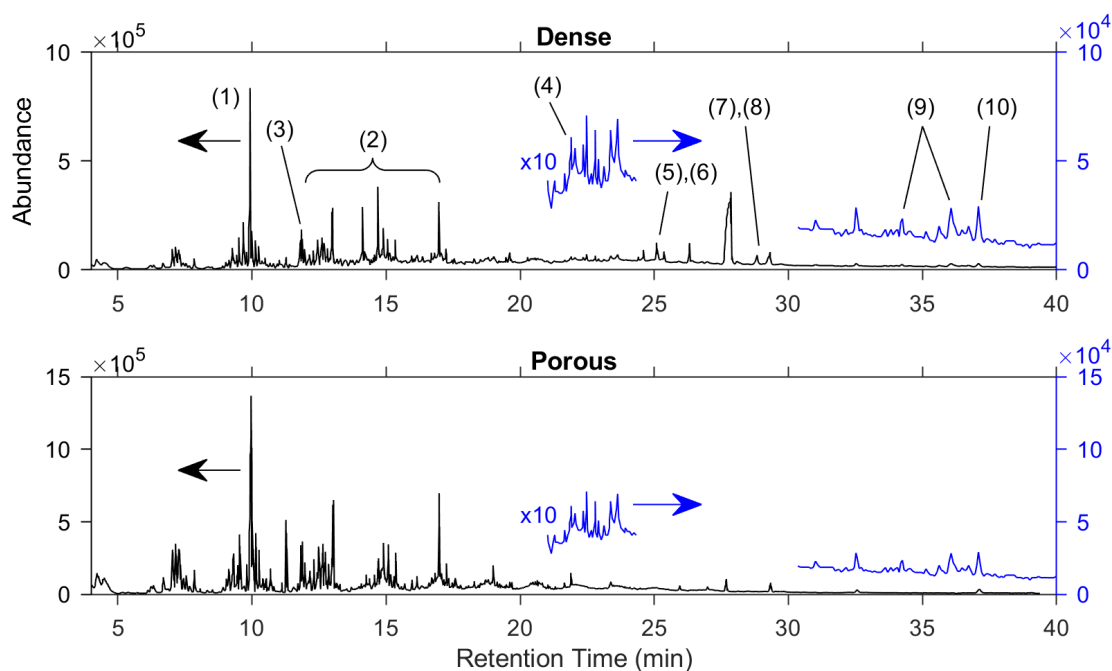


Figure 4.21. Chromatograms of dense and porous samples, with compounds identified by mass spectrometry in Table 4.1. The blue trace, as quantified by the right y-axis, magnifies the smaller peaks in the tail end of the chromatograms.

Table 4.1. Compounds identified by gas chromatography and mass spectrometry in the dense and porous samples, where “P” is present, “NP” is not present, and “T” is trace. “T” was used to denote compounds present in significantly lower quantities than “P.”

Compound	Number	M.W. (g/mol)	Retention Time (min)	Dense	Porous
benzoic acid, 4-ethoxy-, ethyl ester	(1)	194	10	P	P
non-aromatic hydrocarbons	(2)	-	12-17	P	P
cadina-1(10),6,8-triene	(3)	202	12	P	NP
7,12-dihydrobenzo[k]fluoranthene	(4)	252	22	P	T
dibenzo[def,mno]chrysene	(5)	276	24-26	P	T
benzo[ghi]perylene	(6)	276	24-26	P	T
coronene	(7)	300	28-30	P	NP
3,4:9,10-dibenzopyrene	(8)	302	27-30	P	NP
acenaphtho[1,2-j]fluoranthene	(9)	326	34,36	P	NP
dibenzo[fg,ij]pentaphene	(10)	352	37	P	NP

The porous sample chromatogram looked similar to the dense one up to a retention time of approximately 20 min, however the tail end peaks were significantly reduced comparatively. Appendix D shows extracted ion spectra of the PAHs listed in Table 4.1, where detected ion counts were summed in the range $MW-0.3$ and $MW+0.7$ for a given integer molecular weight MW . The extracted ion spectra show that compounds at 300, 302, and 326 g/mol were not present in the porous sample, while the compound at 276 g/mol was present only in trace quantities. The compounds listed in Table 4.1 were identified by comparing fragmentation patterns to NIST standards [79]. For example, Figure 4.22 shows a summation of the dense sample mass spectra from retention times of 29.227 to 29.248 min, which matches the standard mass spectrum of 3,4:9,10-dibenzopyrene well. While extracted ion spectra in Appendix D seem to show compounds (3) at 202 g/mol and (10) at 352 g/mol as present for the porous sample, mass spectra summed over the extracted ion spectra peaks show that the porous chromatogram peaks were not caused by PAHs.

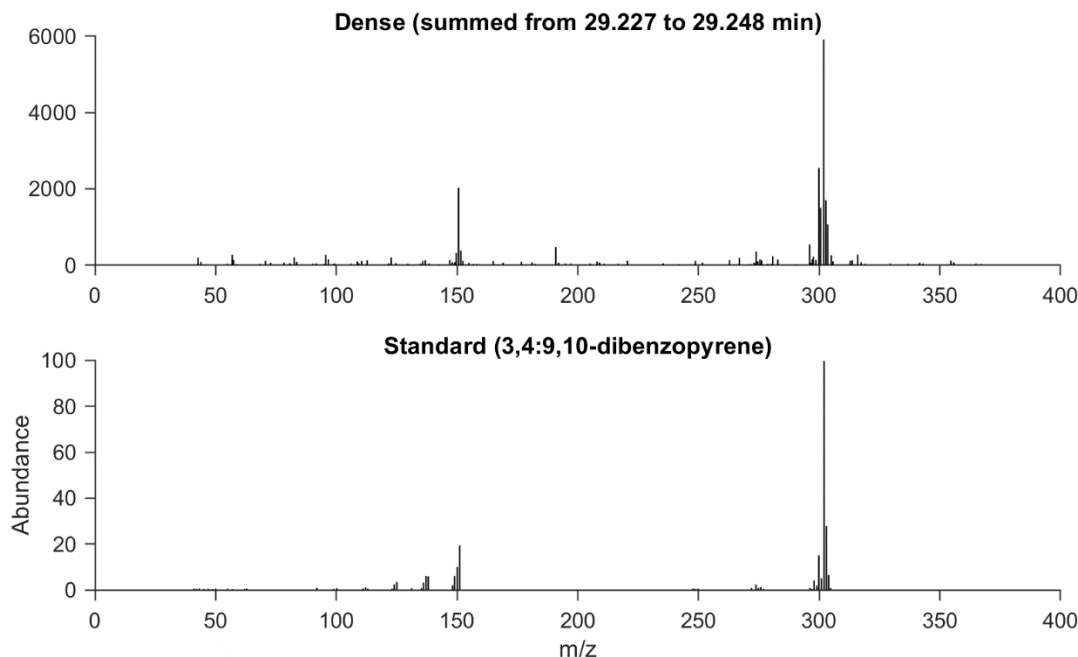


Figure 4.22. The upper spectrum shows the dense sample extracted ion spectra summed between the retention times of 29.227 to 29.248 min. The standard for 3,4:9,10-dibenzopyrene [80] shown in the bottom spectrum matches well.

The presence of PAHs in the dense layer, but not in the porous layer suggests that the dense layer formation mechanism is likely dependent on condensation of PAHs to some extent. The results by Preciado et al. [27], with extraction rates up to 80%, would suggest that condensation was the primary mechanism for formation of their dense deposits in a flat flame burner. The preliminary GCMS data collected for the Task 1 combustor deposits is not yet enough to exclude other mechanisms for dense layer formation. Further work could measure percent extractables from the dense and porous layers as a function of axial distance from the fuel-film injector to more quantitatively determine condensable fraction. Additionally, quantitative GCMS would further support the quantitative extractables data.

4.3.2 Raman Spectroscopy

Carbon allotropes are easily distinguishable by Raman spectroscopy, making it an ideal characterization technique for identifying changes in molecular structure of the carbonaceous deposits as the fuel-film progresses axially from the injector. Raman spectroscopy uses a high intensity laser to excite vibrational modes which result in Raman scattering of light. The Raman

scattered light is resolved from the much more intense Rayleigh scattered light using a holographic notch filter. Raman spectrometers are often coupled with optical microscopes to allow for chemical analysis with a spatial resolution of up to 1 μm . Graphite, diamond, fullerenes, and amorphous forms of carbon all have distinguishable peaks in Raman spectroscopy which can be used to identify short (hybridization), medium (bonding structure), and long range order (number of aromatic rings) [81,82].

The graphite Raman peaks are most relevant to the carbonaceous material formed in this study. Graphite has two main Raman peaks denoted as the G and D (also called D1) peaks at approximately 1575 cm^{-1} and 1355 cm^{-1} respectively, both of which change to varying degrees with incident laser wavelength. The G peak is an in-plane stretching mode that is present in all Raman spectra of crystalline graphite [81]. The D peak can be attributed to scattering from crystallite edges and has a strong dependence on excitation laser wavelength [83]. Spectra for single crystal graphite only feature the G peak, whereas spectra of highly disordered graphite contain both the G and D peaks.

Methods

In this study, I used a Horiba Scientific XPlora Plus Raman Microscope with a 532 nm, 9 mW Nd:YAG laser to attain Raman spectra of the carbonaceous deposits. First order spectra were taken from 300 to 2200 cm^{-1} with a 600 gr/mm grating and an x10 objective (0.25 N.A.). The focused spot size of approximately 3 μm . was considered large enough to smooth soot particle disparity yet small enough to distinguish bulk carbonaceous material types. An estimated penetration depth of approximately 100 nm was adequately large to capture a mixture of surface and bulk deposit chemistry, since the deposits were typically on the order of ones to tens of microns thick. For all data reported the laser filter, acquisition time, and accumulation were 50%, 5 s, and three respectively. The Raman microscope was calibrated with a silicon sample before collecting data to verify that it passed all internal spectrometer self-checks.

Figure 4.23 shows typical Raman spectra as a function of distance from the fuel-film injector, where site 1 was closest to the injector and site 6 was axially furthest from the injector. The spectra D peaks were normalized to one so that minute differences could be determined between the spectra of each site. Three features were evident with increasing distance from the fuel-film injector (increasing site number):

1. The ratio of D to G peak intensity increases.
2. The D peak shifts to lower wavenumbers.
3. The G peak shifts to lower wavenumbers.

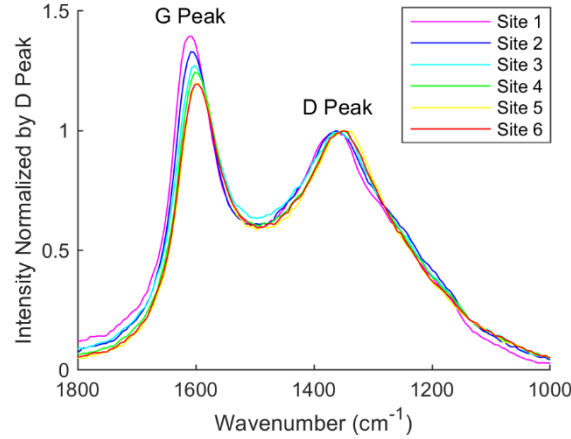


Figure 4.23. Raman spectra for test 54, upper octant B where increasing site numbers occur axially further from the fuel-film injector.

Changes in these Raman spectral features can be related to changes in the soot physical and chemical structure. The first, and most studied Raman spectral feature, is the D to G peak intensity (or area) ratio.

Planar Coherence Length

Tuinstra and Koenig (T&K) [84] correlated intensity ratio of the D and G peaks to the planar coherence length of graphite crystallites in 1970. Planar coherence length, L_a , is defined as the average crystallite size in the hexagonal sheet plane of graphitic carbon materials. T&K determined the following relationship (Equation 4.1) between planar coherence length L_a and D to G intensity ratio (I_D/I_G) for a wide variety of carbon samples with laser wavelengths of 488 and 514.5 nm, using x-ray diffraction to validate the correlation.

$$L_a(\text{\AA}) = 43.5 \left(\frac{I_D}{I_G} \right)^{-1} \quad (4.1)$$

Since 1970, several researchers have validated and improved upon the original T&K relationship. Knight and White [85] compiled Raman spectra from multiple sources to verify that they all fit the same inverse relationship to within the statistical limitations of the data. A 1996 PhD thesis by Dallas [82] describes several limitations of using the original T&K relationship,

namely the peak intensity's dependence on incident laser wavelength, possible contributions of sp^3 carbon and non-six-membered rings, and the limited region of T&K data ($I_D/I_G < 1$). Ferrari and Robertson [86] also noted the limited region of T&K data while explaining the effects of clustering of the sp^2 phase, bond disorder, presence of sp^2 rings or chains, and the sp^2/sp^3 ratio on the Raman spectra of disordered graphitic materials. They showed that amorphous carbon planar coherence lengths of less than 20 Å follow a quadratic relationship with D to G peak intensity ratio as opposed to the T&K inverse relationship for nanocrystalline graphitic carbon. Cançado et al. [87] generalized the T&K relationship as a function of excitation laser wavelength using annealed diamond-like carbon films and five different visible laser wavelengths from 457.9 to 647 nm. Their result, Equation 4.2, has a fourth order dependence on wavelength, where λ_l is the laser wavelength in nanometers. Note that the Cançado et al. wavelength-dependent coefficient does not collapse to the T&K constant coefficient of 44 Å when substituting a laser wavelength of 514.5 nm, instead it is significantly higher. Cançado et al. attribute this discrepancy to using D to G peak area instead of intensity ratio, differing x-ray diffraction instrument widths, and a narrower range of crystallite sizes. Despite the differing absolute results for planar coherence length, both T&K's and Cançado et al.'s data sets matched the general inverse trend quite well.

$$L_a (\text{Å}) = (2.4 * 10^{-9}) \lambda_l^4 \left(\frac{A_D}{A_G} \right)^{-1} \quad (\text{Error! Bookmark not defined.4.2Error! Bookmark not defined.})$$

defined.4.2Error! Bookmark not defined.)

The following analysis of planar coherence length is more concerned with qualitative trends than quantitating numbers. For this reason, I used the T&K relationship for planar coherence length shown in Equation 4.1 as opposed to the more general Cançado et al Equation 4.2. Both equations give the same qualitative information and the latter would require deconvolution of the Raman spectra to determine peak areas. Figure 4.24 compares the planar coherence lengths of carbon deposits from a baseline test, T58, with those from a 4-6-4 oxidized test, T60. The 4-6-4 test autosequence involved four seconds of monopropellant, followed by the standard six seconds of bipropellant burn time, then ending with another four seconds of monopropellant run time. The loose soot particles of the porous layer were removed from the sample surface by the final four seconds of monopropellant run time, however, the dense layer persisted. Therefore, Figure 4.24 is effectively a comparison of the planar coherence lengths of the porous and dense layers. Raman spectra taken at porous versus dense sites were distinguished qualitatively via optical microscopy

and visual inspection, where the site type refers to which layer was exposed at the sample surface. The small spot size of the laser may have resulted in some mischaracterization of the site type.

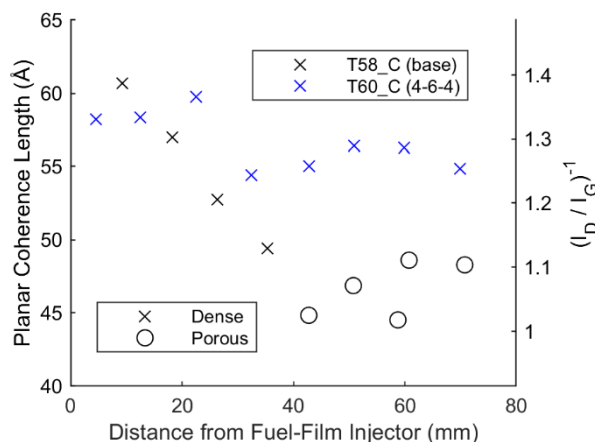


Figure 4.24. Planar coherence length as a function of axial distance from the fuel-film injector for the baseline test sample T58_C compared to an oxidized sample of T60_C.

The deposits closest to the fuel-film injector were consistently of the dense type across all tests, since soot required longer residence times to form compared to condensation of PAHs. The planar coherence length of the dense deposits closest to the fuel-film injector were consistently around 60 Å. Planar coherence length then decreased with increasing distance from the fuel-film injector, leveling off for dense and porous deposits at around 55 and 45 Å respectively. The higher planar coherence lengths of the dense deposits are likely related to the differences between the condensation of heavy PAHs versus thermophoretic diffusion of soot mechanisms. The leveling off of the planar coherence length correlates well to where the liquid fuel-film is presumed to be completely vaporized, where the vaporization process likely created large gradients in soot and condensate formation conditions. Dense layer deposit planar coherence length was relatively constant, which is likely related to the spatially constant wall temperature of the heat sink cooled combustor and low wall temperature's direct effect on the heavy PAH condensation mechanism.

Figure 4.25 shows planar coherence length measured for samples produced on different chamber liner materials, which effectively resulted in different chamber wall temperatures. Note that points with both a circle and an "X" are considered transition deposits, with both dense and porous deposits visible at the surface. All of the samples began at the 60 Å starting point since the chamber liner material was not present until after the fuel-film injection point. Planar coherence length generally decreased with increasing distance from the fuel-film injector, which is the

opposite trend of the expected increasing annealing temperature, and therefore structural order, with distance from the fuel-film injector. As the gaseous fuel-film boundary layer grows, the hot core flow gases mix and heat the fuel-rich soot production zone. I would expect this to result in higher planar coherence length with increased distance from the fuel-film injector, but the opposite was measured. The trends of both S304 and N066 were similar to each other, which is expected since the two metals have nearly identical thermophysical properties of density, specific heat, and thermal conductivity. As the fuel-film progressed axially along the chamber liner, the S304 and N066 tests had slightly lower planar coherence lengths than the C101 baseline test. The explanation for this phenomenon is not clear, since the higher soot formation temperatures of the S304/N066 tests should result in higher planar coherence lengths based on typical Raman spectroscopy of carbon literature [81]. Higher temperatures should result in more carbonization and polymerization, although the temperatures found in fuel-films are likely far too low for graphitization. Polymerization would cause an increase in planar coherence length, as the carbonized materials begin orienting into planar sheets. But the opposite trend is being shown in Figure 4.25, where the higher near-wall temperatures of S304/N066 are causing lower planar coherence lengths.

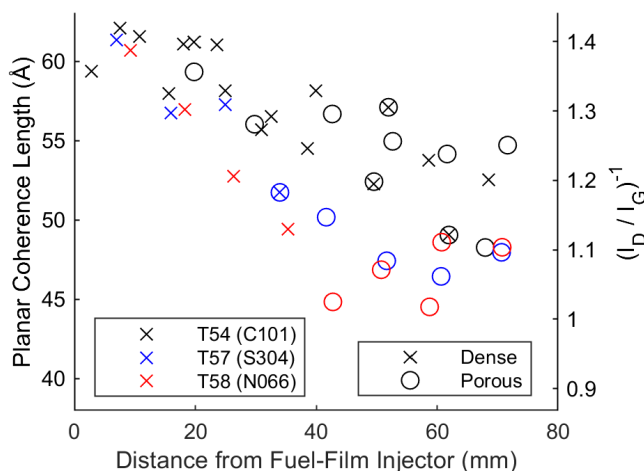


Figure 4.25. Planar coherence length trends for sample materials of oxygen-free high conductivity copper (C101), stainless steel 304 (S304), and Inconel 600 (N066).

Figure 4.26 examines the effect of bipropellant run time on planar coherence length with N066 as the chamber liner material. As with every other sample, the planar coherence length starts at 60 Å near the fuel-film injector. Planar coherence lengths for the nominal and long bipropellant

run times follow similar trends, however the porous deposits seem to have slightly lower planar coherence length than the dense deposits. The longer run time tests had thicker carbon deposits, especially in the near field region, as demonstrated in Section 4.2.1. Thicker deposits should result in higher near-wall temperatures. But again, the measured trend was higher wall temperatures causing lower planar coherence lengths.

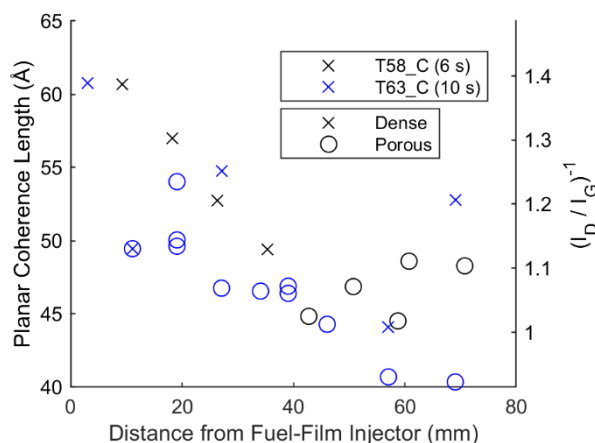


Figure 4.26. Planar coherence length trends with varying fuel types of JP-8 and RP-2.

Structural Parameter Trends via Deconvolution

The G and D (D1) bands are not the only ones that have been associated with the Raman spectra of disordered graphite. The D3 (A) band at approximately 1500 cm^{-1} has been attributed to an odd-numbered ring vibrational mode, whereas the D2 band at 1620 cm^{-1} is thought to be caused by oliphatic structures [82,88]. Dippel et al. [89,90] noted the D4 band at 1200 cm^{-1} in combustion soot, which they postulated was caused by polyene-like structures. Sadezky et al. [88] gives an overview of the five bands (G, D1, D2, D3, D4), along with guidelines for fitting Raman spectra of soot and related carbonaceous material. Table 4.2 shows the first order Raman bands of soot, as described by Sadezky et al. [88], that were used to fit Raman spectra from the Task 1 combustor.

Table 4.2. First order Raman bands of soot as described by Sadezky et al. [88].

Band Names	Location (cm^{-1})	Description
G	1580	Ideal graphitic lattice
D1, D	1350	Disordered graphitic lattice (graphene layer edges)
D2, D'	1620	Disordered graphitic lattice (surface graphene layers)
D3, D'', A	1500	Amorphous carbon
D4, I	1200	Disordered graphitic lattice, polyenes, ionic impurities

Determining the individual band contributions to the total Raman spectra requires deconvolution of the spectra. MATLAB®'s *lsqcurvefit* function was used to deconvolute Raman spectra into combinations of Lorentzian and Gaussian functions, one for each band. Sadezky et al. [88] tried various combinations of Lorentzian and Gaussian fits to determine the best band combination for fitting a wide variety of soot types. Their best fit used Lorentzians for the G, D1, D2, and D4 bands and a Gaussian for the D3 band. After trying the numerous fits attempted by Sadezky et al. [88] on the Task 1 Raman spectra, it was found that their best fit corresponded to the best fit for the Task 1 data as well. Table 4.3 shows the initial guesses, upper bounds, and lower bounds used for each bands center. The lower bounds, initial guesses, and upper bounds of the amplitude and standard deviation were 0, 1e3, 1e5 and 0, 10, ∞ respectively. Appendix E contains MATLAB® the code used to perform the fits.

Table 4.3. Fit parameters for first order Raman bands, where “L” and “G” indicate Lorentzian and Gaussian functions respectively.

Band Names	Type	Lower Bound	Initial Guess	Upper Bound
G	L	1571	1585	1600
D1, D	L	1343	1360	1375
D2, D'	L	1595	1610	1630
D3, D'', A	G	1475	1500	1525
D4, I	L	1127	1180	1250

Figure 4.27 shows a Raman spectrum collected from octant B of test 54, which has been deconvoluted into the five bands previously described. A linear background fit between 800 and 2000 cm^{-1} is shown beneath the spectrum, as well as the deconvolution fit residuals. Similar qualities of fit were achieved for all Raman spectra presented below.

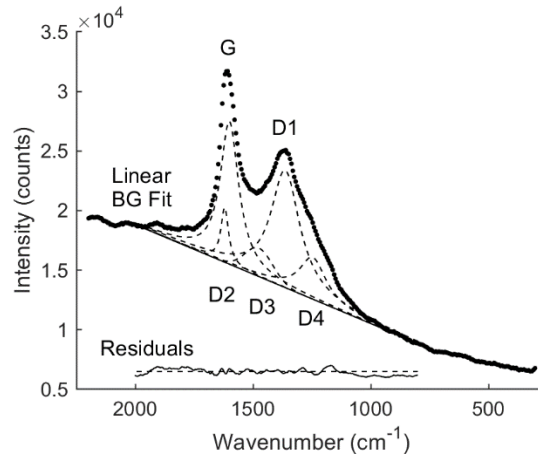


Figure 4.27. Deconvolution fit of Raman spectrum from octant B of test 54.

Several Raman bands have been correlated with microstructural aspects of carbonaceous materials, albeit to significantly lesser degrees than the T&K relationship. Gruber et al. [91] noticed the reduction in FWHM for both G and D bands with increased graphitization of carbon black, as measured by increasing annealing temperature. They also saw a slight downshift in G band position from approximately 1605 to 1595 cm^{-1} for annealing temperatures from 300 to 2600 K respectively, followed by a sudden drop to 1575 cm^{-1} at 3000 K. In contrast, the D band position was found to be relatively constant with increased annealing. Sze et al. [92] outline a theoretical approach for planar coherence length's dependence on D to G intensity ratio in graphite, relating the G band to average volume of ordered graphite crystals and the D band to the total crystal edge area, thus making their ratio approximately proportional to planar coherence length. The average graphite crystal thickness could then be similarly determined by the D2 to G intensity ratio, since they postulated that the D2 band is determined by the surface area of the crystal without accounting for its local surroundings.

As an example of a structural parameter trend, Figure 4.28 shows the G band position versus axial distance from the fuel-film injector for C101, S304, and N066 chamber liner materials. Generally, there was a slight decrease in G band position wavenumber with increasing distance from the fuel-film injector, which was correlated with increased annealing temperatures by Gruber et al. [91]. The G band position results of Figure 4.28 suggest increased annealing and graphitization with distance from the fuel-film injector, whereas the planar coherence length results of Figure 4.25 suggest the opposite. Having said that, the transition from dense deposits to porous soot is analogous to a transition from low to high temperature annealed solid carbon, which

should result in the trend shown in Figure 4.28 since more soot is present in the porous deposits further from the fuel-film injector.

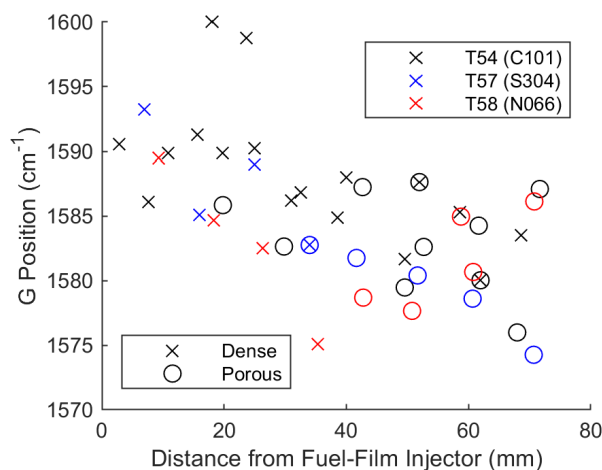


Figure 4.28. G band position structural parameter from Task 1 combustor Raman spectra deconvolution.

Table 4.4 shows changes in deconvolution parameters with axial distance in the Task 1 combustor, against expected changes in the same parameters with increased structural order as determined in literature. A typical experiment characterizing these parameters varies graphitic material annealing temperature in order to induce longer range structural order. Literature concerning the two ratios of peak areas, $R1$ and $R2$, indicate that structural order should increase with decreasing ratio parameter, however the opposite was found as a function of deposit distance from the fuel-film injector. The four parameters concerning full width half maximum (FWHM) and position, as overviewed in Gruber et al. [91], mostly correlated with the expected trend of increased annealing temperature with distance from the fuel-film injector.

Table 4.4. Comparison of expected changes in deconvolution parameters with increased structural order against results from the Task 1 combustor.

Structural Parameter	Change with Increasing Structural Order from Literature	Change with Axial Distance from Fuel-Film Injector in Task 1 Combustor
$R1 = D1/G \propto 1/L_a$	Decrease [84,85,87,92]	Increase
$R2 = D1/(G + D1 + D2)$	Decrease [93]	Increase
G band FWHM	Decrease [91]	Constant
D1 band FWHM	Decrease [91]	Decrease
G band position	Decrease [91]	Decrease
D1 band position	Constant [91]	Decrease

Overall, Raman spectroscopy of the Task 1 carbon deposits seemed to raise more questions than it answered. Planar coherence length seemed to indicate a decreasing soot production temperature as the core flow mixed into the fuel-rich gaseous boundary layer. Raman spectra of carbonaceous deposits on S304 and N066 chamber liners suggested lower soot production temperatures when the near-wall temperatures were known to be higher than the C101 chamber liner baseline case. Ratio-based structural parameters increased with distance from the fuel-film injector, whereas FWHM and position parameters decreased. However, one positive result was the measurement of constant planar coherence length for the dense deposits in Figure 4.24, which indicated a constant deposition temperature consistent with the PAH condensation mechanism.

4.3.3 X-Ray Photoelectron Spectroscopy (XPS)

XPS ejects photoelectrons from a sample surface via incident monochromatic x-rays. Kinetic energies of the emitted electrons are measured in an electron analyzer and corrected for the incident x-ray energy to calculate electron binding energy. Small chemical shifts in measured binding energies, based on the nature of nearby molecular bonds, can then be used to determine the chemical structure which caused a given spectra. XPS is a surface characterization technique due to the exponential attenuation of electrons in materials. Typical XPS measurement depths are on the order of nanometers. More information on XPS can be found in various texts [94]. The following analysis focuses on the C 1s, O 1s, and C KLL spectra collected from carbonaceous deposits produced in the Task 1 combustor.

Methods

A Kratos AXIS Ultra DLD Imaging x-ray photoelectron spectrometer was used to collect XPS surface spectra of samples from tests 38, 39, 54, and 58 as a function of axial distance from the fuel-film injector. Care was taken to select samples which had not been exposed to other post-test analysis instruments. XPS is highly sensitive to small changes in surface chemical structure and various instruments' energy sources, such as the electron beam from an SEM or the laser from a Raman microscope, could change the surface chemistry in a detectable manner. The 150 mW source used x-rays from the K α line of aluminum at 1486.7 eV. Charge neutralizer

current was set to 1.9 A to mitigate sample charging. An elliptical spot size of 400 x 600 μm with its long dimension oriented in the sample's axial direction was large enough to statistically encompass sample surface inconsistencies, such as surface roughness caused by soot particle agglomerates. Acquisition parameters used for wide and narrow spectra are shown in Table 4.5. Data analysis and deconvolution were performed in the CasaXPS program. The NIST XPS database [95] was used to determine suitable binding energies for peak deconvolution.

Table 4.5. XPS acquisition parameters for each spectra.

Spectra Type	Binding Energy Range (keV)	Resolution	Acquisition Time (min)	Sweeps	Step Size (meV)	Dwell Time (ms)
Survey	0-1350	160	11	1	1000	500
Ag 3d	360-382	20	188	16	50	1600
O 1s	525-540	20	24	3	50	1600
C 1s	276-298	20	22	2	50	1600

The XPS spectrum of silver is often used for calibration and resolution determination due to its well separated $3d_{3/2}$ and $3d_{5/2}$ peaks. Silver contamination in the Task 1 combustor came from silver-coated stainless steel screens of the hydrogen peroxide catalyst bed, where silver was the catalyst used to decompose hydrogen peroxide into hot oxygen and steam. The silver was likely present as a mixture of its metallic form and silver oxides. The high temperatures of the catalyst bed likely caused reduction of any silver oxides, but metallic silver may have been reoxidized during the shutdown transient by oxygen from the catalyst bed, resulting in an unknown mixture. Ferrara et al. [86] gives an overview of peak positions for silver and its oxides, which vary from 368.3 eV for the metal to 368.4 and 368.6 eV for Ag(I) in AgO and Ag₂O. The test 54 and 58 narrow silver spectra had Ag $3d_{5/2}$ peak positions ranging from 368.49 to 368.62 eV, with a mean value of 368.56 ± 0.04 eV for the twelve sites. There was not an identifiable trend with axial distance from the fuel-film injector, therefore the variance was attributed to changes in sample charging over the course of measurement. Peak positions were determined by using a Shirley background and the CasaXPS pseudo-Voigt *SGL(30)* symmetric line shape consisting of a linear combination of 70% Gaussian and 30% Lorentzian character. Asymmetric line shapes are often chosen for metal 3d peaks [96], however the *SGL(30)* line shape was chosen based on fitting the given Ag $3d_{5/2}$ peaks best.

Calibration for each sample consisted of shifting all spectra by the difference between each site's Ag $3d_{5/2}$ peak position and the mean Ag $3d_{5/2}$ peak position for each sample octant half

(averaged over three sites). For instance, the mean test 58 upper octant half (T58_D_u) Ag 3d_{5/2} peak position was 368.53±0.04 eV and the site 1 Ag 3d_{5/2} peak position was 368.49 eV, therefore all site 1 spectra binding energies were shifted upwards by 0.04 eV. Such small calibrations in binding energy seem trivial, but they can affect deconvolution of nearby components significantly, as will be seen in the C 1s and O 1s spectra.

Each sample octant half was a separate piece of hardware, therefore the mean peak position could not be taken over multiple octant halves without introducing errors due to differences in charging. This procedure assumed that the metallic silver and silver oxide mixture on each octant half may be different, and is best determined by the average peak position of the three sites. Calibration would be more accurate if the silver composition was better known. The maximum uncertainty of this calibration procedure is reflected in the range (0.13 eV) and standard deviation (0.04 eV) of the Ag 3d_{5/2} peak positions from the previous paragraph, since twelve sites on four different sample octant halves measured hours apart is considered a large enough sample size. The largest calibration shift was 0.04 eV for test 58 site 1, and the mean shift was 0.02 eV.

Additionally, the full width at half maximum (FWHM) of the Ag 3d_{5/2} peak for a sputter-cleaned metallic silver sample is often used as a measure of instrument resolution [97]. The silver composition on the Task 1 combustor samples was unknown, as previously mentioned. However, a mean FWHM for the twelve sites from tests 54 and 58 of 0.91±0.04 eV is reported for completeness, and gives some sense of instrument resolution.

Survey Spectra

A typical survey XPS spectrum is shown in Figure 4.29 with labeled peaks. The C KLL feature is an Auger peak that occurs at kinetic energies around 290 eV. Note that measured electron kinetic energy is equal to incident x-ray energy minus binding energy, therefore we would expect the C KLL feature to occur at a binding energy of approximately 1210 keV. The fluorine F 1s peak was likely caused by decomposition and deposition of Viton o-rings in the Task 1 combustor hydrogen peroxide catalyst bed, as evidenced by post-test visual inspection of the damaged o-rings. The silver Ag 3d peak also came from the catalyst bed, as previously mentioned. The C 1s and O 1s peaks were primarily caused by the carbonaceous deposits, and had the largest signals in all spectra taken.

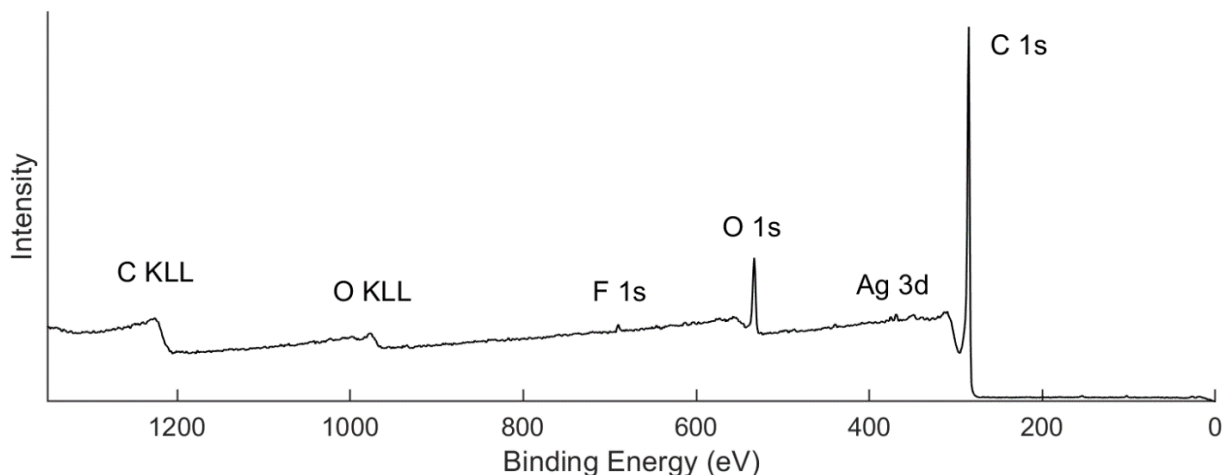


Figure 4.29. Survey XPS spectrum of the test 58, octant D, upper sample at site 2.

The ratio of peak areas from an XPS survey spectrum can be used to determine the ratio of element chemical states. Figure 4.30 shows survey spectra from multiple sites of test 58, where site 1 was just downstream of the fuel-film injector and increasing site number corresponded to increasing distance from the fuel-film injector. The O 1s peak height decreased with distance from the fuel-film injector, whereas the C 1s peak height increased. Other peaks remained fairly constant, although more fluorine was detected closer to the fuel-film injector, presumably because of the lower wall temperatures allowing for condensation of fluorine-containing compounds that formed in the core flow. Shirley backgrounds were used beneath each peak and the area was integrated numerically to more quantitatively determine elemental composition. Table 4.6 lists elemental percent compositions based on the identifiable peaks in the XPS spectra. Due to the resolution of the survey spectra, the results cannot be trusted to better accuracy than around one percent. Two of the trace element peaks, Na 1s and S 2p, were qualitatively detectable in some spectra, but their peaks were so small that they did not even amount to 0.1% elemental composition in the test 58 spectra.

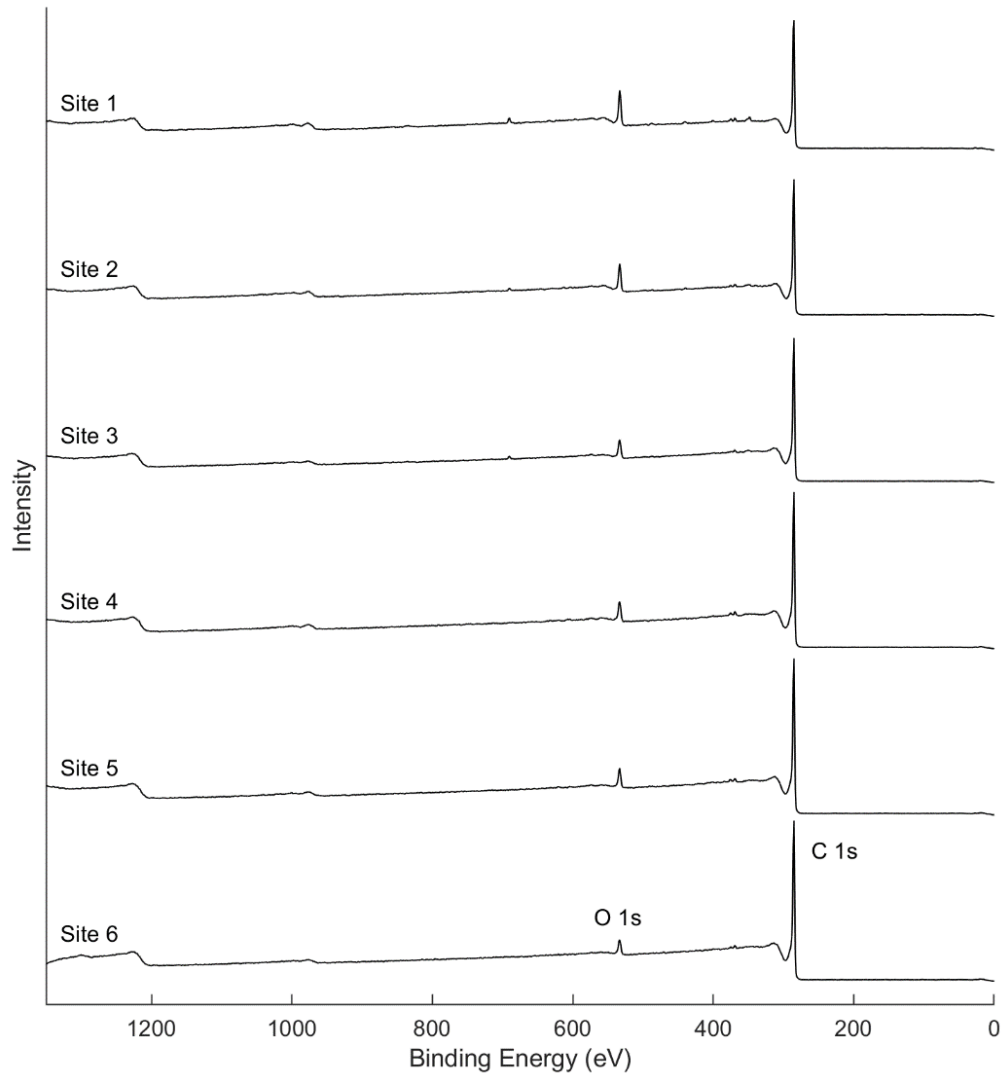


Figure 4.30. Survey spectra of test 58, octant D at multiple axial sites, where increasing site number corresponds to increasing axial distance from the fuel-film injector.

Table 4.6. Elemental compositions from test 58, octant D survey spectra as a function of axial distance from the fuel-film injector.

Site Num	Distance from Fuel-Film Injector (mm)	C 1s (%)	O 1s (%)	F 1s (%)	Na 1s (%)	Ca 2p (%)	S 2p (%)	Si 2p (%)	Ag 3d (%)	N 1s (%)
1	9.6	86.8	10.6	1.0	0	0.7	0	0.3	0.1	0.6
2	19.6	91.1	7.9	0.4	0	0.1	0	0.4	0.1	0
3	29.6	93.4	5.3	0.5	0	0.2	0	0.2	0.1	0.4
4	48.2	94.1	5.4	0.1	0	0.1	0	0.1	0.1	0.2
5	57.2	94.4	4.9	0.1	0	0.1	0	0.1	0.1	0.4
6	67.2	95.0	4.0	0.0	0	0.1	0	0.1	0.1	0.6

A decrease in oxygen content with increasing distance from the fuel-film injector can likely be attributed to the transition from dense to porous deposits exposed on the sample surface. Dense deposits condensed from heavier compounds in the fuel-film boundary layer contained more oxygen than soot formed in the fuel-rich combustion region, which was mostly dehydrogenated carbon. Saito et al. [25] also found that deposits from earlier in the flame structure had higher oxygen content when examining O 1s peaks from electron spectroscopy for chemical analysis (ESCA), which was an earlier name used for XPS. They cited the number of trapped radicals in the condensed phase, which are known to decrease with increasing environment temperature, as an explanation for the increasing carbon-to-oxygen ratio in soot as the flame progresses.

C 1s Spectra

The C 1s feature, when deconvoluted, can be used to determine carbon hybridization and bonding information. It has been thoroughly studied in XPS literature due to the wide variety of carbon allotropes. Additionally, its omnipresence in XPS samples as adventitious carbon contamination makes it a common sight in survey spectra. Figure 4.31 shows the C 1s spectra of test 58, where site positions are detailed in Table 4.6. The C 1s feature narrows and shifts to lower binding energies with increased distance from the fuel-film injector. The narrowing of the high binding energy shoulder can likely be attributed to decreasing oxygen-containing functional groups, as supported by the decreasing oxygen content evident in the survey spectra.

The shift of the primary peak position to lower binding energies is more difficult to understand, since multiple components occur within close proximity in the 284-285 eV range. Blume et al. [98] investigated the C 1s spectra of several carbon allotropes with the goal of distinguishing carbon-based components in the 284-285 eV range from carbon-oxygen-based functional group components, which typically occur as a shoulder at binding energies over 285 eV. The primary C 1s peak has been typically considered sp^2 (at 284.3 eV), sp^3 (at 284.8 eV), or some combination thereof. The sp^3 component position has been determined from diamond crystals or diamond-like-carbon films, both of which do not directly apply to the disordered carbon structures expected in soot. Instead of using a sp^3 component, Blume et al. considered disordered and defect carbon components. The disordered carbon component can be attributed to carbon without long-range order whereas defect carbon can be attributed to defects in the graphite lattice.

Blume et al. found that sp^2 , disordered, and defect carbon occurred at 284.35, 284.75, and 284 eV respectively for a variety of carbon allotropes. Note that defect and disordered carbon occur on either side of the primary sp^2 peak. [98]

The shift of the main peak position to lower binding energies can be interpreted as a shift in disorder and defects of the deposited carbon, likely related to the shift from dense to porous deposits as described in Section 4.2. It seems as though disorder and defects should increase with the transition from condensed PAHs to soot. Additionally, as the soot matures, increased carbonization and dehydrogenation should result in the formation of more graphitic soot with less disorder and defects. The former condensables-to-soot trend follows the trend of decreasing planar coherence length with distance from the fuel-film injector, as seen in Section 4.3.2, whereas the latter soot maturation trend directly conflicts the Raman results.

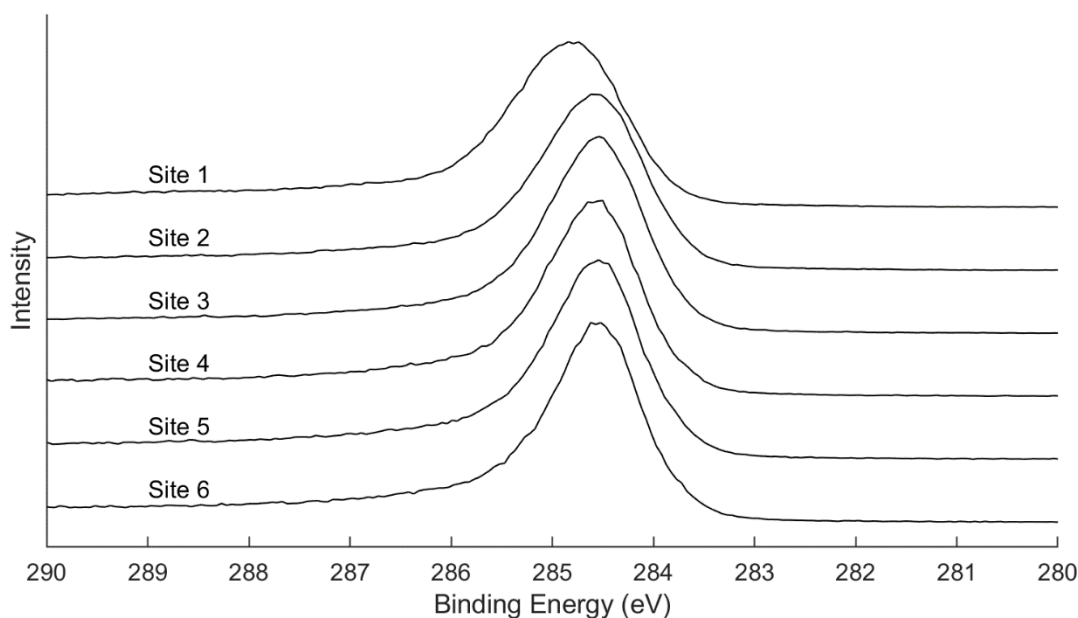


Figure 4.31. C 1s spectra for test 58, octant D, where larger site numbers were axially further from the fuel-film injector.

A satellite feature was found in test 54 sites 1 and 2, occurring in the high binding energy tail of their C 1s spectra as shown in Figure 4.32. This component, located at approximately 293.3 eV, is a shake-up feature likely due to the delocalized electrons of PAHs present near the fuel-film injector. Saito et al. [25] also noticed a PAH satellite feature in their ESCA spectra for soot. They found that the satellite feature occurred only in deposits collected from the early flame structure, which matches the axial positions found in the Task 1 combustor XPS data. Additionally,

the PAH shake-up feature was not found in the test 58 data, which had higher near-wall temperatures than test 54 since it used a N066 chamber liner as opposed to test 54's C101 chamber liner. Higher near-wall temperatures would have resulted in less condensation of PAHs, as outlined in Section 4.3.1, and the lack of a PAH shake-up feature follows. Therefore, this satellite feature is consistent with the conclusions drawn from the GCMS analysis in Section 4.3.1. Further GCMS testing on N066 and S304 samples could be completed to verify this XPS result.

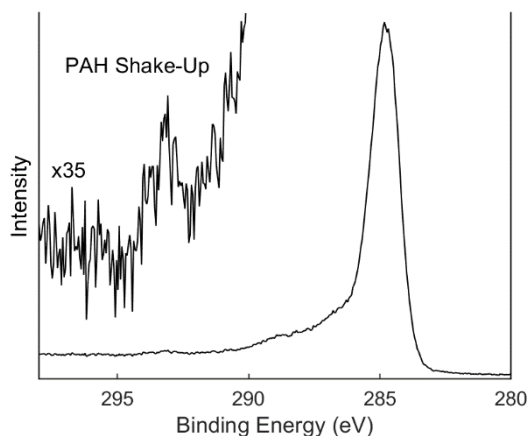


Figure 4.32. Test 54, octant D satellite feature found in site 1, which was closest to the fuel-film injector.

O 1s Spectra

In carbon-based samples, the O 1s spectra is often used to compliment information found in the high binding energy shoulder of the C 1s spectra, where oxygen-containing functional groups are found. Figure 4.33 shows the corresponding O 1s spectra to the C 1s spectra presented in Figure 4.31. Peak amplitude decreases significantly from sites near the fuel-film injector to those further away, indicating a decrease in oxygen atoms with distance from the fuel-film injector, and complimenting the survey spectra data in Figure 4.30. The primary components typically used to deconvolute O 1s spectra with carbon-oxygen bonds are the single (C-O) and double (C=O) oxygen bonds with carbon, which occur at approximately 533 and 531.75 eV respectively [95]. Asymmetry of the O 1s spectra in Figure 4.33 shifts from lower to higher binding energies with distance from the fuel-film injector, corresponding to a shift towards more singly bonded carbon. The transition towards less double bonded oxygen with carbon may be related to the change in benzoic acid (found in GCMS from Section 4.3.1.) concentration as the porous layer grows on top of the dense layer.

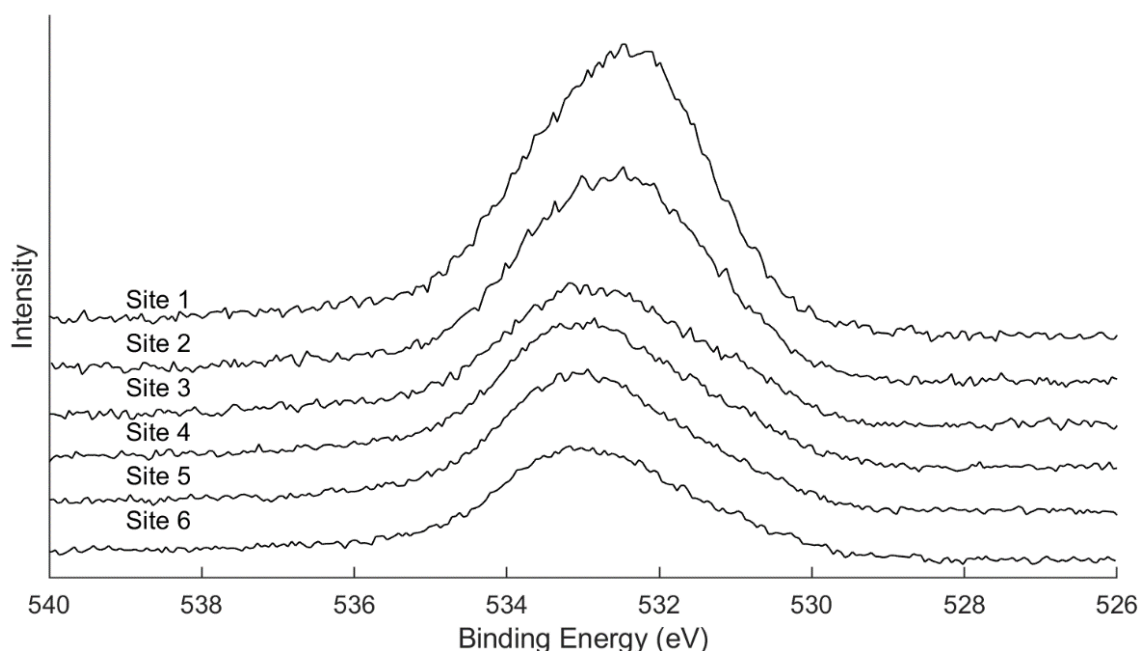


Figure 4.33. O 1s spectra for test 58, octant D, where larger site numbers were axially further from the fuel-film injector.

C KLL Spectra

X-ray photoelectron spectrometers also capture x-ray induced Auger lines in an analysis technique called x-ray induced Auger electron spectroscopy (XAES). Auger electrons are ejected from an atom when an inner shell vacancy is filled by an outer shell electron. The kinetic energy of the emitted electron is independent of incident x-ray energy, therefore Auger lines are best viewed with kinetic energy as the independent variable, as opposed to binding energy which is used for XPS peaks. The carbon C KLL Auger line is caused by emission of an electron in the L shell of a carbon atom when a different L shell electron drops down to fill a K shell vacancy. The K shell vacancy would have been caused by the incident x-rays, and would be detectable as the C 1s XPS peak. Auger electron spectroscopy (AES) uses electron radiation to induce emission of Auger electrons, whereas XAES uses x-ray radiation. AES causes more surface damage than XAES due to the higher mass of electrons compared to photons.

Carbon of sp^2 and sp^3 hybridization can be difficult to distinguish in the C 1s spectra due to their close proximity of approximately 1 eV. In contrast, the carbon KLL Auger line energy separation is on the order of 10 eV. Mizokawa et al. [99] compared first derivative XAES spectra to AES spectra, noting similar C KLL structures for diamond-like-carbon films, graphite, and

β -SiC. Due to the similarity in results, XAES could be used in place of AES such that less sample degradation would occur. They found that the highest-to-lowest peak width with increasing kinetic energy for the C KLL feature was broader for graphite (23 eV) than diamond-like-carbon (14 eV) and SiC (10 eV). Most notably, the width was the same in all samples for both XAES and AES, despite a slightly different peak structure. Lascovich et al. [100,101] compared XPS and XAES features for the determination of graphite, diamond, and amorphous carbon samples, noting that the presence of oxygen can also vary the characteristic feature width. They linearly interpolated between the graphite and diamond widths to approximate amorphous carbon film sp^2 to sp^3 ratio. The larger feature sizes of the C KLL line allow for determination of carbon hybridization with lower instrument resolution requirements.

XAES narrow scans of Task 1 combustor samples were not performed at the time of data collection, therefore the survey spectra were used despite their low resolution. A five-point Savitzky-Golay filter quadratic polynomial derivative function was used to convert the $N(E)$ spectra into $dN(E)/dE$ spectra. Typical high-to-low peak excursions were approximately 20 eV, as demonstrated by the spectra in Figure 4.34. The low resolution of the survey scans precluded further conclusions from being drawn. Suggested future work includes high resolution scans of the C KLL feature to definitively refute the presence of sp^3 carbon.

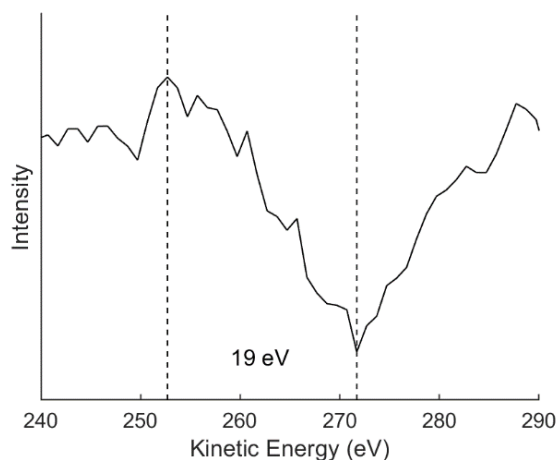


Figure 4.34. First derivative XAES spectrum of carbonaceous deposits at test 58, octant D, site 6.

4.3.4 X-Ray Diffraction

An x-ray diffractometer measures the scattering pattern of a sample's crystallographic structure by irradiating it with x-rays. The angle between the source and detector is varied to measure the change in intensity with included angle based on Bragg's law.

Dikio [102] gives XRD patterns for soot-like carbon from kerosene combustion at atmospheric pressure. Figure 4.35 shows data collected from the Task 1 combustor. The wide peak at approximately 23° can be attributed to mostly amorphous carbon, typical of soot. At approximately 45° , a copper peak overshadows a secondary carbon peak due to the prevalence of copper in the examined sample area. The x-ray diffractometer's penetration depth was significantly larger than the carbon layer thickness due to the carbon's low density, thus preventing examination of only the carbonaceous deposits. Additionally, the XRD's alignment procedure precluded axial site selection on a given sample, likely because it has a significantly large spot width (typically 10 to 20 mm). Deposits could have been scraped from the sample surface for analysis as powders at the cost of destroying any longer-range order and anisotropies. Neither of these would have been expected in the dense nor porous layers, however, x-ray diffraction was not pursued further due to more relative success with GCMS, Raman spectroscopy, and XPS.

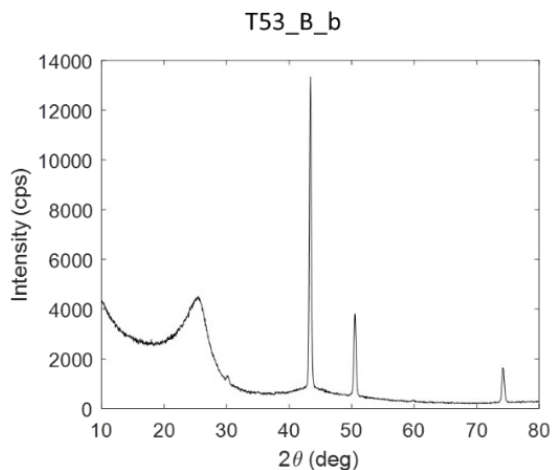


Figure 4.35. XRD data from the C101 substrate, lower octant half of test 53, octant B.

4.4 Thermophysical Properties

Thermophysical property measurements are necessary for accurate modeling of the carbon deposition process. Due to differences in chemical and physical structure, we can expect the dense

and porous deposits to have different properties. Therefore, all relevant measurements were attempted on both deposit layers where possible.

4.4.1 Density

The heat diffusion equation depends on thermal diffusivity and conductivity in its transient and steady forms. Thermal diffusivity is inversely proportional to density and thermal conductivity can have a density dependence, typically decreasing with lower density.

Density can be quantified in several different manners for powders and other materials with voids. Absolute density excludes the volume of both closed and open pores, and can be thought of as a measure of the density of only the solid portion of the powder. Envelope density includes the pore volume, and is therefore always lower in value compared to absolute density.

Graphite has a theoretical single-crystal density of 2266 kg/m^3 , however typical engineering graphite has a density of around 1800 kg/m^3 due to its small crystallite size [103]. Soot agglomerate effective density from diesel engine exhaust was measured by Park et al. [104], with values ranging from 300 to 1600 kg/m^3 . Larger agglomerate mobility diameters resulted in lower effective densities. Note that effective density is not the same as apparent or envelope density.

A Micromeritics AccuPyc II 1340 pycnometer was used with helium to determine the absolute density of porous and dense carbon deposit powder samples. The pycnometer 3.5 cm^3 sample cup was calibrated with a metal sphere standard, as per the operator manual [105]. Sample collection involved lightly scraping porous deposits from octant halves, requiring four or more octant halves to get enough volume for analysis. The dense deposits could not be removed in sufficient volume for gas pycnometry analysis.

In-situ envelope density, which accounted for porous volumes, was determined by measuring layer mass and layer volume. Layer mass was measured gravimetrically by progressively cleaning the porous and dense layers off of each octant half. Light cleaning with isopropyl alcohol removed the porous layer while leaving the dense layer mostly intact. However, the distinction between dense and porous layer can often be ambiguous, even when imaging with the SEM. For instance, some dense layer SEM cross sections showed multiple dense layers with air gaps between them, which would manifest as a lower total density when integrated across the entire sample surface area (see Figure 4.13). The more tenacious dense layer was removed by

ultrasonic cleaning in Ensolv®, a n-propyl bromide solvent, for 60 minutes. Layer depth was measured by integrating scanning electron microscopy (SEM) and optical profilometry depth measurements as a function of axial distance from the fuel-film injector. Layer volume could then be calculated by measuring the sample surface area and assuming an axisymmetric deposition profile. The porous layer volume was calculated by subtracting the dense layer volume (measured with SEM) from the total volume (measured with profilometer). The largest uncertainties in this analysis were likely from sample sectioning, porous layer cleaning, and the axisymmetric deposition profile assumption.

Apparent density measurements from tests 40, 58, and 63 resulted in similar values to those expected for engineering graphite, as shown in Table 4.7. Apparent and envelope densities of the porous and dense layers were approximately constant across tests 57, 58, 60, and 63. Test 60 apparent density likely isn't comparable with tests 57, 60, and 63 because the 4-6-4 test structure, with its four second monopropellant firing occurring after bipropellant shutdown, likely resulted in the removal of the dense layer transition to the porous layer more effectively than a light isopropyl alcohol cleaning. Similar data precision was noted for both the porous and dense layer envelope densities after neglecting T60. Dense layer envelope densities approached the apparent density of the porous layer, where the deviation occurred due to the dense-porous transition region and intra-dense-layer air gaps. The porous layer was almost an order of magnitude less dense than the dense layer, and is therefore expected to be the primary contributor to thermal insulation.

Table 4.7. Apparent and envelope densities of Task 1 combustor carbonaceous deposits. Test 60 used a 4-6-4 test autosequence (see Appendix A) and did not match data from the other tests.

Test Number	Porous Layer Apparent Density (kg/m³)	Dense Layer Envelope Density (kg/m³)	Porous Layer Envelope Density (kg/m³)
40	1929	-	-
57	-	1336	202
58	1935	1639	244
60	-	1835	172
63	1874	1419	203

4.4.2 Specific Heat

Measurement of carbonaceous deposit specific heat via powder samples was unsuccessfully attempted using differential scanning calorimetry (DSC) with a sapphire calibration standard. The primary issue was instrument age. The PerkinElmer Jade DSC did not produce repeatable results, even for the calibration standard. An additional issue, had I gotten far enough, would have been the difference in sample type between the calibration standard (crystalline) and sample (powder). Literature has covered measurement of soot specific heat, with results typically within 10% of engineering graphite [106].

4.4.3 Thermal Conductivity and Diffusivity

From an experimental point of view, thermal conductivity and diffusivity are typically measured in steady and transient systems respectively. In terms of carbonaceous deposits, thermal conductivity is the more useful measurement since ORSC engines can be considered quasi-steady-state thermal devices for the majority of their operation time. Unfortunately, both thermal conductivity and diffusivity were difficult to measure primarily due to the micron depth scale of the Task 1 combustor deposits. The following measurement techniques were attempted on Task 1 deposits: laser flash analysis, time-domain thermoreflectance, modulated differential scanning calorimetry, infrared microscopy. Only infrared microscope measurements of thermal conductivity were successful, albeit with carbon deposit samples not from the Task 1 combustor. While what follows is not my work, the results are included due to their relevance to the topic.

Infrared images were captured with a high resolution (1.7 $\mu\text{m}/\text{pixel}$) infrared microscope to measure thermal conductivity from carbonaceous deposit samples from a high-pressure fuel-rich gas generator environment. The approximately millimeter sized chunks were cast in polydimethylsiloxane (PDMS) which was allowed to set before grinding to a rectangular prism shape. The PDMS/carbon sample was then placed between two aluminum plates (see Figure 4.36) which acted as constant temperature boundary conditions for a steady-state 1D heat diffusion problem. The hot-side aluminum plate was attached to an electric heater and the cold-side aluminum plate was convection cooled. An emissivity calibration was performed at a reference temperature of 60°C. Temperature distributions were imaged after reaching steady-state, and at two different heater power levels in order to verify acceptable precision.

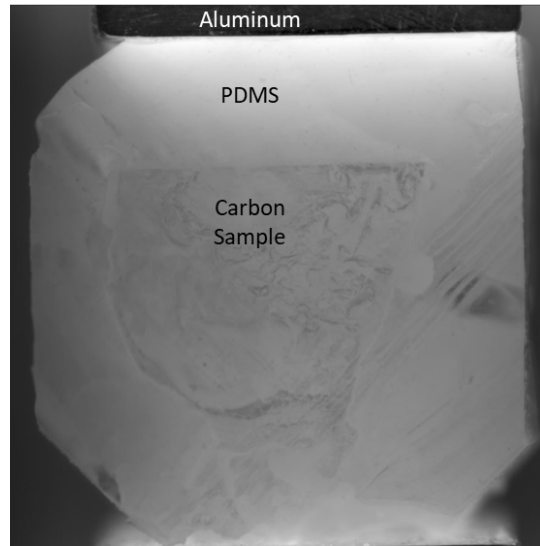


Figure 4.36. Carbonaceous deposit sample embedded in PDMS, sandwiched between two aluminum blocks (only top one shown).

Figure 4.37 shows typical temperature data obtained from the infrared microscope using hot and cold temperatures of approximately 80 and 60°C respectively. Sample thermal conductivity was measured using a 1D steady-state heat diffusion equation model, where heat flux was determined by direct comparison with the PDMS reference. A PDMS thermal conductivity of 0.15 W/m-K was used for the given temperature range [107]. Uncertainty due to the emissivity calibration was approximated by running the experiment at multiple temperatures. Where possible, measurements were taken at multiple sites to confirm reference and sample thermal gradients.

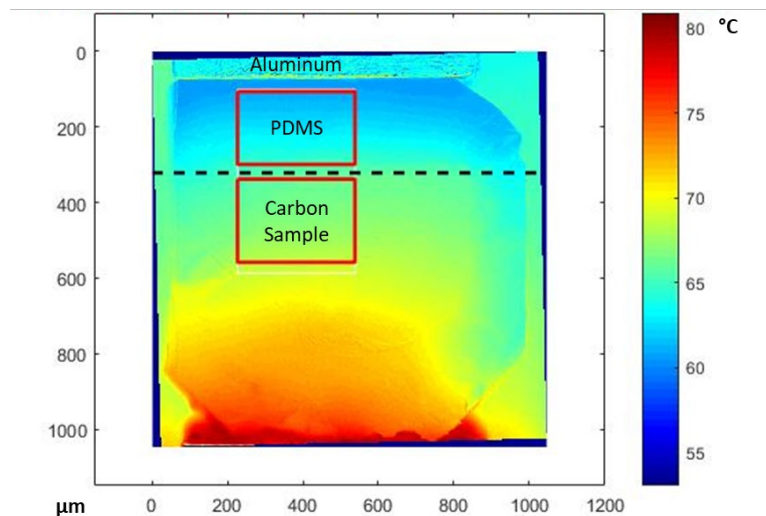


Figure 4.37. 2D temperature map of the PDMS-encased carbon sample shown in Figure 4.36. Red rectangles indicate the regions used for thermal conductivity determination.

Measured thermal conductivity values ranged from 0.2 to 1.1 W/m-K depending on the sample, with relative uncertainties of approximately 10%. The gas generator samples most closely resembled the dense deposits from the Task 1 combustor. They were solid carbon chunks, similar to graphite albeit with less strength, that had been chipped away from the metal substrate on which they were formed.

4.4.4 Emissivity

The infrared microscope from Section 4.4.3 was used in conjunction with a temperature-controlled stage to measure two-dimensional emissivity profiles of carbon deposits in the infrared wavelength region. The emissivity profile is particularly useful for high fidelity CFD models since radiative heat emission is proportional to the emissivity of a surface, which can increase drastically when a polished metal surface is covered in black carbon deposits. Figure 4.38 shows a virgin copper sample on the left and a carbon-covered copper sample from test 35 on the right for a sample temperature of 40°C. Small emissivity changes from the peaks and valleys of the lathe boring bar are visible in the left image, where the mean emissivity of the sample surface is approximately 0.2. The rightmost point of the image on the right of Figure 4.38 is where the fuel-film was radially injected onto the sample. Note the transition from an emissivity of approximately 0.45 to 0.65 as the carbon depth increases from right to left. Approximately 6 mm (0.24 inch) downstream of the fuel film injection point, the emissivity was nearly constant at 0.65, since increasing the carbon depth past a few microns does not affect the surface emissivity.

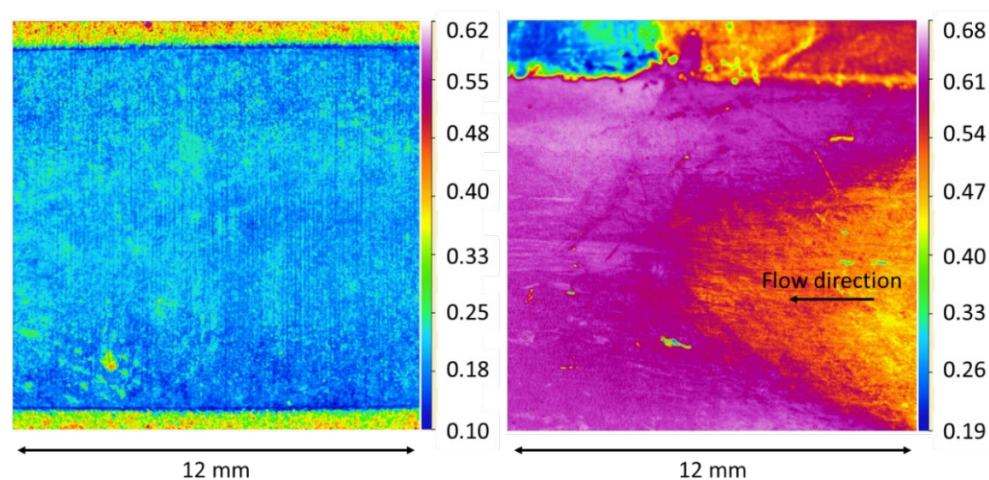


Figure 4.38. Emissivity of a bored copper sample (left) versus carbon deposits on a copper substrate from test 35 (right).

5. TASK 4 COMBUSTOR

The Task 4 combustor, also known as the fuel-film oxygen-kerosene carbonaceous deposit combustor (FFOKCDC), was a logical next step based on the shortcomings of the Task 1 combustor. Its primary goal is to obtain deposit samples similar to those of the Task 1 combustor, but at conditions more relevant to ORSC, all while maintaining axisymmetry to enable rapid CFD validation for carbon deposition model building.

5.1 Requirements

The following set of requirements was developed for FFOKCDC based on the successes and shortcomings of the Task 1 combustor:

1. The propellants will be gaseous oxygen and kerosene to obtain representative adiabatic flame temperatures and combustion chamber species.
2. The maximum chamber pressure will be 20.7 MPa (3000 psia) to match chamber pressures expected in ORSC engines.
3. The design mixture ratio will maximize specific impulse at each chamber pressure to match the conditions expected with changing chamber pressure (throttling).
4. The sample will be easily removable from the combustor.
5. The sample shape will be sized appropriately for instruments used in post-test analysis of the Task 1 combustor samples.
6. The combustor will operate at a mass, momentum, and energy steady-state with short startup and shutdown transients.
7. The combustor will have a contraction ratio representative of ORSC engines.
8. The combustor will be axisymmetric with well-defined inlet and outlet mass, momentum, and energy boundary conditions.
9. The fuel-film will be injected downstream of the injector face to allow for appropriate mixing and boundary layer development.
10. The combustor will be designed for compatibility with the ZL1 108A test cell for low pressure testing (up to 1500 psia) and ZL3 rocket cell for high pressure testing (up to 3000 psia).

The following conditions will be varied to determine their effect on carbon deposition:

1. Chamber pressure at constant contraction ratio by adjusting mass flow rates with the same throat diameter nozzle (three set points).
2. Contraction ratio at constant chamber pressure by changing the nozzle throat diameter and adjusting mass flow rates to compensate (two set points).
3. Core flow mixture ratio at constant chamber pressure and contraction ratio by adjusting the main injector fuel flow rate.
4. Fuel olefin and aromatic content by using JP-8 and RP-2.
5. Sample wall temperature by changing coolant mass flow rate.
6. Sample surface roughness by roughing and smoothing finishing procedures.
7. Oxidizer injection temperature.
8. Fuel-film injection temperature.

5.2 Design

The requirements and variables from the previous section significantly limited the design space of FFOKCDC. The most limiting requirements pertained to CFD validation. Maintaining axisymmetry and well-defined boundary conditions through ignition transients and steady-state was a difficult problem to solve. The extreme cooling requirements of such a small combustor compounded the design problems, requiring careful dimensioning and tolerancing of cooling jacket parts. FFOKCDC was designed with modularity in mind. Multiple chamber pressure and contraction ratio set points can be achieved with the replacement of only one or two parts. The chamber can be lengthened or shortened with modular water-cooled calorimeter segments. Even the film injector is modular, such that multiple axial film injection points can be used to establish the effect of the gaseous boundary layer of an upstream film injector on the liquid injection of a downstream film injector.

A cross section of the FFOKCDC hardware is shown in Figure 5.1. Stainless steel, brass (UNS C36000), and copper (UNS C10100) parts are displayed in gray, yellow, and orange respectively. The stainless steel parts are mostly of the free-machining variety (UNS S30300), except for a few film injector parts which needed to be brazed, and were therefore UNS S30400. A yttria (Y_2O_3) coating, as shown in bluish-gray, was applied to parts that would experience the highest heat fluxes, namely those between the main injector and the first fuel-film injector. The

small black annulus located just upstream of the main nozzle converging section is a graphite gasket thermal expansion joint, which used Grafoil purchased from McMaster-Carr.

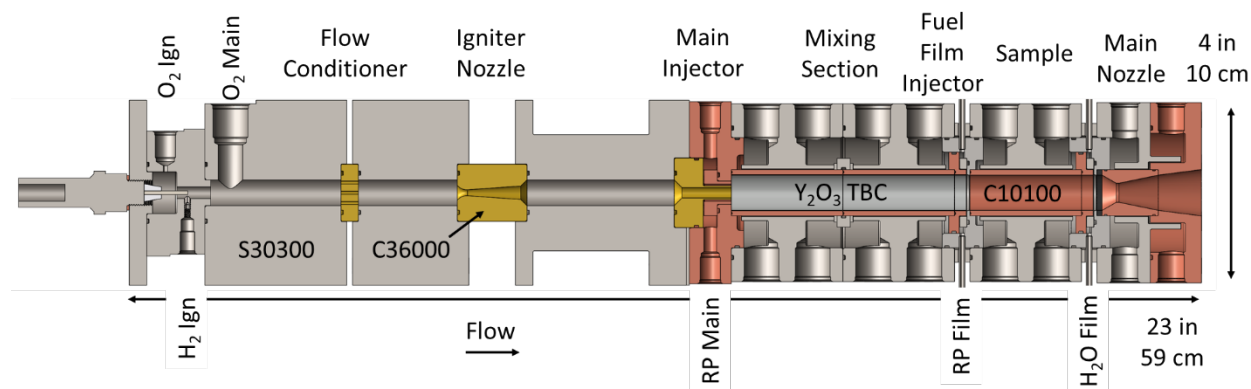


Figure 5.1. FFOKCDC cross section with annotated parts and fluid inlets.

The requirement for an axisymmetric flow domain with well-defined boundary conditions drove the design of FFOKCDC. The principle design feature of FFOKCDC is that the igniter nozzle also acts as the O₂ sonic nozzle used for mass flow rate measurement. The igniter nozzle can then act as a CFD boundary condition for the axisymmetric flow domain downstream of it. An orifice plate between the igniter and the igniter nozzle helps straighten the flow before this boundary condition. The main injector is an inverted (compared to typical ORSC swirl elements) shear coaxial element, where the oxidizer is on the inside and the fuel is on the outside. Injector choice was driven by introducing the igniter and main oxidizer to the combustor in an axisymmetric manner. Modular calorimetric chambers cooled by water house copper chamber liners, some of which have the option of being coated with a yttria thermal barrier coating. Multiple film injectors can be placed between chamber segments, allowing for the introduction of kerosene or water films. A film injector is situated just upstream of the nozzle, which is cooled both internally and externally by water. Lastly, a conical converging-diverging copper nozzle expands the flow to near-atmospheric conditions. Due to the much higher temperatures expected in the inner chamber liner than the outer calorimetric chamber segments, a graphite gasket introduces some compliance into the inner structural stackup to allow for thermal expansion.

Table 5.1 details the startup transient, which goes through the following states in the given order before reaching nominal operating conditions: double ignition, igniter off, O₂ ramp, H₂+fuel. Double ignition occurs in both the igniter and the main chamber at the same time using O₂-H₂ propellants, where the igniter operates oxygen-rich and the combustor operates fuel-rich. At this

point, the combustor main injector is flowing hydrogen through the same fuel manifold that will eventually be flowing kerosene. Then the igniter is turned off by stopping the igniter hydrogen mass flow rate, while the main combustor stays lit at a fuel-rich condition with hydrogen. The oxygen flow through the igniter nozzle, which doubles as the oxygen sonic nozzle, is ramped up significantly thus changing the combustor fuel-rich flame to an oxygen-rich flame. The fuel main run valve is opened in the H₂+fuel state, which quickly transitions to the nominal conditions after the hydrogen main run valve is turned off. Ideally, the H₂+fuel state will be kept as short as possible due to concerns about instabilities with the injection of a two-phase mixture. The feed system was designed for main oxygen and main kerosene mass flow rate ramps in case the combustor encountered flame holding difficulties in the O₂ ramp and H₂+fuel states.

Table 5.1. Expected mass flow rates, chamber pressures, mixture ratios, and run times for states in the FFOKCDC startup sequence for the low pressure, low contraction ratio arrangement. Pressures were calculated from NASA's CEA [57]. Film coolant flows were neglected in pressure and mixture ratio calculations.

State	Double Ignition	Igniter Off	O ₂ Ramp	H ₂ +Fuel	Nominal
$\dot{m}_{O_2,ign}$ (g/s)	10	10	-	-	-
$\dot{m}_{H_2,ign}$ (g/s)	0.13	-	-	-	-
$\dot{m}_{O_2,main}$ (g/s)	-	-	75	75	75
$\dot{m}_{H_2,main}$ (g/s)	1.88	1.88	1.88	1.88	-
$\dot{m}_{fu,main}$ (g/s)	-	-	-	31.9	31.9
$\dot{m}_{fu,film}$ (g/s)	-	-	-	24.5	24.5
$\dot{m}_{H_2O,film}$ (g/s)	28	28	28	28	28
P_{ign} (psia)	178	-	-	-	-
P_{main} (psia)	81	80	179	341	321
O/F_{ign}	75	∞	∞	∞	∞
O/F_{main}	4.98	5.33	40.0	2.22	2.35
Time (s)	up to 2	0.5	2	0.5	up to 40

Appendix F tabulates the run conditions for the low, medium, and high pressures of the low and high contraction ratio combustor arrangements respectively. Contraction ratio was adjusted by changing the main and igniter nozzles, whereas chamber pressure was changed by adjusting mass flow rates. Gaseous propellants required no injection geometry changes for mass flow rate changes since injector pressure drop increased proportionally with chamber pressure. On the other hand, the square root of liquid injector pressure drop increases proportionally with chamber pressure as mass flow rate increases with a constant throat area, requiring hardware changes. The medium and high pressure set points of the low contraction ratio hardware arrangement matched the low and medium pressure set points of the high contraction ratio arrangement. The high contraction ratio value was matched to the Task 1 combustor value of 6.8, such that carbonaceous deposit comparisons between combustors could be considered more valid. Additionally, the low and medium pressures of the high and low contraction ratio arrangements respectively were designed to match the Task 1 combustor chamber pressure for the same reason of comparison. A typical autosequence for FFOKCDC, as proven by qualification testing, is shown in Appendix G.

Figure 5.2 shows the long chamber, dual film injector hardware configuration of FFOKCDC. Fluids have two inlets on either side of the combustor to more equally distribute propellant and coolant in their respective manifolds. An additional benefit of the dual inlet geometry is a simplification of combustor installation on the test stand, especially given the many hardware configurations of FFOKCDC which require inlets at different axial levels.

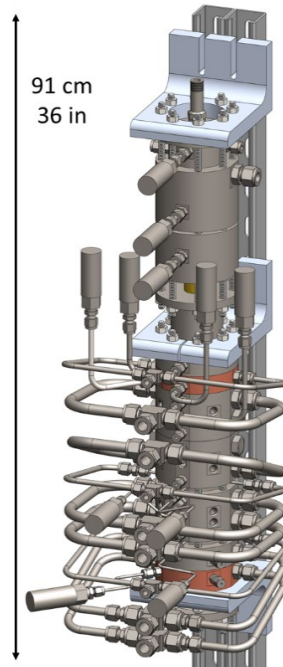


Figure 5.2. FFOK CDC CAD with propellant and coolant inlet tubes.

5.2.1 Igniter

A hydrogen-oxygen torch igniter was selected for FFOK CDC due to its simplicity and familiarity. The FFOK CDC startup transient was considered complicated enough without having to contend with ignition issues from an unfamiliar ignition source. Additionally, a choked torch igniter could be designed for axisymmetry downstream of its throat, which could then be taken as the inlet boundary condition for the main combustor, as previously explained.

The Repas [108] hydrogen-oxygen torch igniter design often acts as a starting point for torch design due to its availability online. Repas used an oxygen-rich main chamber with an annular hydrogen cooling flow that, when mixed with the oxygen-rich core flow, transitioned the torch exhaust to near-stoichiometric combustion. The torch tube which connects the igniter chamber to the main combustion chamber had no well-defined throat, and was therefore near-sonic throughout its entirety. While relatively simple in terms of part count, the Repas design suffers from several expensive design choices:

- High precision machining is required for the torch tube.
- The torch tube must be electron-beam welded to the igniter main chamber.
- Metal o-rings are used to seal between parts.
- The Champion surface gap spark plug can cost thousands of dollars each.

Zucrow Laboratories at Purdue University gained considerable experience with hydrogen-oxygen torch igniters during the Hydrogen-Oxygen Multi-Element Experiment (HOMEE) project. An igniter design and operation manual was written by Helderman [109] to document the experience. The Repas igniter design was manufactured and tested with some success, however, some hardware damage occasionally occurred when the metal o-rings were seated improperly. A new design improved upon the Repas design by using a low-cost furnace igniter (Auburn SI-140) and radially injecting hydrogen downstream of the oxygen inlet to prevent combustion in uncooled portions of the igniter. It is unclear whether the flame was intended to be held beneath the spark plug electrode, where the main hydrogen was injected, or downstream of the hydrogen coolant flow, where stoichiometric conditions existed (if considered well-mixed). This igniter had no throat, therefore the hydrogen-cooled torch tube would operate near sonic velocity, similarly to the Repas design. Zucrow Lab's more recent designs (not detailed) have adjustable spark gaps, among other improvements to the HOMEE igniter design [110].

As a final note on igniter literature, some design inspiration was taken from a NASA presentation by Marshall [111] on igniter systems for methane engines. The primary takeaway was that the spark igniter could be used in what was termed a "plasma-assist" mode, where it ionized pure oxygen which would then ignite a fuel once mixed further downstream. This presentation also contained several references to other NASA igniter work, although most of it concerned the main combustion chambers that the igniters were used to light.

A CAD cross section of the FFOKCDC igniter is shown in Figure 5.3 without the downstream flow conditioner and igniter nozzle, both of which were already shown in Figure 5.1. The igniter nominally operates at a mixture ratio of 75, with chamber pressures of 1.23 and 2.41 MPa (178 and 349 psia) for the low and high contraction ratio arrangements respectively. Similar to the Helderman design, oxygen is injected upstream of the spark location whereas hydrogen is injected just at or downstream of it. The Auburn SI-140 furnace spark igniter was used due to its low cost compared to Champion spark plug alternatives. The SI-140 has been used at Purdue extensively due to its low cost, although its primary drawback is that the ceramic sheath can crack when testing at higher pressures (3-5 ksi) and when exposed to high temperatures [110]. The spark gap was placed between the Auburn flame rod and an adjustable set screw, where the primary hydrogen flow was radially injected through a hole in the latter. A second "jam" set screw was used to preload threads of the spark gap set screw such that it did not move during tests. No

secondary hydrogen coolant flow was deemed necessary because this injector only needed to ignite a relatively low-pressure hydrogen-oxygen flow in the main combustion chamber, which was one of the perks of the convoluted FFOKCDC startup sequence. The majority of the igniter was machined from free-machining stainless steel (UNS S30300) to reduce manufacturing costs.

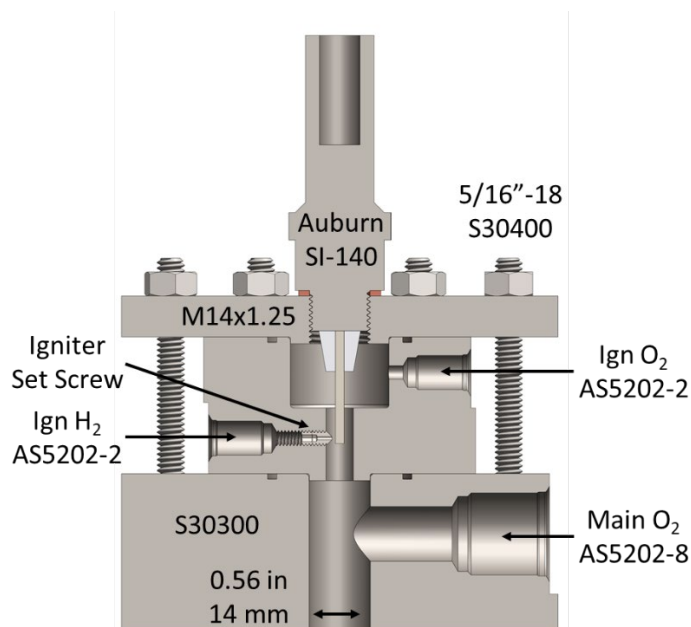


Figure 5.3. Igniter injector CAD cross section view.

The ignition sequence started with mass flow rate limited nitrogen purges through the igniter O₂, igniter H₂, and main O₂ inlets. The igniter was started oxygen-rich by opening the igniter O₂ run valve first. Next the spark was turned on, followed by injection of hydrogen through the spark gap set screw. Once ignition occurred, the flame anchored at the recirculating step just downstream of the hydrogen injection point. The igniter H₂ manifold was briefly purged with nitrogen, after which oxygen was allowed to backflow up to the igniter H₂ check valve, and should that fail, closed run valve. A downstream nozzle choked the igniter flow, thus reducing upstream Mach numbers and heat transfer considerably. The heat sink cooled igniter nozzle was manufactured from free-machining brass (UNS C36000) for a combination of inexpensive manufacturing, oxygen ignition resistance, and heat transfer properties. See the autosequence in Appendix G for more details on igniter timings.

Modeling of spark gap breakdown voltage was deemed largely unnecessary due to the low-pressure design of the igniter and adjustability of the spark gap set screw. Higher pressure igniters have higher pre-ignition cold flow pressures, resulting in larger breakdown voltages and

the need for higher voltage sparking electronics. The low and high contraction ratio igniter cold flow chamber pressures were expected to be 0.77 and 1.52 MPa (112 and 221 psia) respectively. Back-of-the-napkin breakdown voltage calculations were enough to confirm considerable safety factor in necessary spark gap lengths, with Paschen's Law adjustments based on Nugent's dissertation [112] on breakdown voltages at typical rocket igniter conditions.

A 1D, radial, transient heat diffusion equation model confirmed operability of the igniter for up to 2 seconds, where the highest temperatures occurred in the brass igniter throat as shown in Figure 5.4. Hot gas side heat transfer coefficients were calculated from the Dittus-Boelter equation [59] using properties calculated from NASA's CEA [57] and the cool side was considered adiabatic. Additional heat transfer calculations were completed to confirm adequate cooling of the flow conditioning orifice plate and igniter nozzle after the igniter turned off such that they did not affect main O₂ mass flow rate measurements through the sonic nozzle.

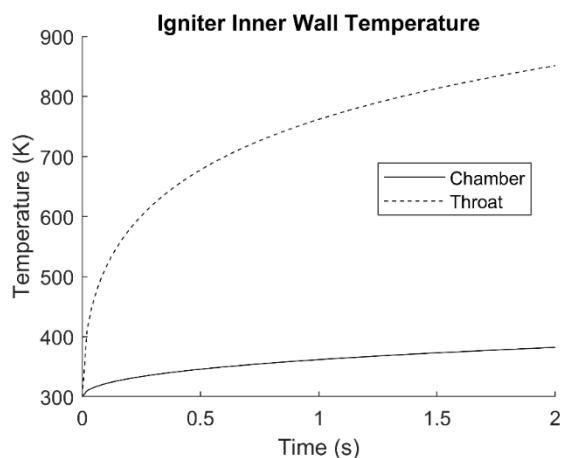


Figure 5.4. Igniter 1D, radial, transient heat transfer results.

Chamber pressure measurements were taken at the following locations: in the O₂ manifold, upstream of the orifice plate, upstream of the sonic nozzle, and downstream of the sonic nozzle. Square-edged orifices were used to limit mass flow rate for the igniter oxygen and hydrogen streams. While square-edged orifices cannot be operated in a choked mode like sonic nozzles [113], they were assumed to operate as such with a discharge coefficient of 0.6 for simplicity. The hydrogen mass flow rate was so low that a sonic nozzle would not have been feasible to manufacture, and using orifices reduced expenses at the cost of increased uncertainty in the igniter mixture ratio. Assuming the same discharge coefficient for both the hydrogen and oxygen “sonic” orifices likely reduced this mixture ratio error to some extent. Chamber temperature was not

measured for fear of melting thermocouples, which could then block the igniter nozzle during operation. Igniter exhaust temperature was measured just outside of the igniter nozzle during qualification test series T1, as outlined in Section 5.3.1.

5.2.2 Main Injector

The main injector design was constrained by the axisymmetric requirement, resulting in a shear coaxial gas-core liquid-annular injection scheme. In order to keep the ignition transient axisymmetric, the igniter had to be the center element of the main injector. Since the igniter could not operate with kerosene, it would have to be oxygen-rich and the center portion of the main injector element would have to be gaseous oxygen. Typical ORSC injectors use swirl coaxial elements with fuel on the inside and hot oxygen-rich gas on the outside. Unfortunately, the swirl element could not be made compatible with the FFOKCDC requirement for axisymmetry. In a similar manner, discrete hole elements such as impinging jet and pintle injectors could not be made compatible with the requirements.

Literature for the gas-core, liquid-annular injector scheme is scarce, especially in the rocket propulsion field. Li and Shen [114] measured Sauter mean diameter (SMD), mean velocity, velocity fluctuation, and droplet number density at radial and axial locations of an annular liquid water stream surrounding a coaxial gaseous air jet. They found that the droplet velocity had a self-similar spatial distribution, with a maximum value at the axial centerline. A further investigation by Li and Shen [115] defined the following regimes of operation for an annular liquid water stream surrounding a coaxial gaseous air jet: bubble formation (instability), annular jet formation, and atomization at low, medium, and high air injection velocities respectively. Leboucher et al. [116] later confirmed this Rayleigh instability mode, but mostly focused on swirling gaseous jets. One commonality between these investigations was that they were completed at atmospheric pressure conditions, i.e. not representative of FFOKCDC conditions.

Based on this literature, it is clear that a tradeoff will need to be made between obtaining adequate atomization at a high oxygen injection velocity and insuring suitable mixing in the given combustor length. Too high of an oxygen injection velocity could result in a largely oxygen core flow pushing the liquid kerosene against the chamber wall, thus resulting in poor mixing. The final design settled on oxygen injection velocities of 50 and 100 m/s for the high and low contraction ratio hardware arrangements, resulting in injector oxygen-fuel momentum ratios of approximately

30 and 60 respectively. Gaseous oxygen injection velocity remained constant with change in chamber pressure, and different fuel collars were machined for each pressure set point to maintain comparable injector characteristics.

Figure 5.5 shows a CAD cross section of the FFOKCDC main injector, where gray parts are free-machining stainless steel (UNS S30300), yellow parts are free-machining brass (UNS C36000), orange parts are oxygen-free high conductivity copper (UNS C10100), and the bluish-gray coating on the bottom-most-center part is a yttria thermal barrier coating. An interpropellant seal between the fuel and oxygen manifolds is vented by a rectangular radial notch visible on the left of Figure 5.5. Threaded rods (not shown) preload the structure thus compressing o-ring face seals. The oxygen post inner diameter is sized for a 20% chamber pressure drop to prevent combustion products backflow into the oxygen manifold and igniter. Radial slots machined into the face of the fuel collar are sized for a 10% chamber pressure drop to prevent backflow into the fuel manifold. The main kerosene mass flow rate was set with a cavitating venturi, which would also prevent backflow due to the incompressibility of liquid kerosene.

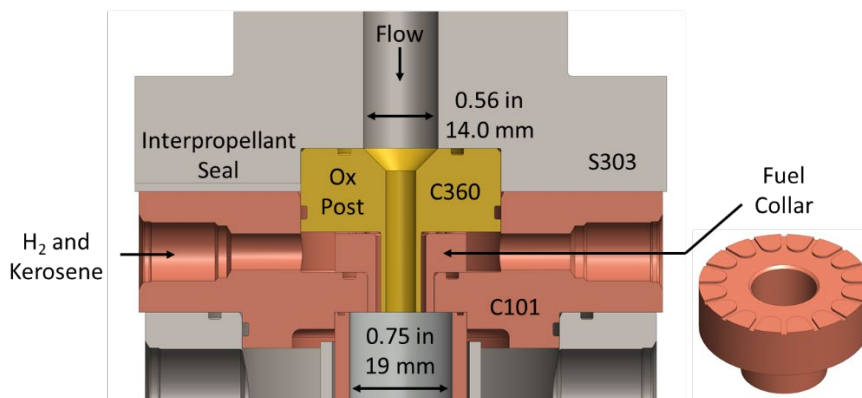


Figure 5.5. CAD cross section of the FFOKCDC shear coaxial main injector.

During double ignition, igniter exhaust products enter through the oxygen post while hydrogen is injected through the fuel collar. When the igniter is turned off, the combustion chamber flame stays anchored at the main injector face. The O₂ ramp state considerably increases the oxygen flow rate through the main injector while keeping hydrogen flow rate constant. Lastly, the hydrogen is switched to kerosene (with some overlap) to achieve nominal run conditions.

5.2.3 Combustion Chamber

The S303 calorimeter chamber, as shown in Figure 5.6, was designed with modularity in mind. It has a segment length of 6.1 cm (2.4 in) as constrained by the thermal barrier coating plasma spray operation which was used on the internal C101 chamber liners. High pressure coolant water counterflows with respect to the combustion chamber gases in a 0.51 mm annular gap between chamber liner exterior and calorimeter interior. Bore seals are used for all interior components such that the chamber liner and film injectors can thermally expand while testing. A graphite gasket, shown as black in Figure 5.6, is preloaded prior to testing and compresses as the inner chamber liners thermally expand while firing. The sample liner was too radially thin for conventional o-ring sizes, therefore Apple Rubber MicrOring® seals were used to seal between the combustion gases and cooling water. The nozzle assembly also used MicrOring® seals, albeit in a bore configuration due to the thermal expansion gasket. Thermal barrier coated parts are used upstream of the first fuel-film injector since heat fluxes are expected to be higher there.

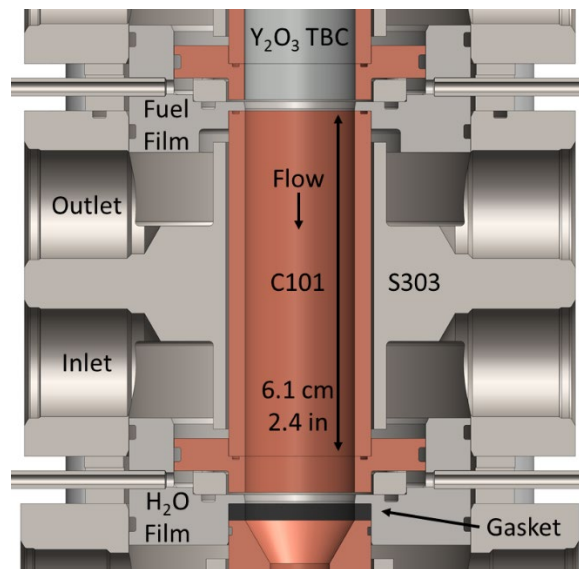


Figure 5.6. FFOKCDC calorimeter chamber CAD with fuel-film injector above it and H₂O film injector beneath it.

Pressure and temperature are measured in the calorimeter chamber inlet and outlet manifolds. Cavitating orifices were placed downstream of the calorimeter chambers to choke the coolant water flow and measure mass flow rate. The orifices were placed downstream, as opposed to upstream, of the calorimeter chamber to maintain high pressures, and therefore saturation temperatures, in the coolant jackets and prevent boiling. The main downside of placing cavitating

orifices downstream of the coolant jacket was a form of positive feedback that could lead to rapid coolant jacket failure. Cavitating orifice mass flow rate depends on upstream pressure, which would decrease if any boiling occurred, thus increasing boiling and potentially causing failure. All cooling jacket circuits had to be pressurized and operated together, otherwise sample liner face seals would slip out of place as the thermal expansion gasket improperly compressed. Intra-channel thermocouple holes accessible from AS5202-2 ports were machined to attempt calorimetry on a shorter length scale than the calorimeter segment length of 6.1 cm (2.4 in). Kirchberger et al. [117] previously attempted intra-channel calorimetry to limited success, and inspired this design.

A 2D axisymmetric, transient COMSOL heat transfer model was used to calculate chamber liner, main injector, and nozzle temperatures with a similar set of assumptions as those used in the Task 1 combustor COMSOL model (see Section 3.4.2). Figure 5.7 shows temperature profiles from the injector head end. The geometry shown is somewhat outdated, as bore seals are used for the sample chamber liner as opposed to the MicrOring® face seals, however the main results are the same. The model predicts a small hot spot on the injector face, which is cooled significantly less than the chamber liner. However, I would expect fuel-rich combustion to take place in this recirculation zone due to the exterior fuel annulus injection scheme, thus reducing the heat transfer to the injector face predicted by the overly-conservative COMSOL model assumptions. Additionally, both Volkmann [48] and the Technische Universität München team [118] noticed lower heat fluxes near the injector head end of similar combustors, likely due to kerosene's characteristically long combustion time with oxygen. Similar analysis was carried out for the film injectors and nozzle, albeit without a liquid film injection model. Their results suggest that the following temperature profiles are overly conservative.

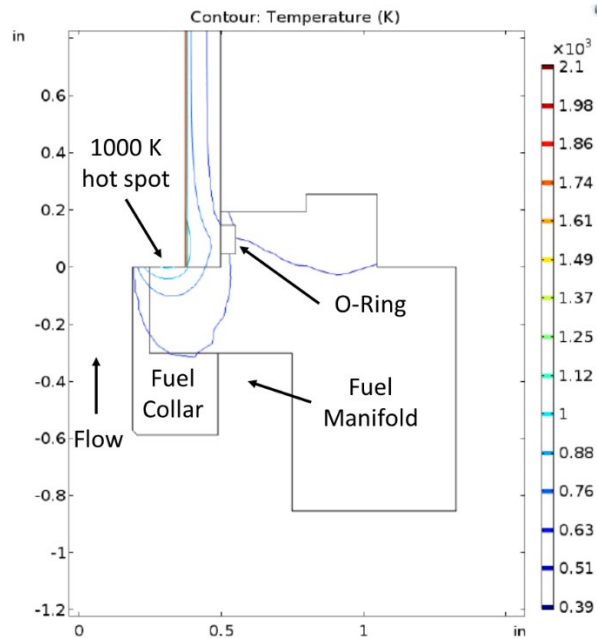


Figure 5.7. COMSOL temperature profile results for the FFOKCDC main injector. Note that the geometry is from a previous FFOKCDC CAD revision where the chamber liner was sealed with standard sized o-rings in a bore seal configuration.

5.2.4 Film Injector

The Task 4 film injector radially injects an annulus of kerosene or water at low velocity such that the high velocity core flow keeps it wetted against the chamber wall, similar to the design for the Task 1 combustor. The primary difference was an injection plate (see Figure 5.8), similar to the fuel collar of the main injector (see Section 5.2.2), which was designed for a 10% of chamber pressure drop. Two different fuel-film injection mass flow rates were designed into the test matrix: 24.5 g/s and 34.1 g/s. These flow rates were selected because they matched the nominal and high Task 1 combustor fuel-film mass flow rate per chamber circumference. Fuel and water films had their mass flow rates measured by cavitating venturis.

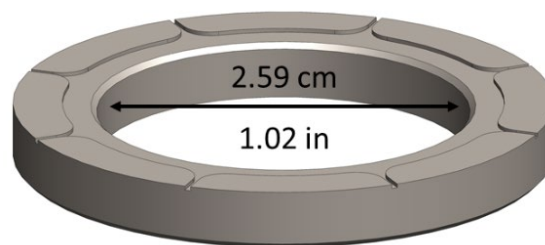


Figure 5.8. Film injection plate with 10% pressure drop flow passages.

5.2.5 Structure

The FFOKCDC structure can be thought of in two parts: the cooling jacket exterior and interior. The exterior consists of the main injector, calorimeter chambers, and nozzle holder. The interior consists of the chamber liners, film injectors, thermal expansion joint, and nozzles. Eight 5/16-18 threaded rods spaced 45° from one another preload the exterior structure to 140 and 280 MPa (21000 and 40000 psi) for the low and high contraction ratio tests respectively. The large preload is required to overcome the internal forces produced by the cooling jacket, whose largest diameter o-ring measures 7.6 cm (3.0 in) in diameter. Water jacket pressures must be kept above or near the chamber pressure to reduce hoop stress in the chamber liner, which can become a failure mechanism at high chamber liner temperatures. The interior structure dimensioning results in a much smaller preload which corresponds to 17% pre-compression for the thermal expansion gasket. This results in just enough force to preload the MicrOring® face seals, but is low enough that the thermally expanded compression of the gasket is only 40%. As mentioned previously, the entire internal structure uses bore seals to allow for it to slide within the exterior structure as it thermally expands.

5.3 Qualification Tests

FFOKCDC qualification testing verified the igniter and combustor operability. Qualification testing was more involved for FFOKCDC than the Task 1 combustor due to the complex nature of the FFOKCDC startup transient. The following test series all operated at the low pressure set point and demonstrated the operability of FFOKCDC. Conditions and notes for each individual test can be found in Appendix H.

- T1: Igniter qualification tests
- T2: Combustor cold flows with N2 and kerosene
- T3: Combustor open-face injector hot fires
- T4: Short chamber, low contraction ratio double ignition and O₂ ramp up
- T5: Short chamber, low contraction ratio fuel switch resulting in nominal run condition
- T6: Long chamber, low contraction ratio
- T7: Long chamber, high contraction ratio

5.3.1 T1: Igniter

The FFOKCDC igniter was assembled on the test stand with a cheap nozzle mockup, which was essentially a high length-to-diameter orifice plate drilled at the lab. The nozzle is the most likely point of hardware damage, therefore I considered it prudent to use an inexpensive nozzle on the first few tests. The nozzle throat diameter was matched to the precision-machined brass ASME venturi nozzle with a correction for differing discharge coefficient. Figure 5.9 shows the chamber pressure for the igniter in a nominal test. The igniter runs oxygen-rich with a mixture ratio of approximately 75, therefore we lead with oxygen to prevent the igniter from reaching a mean stoichiometric mixture ratio.

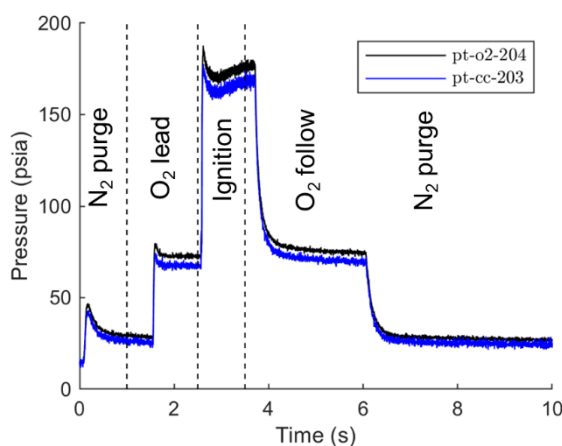


Figure 5.9. Test 1.5 pressure traces for igniter qualification testing. “pt-o2-204” is in the oxygen manifold while “pt-cc-203” is just upstream of the igniter nozzle.

The primary lesson learned from igniter testing was that a rapid chamber pressure spike (often not picked up by our 500 Hz DAQ) to no more than 150% nominal chamber pressure could occur at ignition. This pressure spike happened because the hydrogen sonic orifice was upstream of the run valve, resulting in a high-pressure volume of hydrogen between the sonic orifice and the run valve which was unrestricted in mass flow rate once the run valve was opened. This “slug” of hydrogen could enter the chamber when the spark was not present because the spark plug operated at 60 Hz. Therefore, the chamber pressure spike varied from test to test depending on when the hydrogen run valve was opened in relation to the wall electricity peaks at 60 Hz. No hardware damage occurred due to the pressure spike, however we identified the following solutions for reducing it, where only the second solution was later implemented.

1. Move the sonic orifice after the run valve, at the cost of a slower ignition transient. The slower ignition transient could be sped up by then moving the sonic orifice closer to the igniter hardware, as was done in the HOMEER igniter [109].
2. Increase the hydrogen sonic orifice throat diameter to reduce the upstream pressure for the same mass flow rate, thus resulting in a smaller hydrogen mass flow rate transient upon opening the run valve.
3. Purchase a sparking system that could operate at a higher frequency.

5.3.2 T2: Open-Face Cold Flow

The main injector was cold flow tested with kerosene and nitrogen to image the coaxial shear flow formation and verify injector pressure drops. A larger diameter acrylic tube was used to contain the kerosene spray. Better images were captured during test series three when kerosene failed to ignite, as shown in Figure 5.10. The spray structure looks axisymmetric, however the oxygen core does not seem to mix well with kerosene until multiple inches downstream of the injector face.

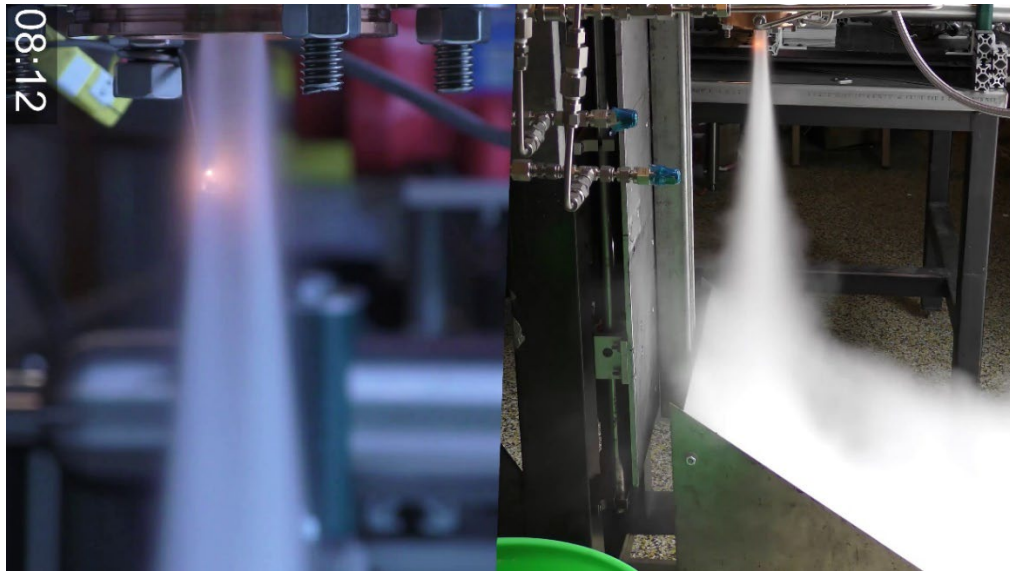


Figure 5.10. Kerosene failing to ignite in test 3.6, thus revealing the main injector spray structure. The bright point in the left closeup image is an expendable thermocouple that was melted during the O₂ ramp state.

5.3.3 T3: Open-Face Hot Fire

One concern was that FFOKCDC was designed to maintain a flame in the combustion chamber while drastically increasing the oxygen flow rate and switching from hydrogen to kerosene as primary fuel. The combustor was tested in an open-face configuration to verify that the flame could be held during these changes in propellant flow rates, albeit at different conditions due to the atmospheric pressure, lack of a recirculation zone, and absence of containment. Despite these shortcomings, verification of double ignition, flame holding in the combustor while turning the igniter off, and an oxygen ramp up to high flow rates was successful. The switch from hydrogen to kerosene as primary fuel did not hold a flame, likely due to the shortcomings mentioned before. Figure 5.11 shows the combustor in test 3.6, just after it transitioned from a fuel-rich flame to oxygen-rich by ramping up the oxygen mass flow rate by an order of magnitude.

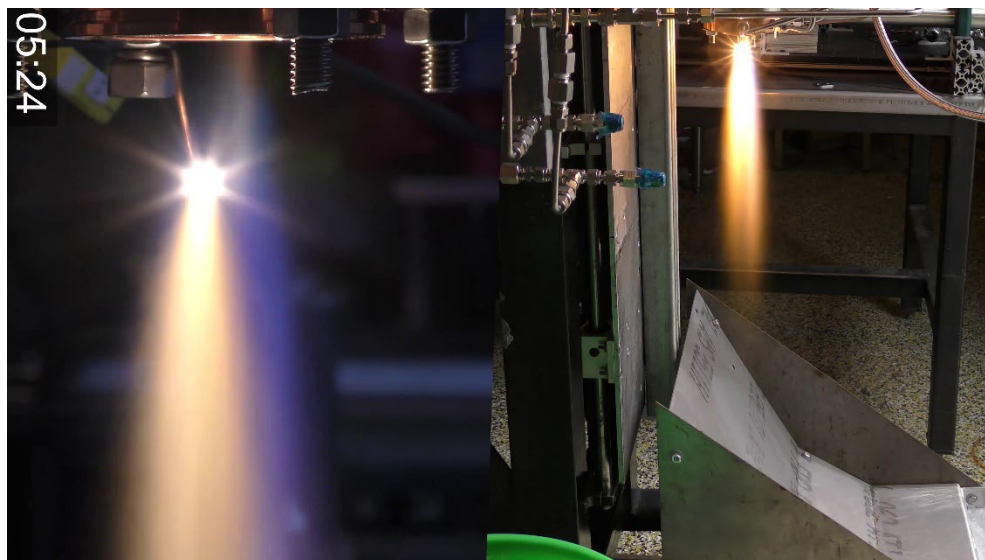


Figure 5.11. Main injector open-face hot fire test 3.6, shown during the O₂ ramp state which is highly oxygen-rich (O/F of 40). The bright spot in the plume is a melted thermocouple which was being used to verify ignition and combustion.

5.3.4 T4 and T5: Short Chamber Combustor

Test series T4 and T5 focused on repeating the build-up from double ignition to fuel switch which was done in series T3, but with a calorimeter chamber and nozzle downstream of the main fuel injector. Figure 5.12 shows the chamber pressure curve for the final test which demonstrated all combustion states and steady flame holding at the nominal kerosene-oxygen run conditions. Note the chamber instability during the O₂ ramp and fuel switch states, which occurred due to the

main injector fuel collar running with hydrogen. Further tests will be needed to tighten the timing on the autosequence such that it takes significantly less than eight seconds to reach the nominal flow condition. The C^* efficiency of this combustor in the nominal state was about 50% because all chambered qualification tests were completed with the minimum amount of hardware possible on the stand, resulting in a short chamber length. Test series 6 and 7 used a longer chamber length configuration to verify an increase in C^* efficiency.

The calorimeter cooling water was run at the maximum flow rate that the system could handle in order to reduce the likelihood of combustor failure during qualification testing. The initial heat flux data from the calorimeter chamber had poor uncertainty due to the high cooling water mass flow rates. As a result of the minimum hardware qualification testing premise, T4 and T5 were completed without a fuel-film injector installed.

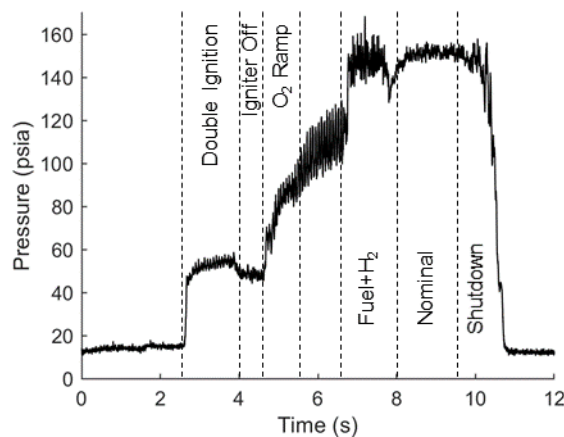


Figure 5.12. Test 5.4 combustor chamber pressure showing various state transitions.

5.3.5 T6 and T7: Long Chamber Combustor

Test series six and seven had the combustor installed in the long chamber configuration with no fuel-film injector. The water coolant mass flow rate was reduced by approximately 30% due to the lower than expected heat fluxes measured in test 5.4. The main benefit of running a lower (less conservative) water cooling jacket mass flow rate is increased heat flux measurement accuracy due to the larger temperature rise between the calorimeter chamber coolant manifolds. Test 6.1 ran the double ignition state to verify that the heat fluxes matched between the higher and lower coolant mass flow rates. The only difference between tests 5.4 and 6.2 was the chamber length. Test 7.5 kept the long chamber length of test 6.2, but also used the high contraction ratio

igniter and main nozzles, resulting in double the chamber pressure of test 6.2. Additionally, the water film mass flow rate was halved in test 7.5 compared to test 7.4, the latter of which didn't stay lit during the O₂ ramp, likely due to the higher oxygen post velocity of approximately 100 m/s instead of 50 m/s in the low pressure case. Tests 7.4 and 7.5 showed that the water film, though nearly 15 cm (6 in) downstream of the main injector, has a considerable impact on the flame holding characteristics of the main injector. Figure 5.13 shows the chamber pressure traces from tests 6.2 (left) and 7.5 (right). The slow shutdown occurred due to a relatively large kerosene dead volume and low volumetric flow rate. A small drop in pressure just as the main fuel run valve is closed can be seen in the test 7.5 chamber pressure curve.

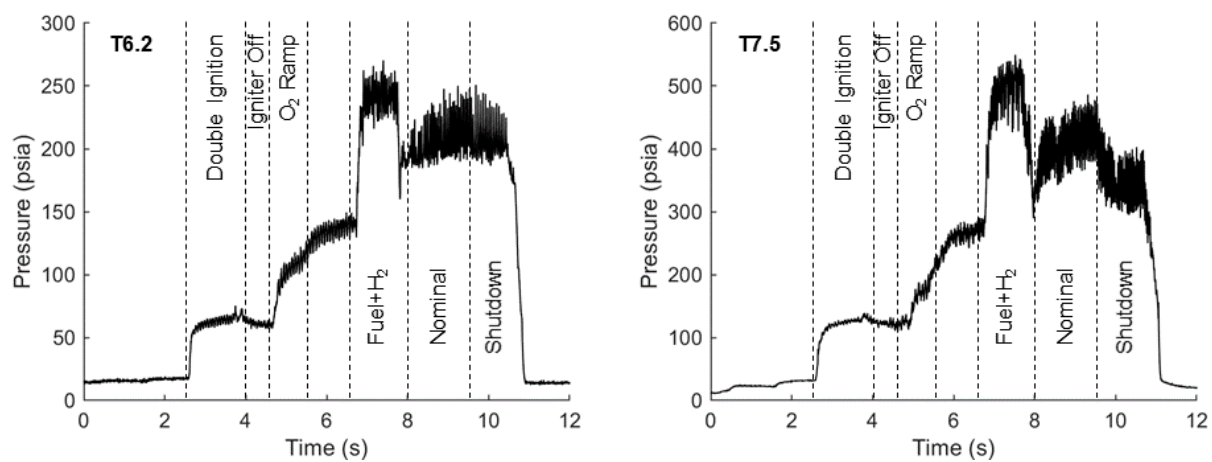


Figure 5.13. Chamber pressures from tests 6.2 and 7.5, both of which used a long chamber configuration. Note the different y-axis scales.

Both tests 6.2 and 7.5 were considerably more unsteady than test 5.4, which did not have a well-defined instability frequency. Figure XXX shows pressure traces for tests 6.2 and 7.5 in the nominal combustion state, where a low frequency instability had a considerable amplitude. The instability was caused by the switch to the longer chamber length, along with a lack of mixing in the main injector element. Additionally, the oxygen density of test 7.5 was approximately double that of test 5.4, resulting in half the pressure drop across the oxygen injector element. Since the nominal chamber pressure doubled between tests 7.5 and 5.4, the percentage pressure drop across the oxygen injector decreased by a factor of four overall. Fixing the instability problem requires a combination of increasing mixing in the main injector and adjusting the oxygen injector geometry to provide a higher pressure drop in the high contraction ratio, high pressure hardware configuration.

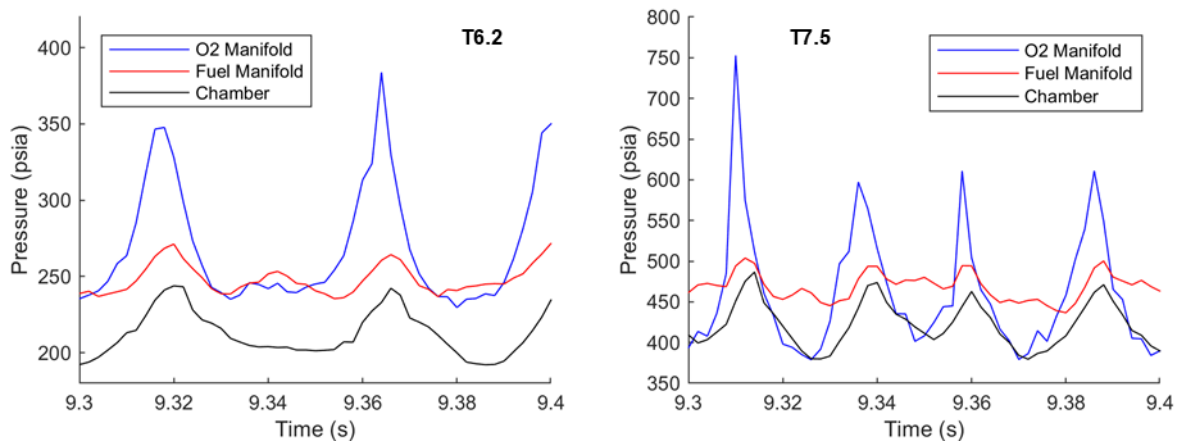


Figure 5.14. Chamber pressure instability from tests 6.2 and 7.5.

Table 5.2 lists instability frequencies calculated via a fast Fourier transform, as well as C^* efficiencies at various combustor states. C^* efficiency was higher than 100% in the double ignition state due to the water film which was not accounted for in the NASA CEA [57] calculations and likely vaporized to some extent. C^* efficiency decreased with increasing mass flow rate, which corresponds to increasing main injector velocity. Additionally, the switch from oxygen-rich hydrogen-oxygen combustion in the O_2 ramp state to near-stoichiometric kerosene-oxygen in the nominal state incurred a second C^* efficiency drop. Note that tests 6.2 and 7.5 had nearly identical C^* efficiencies, corresponding to an exact doubling of the chamber pressure. The main injector momentum ratio changed by a factor of two due to the higher pressure oxygen inlet, indicating that the main injector momentum ratio has little to no effect on C^* efficiency in this regime.

Table 5.2. Chamber pressure instabilities and C^* efficiencies for tests 5.4, 6.2, and 7.5. Instability frequencies were calculated with a fast Fourier transform and C^* efficiencies were calculated using NASA's CEA [57] code.

Test Number	Chamber Length	Nominal Chamber Pressure (psia)	Nominal Instability Frequency (Hz)	C* Efficiency (%)		
				Double Ignition	O_2 Ramp	Nominal
5.4	short	152	-	109	76	46
6.2	long	211	25	126	90	64
7.5	long	417	43	127	90	62

The C^* efficiency and chamber instability problems must be fixed before collecting carbon deposition data, otherwise FFOKCDC will not reach the necessary conditions set out in the

requirements. All three tests that reached nominal conditions had low C^* efficiencies, indicating an injector mixing problem. A switch to radial kerosene injection in an oxygen cross flow seems most prudent, since it will only require machining of one part per pressure set point (three parts total) and has been proven, albeit at different conditions, in the Task 1 combustor. Of course, discretely injecting multiple kerosene streams will completely invalidate the axisymmetric assumption which so much effort was put into upholding. Increasing the number of discrete fuel injection holes would decrease the 3D CFD domain required to simulate this injection scheme. However, it would still be considerably more expensive than a 2D axisymmetric domain.

Future tests will install the fuel-film injector upstream of the sample tube to produce carbonaceous deposit samples similar to those produced in the Task 1 combustor. Additionally, intra-channel thermocouples between cooling water manifolds can be installed to gain better spatial fidelity in heat flux measurements.

5.4 Calorimetry

The calorimeter sections, including the nozzle holder, were used to calculate heat flux for test series four through seven. Series four and five had a single calorimeter chamber in the “short” hardware configuration, whereas series six and seven had two calorimeter chambers. Cavitating orifices were used to measure mass flow rate. All orifices were calibrated in the same water flow test because flowing through individual cooling circuits unseated seals in the FFOKCDC stackup. The orifices used for each calorimeter were identical, allowing for calculation of a discharge coefficient from the aggregate mass flow rate. Individual upstream orifice pressures were measured for each cooling circuit, although they were always within 5% of each other due to the similar geometry of the calorimeter and nozzle holder cooling channel. As a reminder, the cavitating orifices were downstream of the calorimeters to maintain high saturation temperatures in the cooling circuits, therefore the pressure transducers were located between the calorimeter outlet and the cavitating orifice inlet. Future calibration could measure orifice discharge coefficients in a separate calibration circuit, however this would not appropriately account for the pressure drop between the calorimeter outlet manifolds, where pressure transducers are located, and the cavitating orifice inlets. To combat this issue, pressure transducer locations could be moved from the outlet manifolds to the cavitating orifice inlets easily enough.

Calorimeter inlet and outlet manifold temperatures from test 7.5, calorimeter one (upper) are shown in Figure 5.14. Outlet temperature rapidly increases at double ignition, then remains relatively constant for the rest of the test duration. Data from the first 0.2 seconds was used to calibrate out the temperature offset between the two thermocouples. Mean temperature differences at the end of each respective run state could then be used to calculate heat fluxes, with water mass flow rates calculated from the calibrated cavitating orifices.

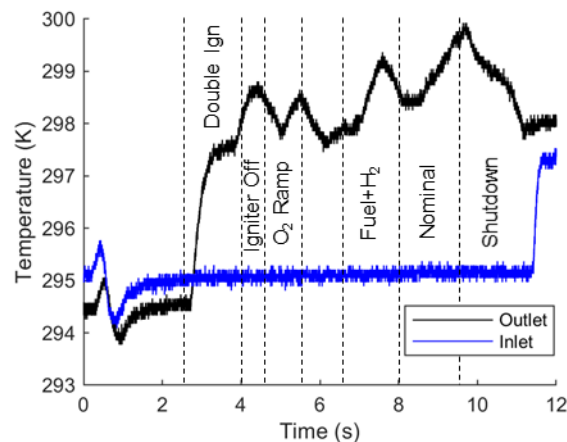


Figure 5.15. Upper calorimeter inlet and outlet temperatures for test 7.5, which had a long chamber and high contraction ratio hardware configuration.

An increase in heat flux as the igniter turned off occurred due to the hydrogen-oxygen flame moving closer to stoichiometric combustion. Heat flux was relatively constant through the O₂ ramp state, somewhat surprisingly, since the mass flow rate increased significantly during this state. Introducing kerosene to the combustor caused a small increase in heat flux, although much less than expected for near-stoichiometric combustion of kerosene and oxygen. The kerosene was likely being blown onto the wall before it could mix with oxygen, thus keeping the measured heat flux much lower than expected.

Heat flux data for each run state of each calorimeter segment has been compiled in Appendix H, from which a few noticeable trends appear. The second, lower calorimeter chamber in test series six and seven had noticeably higher heat flux than in the upper chamber. Poor mixing in the main injection element is gradually rectified with increased chamber length. Test 7.5 had half the nominal water film coolant mass flow rate just upstream of the nozzle, which resulted in lower heat fluxes than those seen in test 6.2, with the latter also occurring at lower chamber pressure. Higher water film flow rates may have been leading to significant entrainment in tests

before 7.5. Reducing the coolant mass flow rate in tests six and seven resulted in less uncertainty due to higher temperature differentials between inlet and outlet manifolds. Despite this improvement, repeatability was still difficult to achieve across all run states. Poor mixing from the inverted coaxial shear injection element causing instabilities is likely the culprit. Calorimetry data is expected to improve significantly once the main injector element has been fixed.

5.5 Lessons Learned

Several areas for improvement have been identified from FFOK CDC qualification testing:

- **60 Hz spark:** Low sparking frequencies can allow propellants to build up before ignition.
- **Venturi location:** Cavitating venturis should be placed upstream of run valves so as to be pre-wetted, which prevents water hammer phenomenon for incompressible fluids. Sonic venturis should be placed downstream of run valves to prevent a high mass flow rate transient upon valve opening, at the cost of a slower startup transient.
- **Coolant water hammer:** Placing a coolant run valve downstream of the test hardware allowed for vacuuming, pre-wetting, and pressurization of the coolant passages to prevent two-phase flow transients. An upstream valve was also required for preventing water hammer when turning off the coolant flow.
- **Thermal expansion joint:** By definition, thermal expansion joints introduce compliance into a normally rigid structure. Carefully dimensioning and tolerancing the expansion joint and face seals is required to prevent leaks. Pressurization transients should be considered, as they have the potential to unseat seals. Bore seals should be preferred, because they decouple the required o-ring preload from the thermal expansion axis.
- **Mixing fuels:** Hydrogen and kerosene were used in the same propellant lines and manifolds, sometimes at the same time. Leftover kerosene from previous tests would contaminate the flow when it was supposed to be only hydrogen. This prevented flame holding at highly fuel-rich conditions. The solution was to purge the main fuel manifold with hydrogen multiple times before firing to clear out the excess kerosene from the previous test.

- **Water film cooling:** A water film injected to cool the nozzle had significant effects on flame holding at the main injector. Film injector design should be careful to avoid mass flow rates so high that they cause entrainment into the core flow.
- **Unproven injector element:** Perhaps the biggest lesson learned from FFOKCDC was that unproven injection elements may not work. Literature with tests at atmospheric conditions suggested sufficient atomization and mixing of the inverted shear coaxial element, but testing with FFOKCDC proved otherwise. Designing with modularity in mind, as well as a backup plan, was crucial to FFOKCDC's future success. The radial liquid injection into a gaseous cross flow design will require minimal changes to the hardware, because the main injector was adapted for it before it was ever needed.

6. CONCLUSIONS

A better understanding of carbonaceous deposits in fuel-film flows was pursued by focusing on deposits' thermal resistance and physical/chemical characteristics. The goal of this research was to gain insight into deposition mechanisms that could predict deposition's effect on heat flux at ORSC conditions. The three objectives from Section 2 are repeated below as a reminder of the problems this research set out to solve.

1. How do ORSC conditions affect fuel-film carbon deposition thermal resistance?
2. What are the carbonaceous deposits' physical and chemical structure?
3. What mechanisms contribute to carbon deposition?

6.1 Task 1 Combustor

The Task 1 combustor was designed to measure heat flux while also enabling post-test analysis of carbon deposition on imaging and spectroscopy instruments. Heat flux was measured using up to 50 null point calorimeter thermocouples embedded within a heat-sink cooled copper sample chamber.

6.1.1 Heat Flux Measurements

High sample chamber thermal conductivity and low inner wall heat flux simplified the inverse heat problem solution due to a lumped capacitance assumption. The direct problem required a numerical solution because heat flux was solved for at every temperature data point. The inverse problem was solved with a Gauss-Newton algorithm using a constant Jacobian matrix. Solutions to the inverse problem matched thermocouple data to within 0.25 K (0.45 R) at every data point except for startup transients, which were typically matched to within 0.5 K (0.9 R).

Heat fluxes calculated at multiple azimuthal locations within the same axial level varied by up to 2 MW/m² (1.2 Btu/s-in²) during startup transients, but converged to within 0.1 MW/m² (0.061 Btu/s-in²) during quasi-steady-state operation of the heat sink cooled combustor. The effects of carbonaceous deposits were clearly visible in the heat flux profiles plotted at different axial locations, resulting in increased heat flux reduction with time for axial locations further away from the fuel-film injector, where carbon deposition was thickest. Repeatability of the heat flux

measurement system was established by testing at the same conditions multiple times. Varying chamber liner material from copper to stainless steel and Inconel resulted in lower heat fluxes during the startup transients, but similar heat fluxes during quasi-steady-state operation. The benefit of carbon deposition during kerosene fuel-film cooling was reduced for low thermal conductivity metals because the carbon deposition thermal resistance was of the same order of magnitude as that of the chamber liner. Chamber liner surface roughness may have influenced the initiation of a carbon deposition layer. However, heat flux was unaffected by surface roughness once the carbon layer seemed to be fully established. Further investigation of the carbonaceous deposits is required to support surface roughness conclusions based solely on the measurement of heat flux.

Heat flux measurements gave a preliminary answer to objective one by quantifying heat flux reduction in a similar manner to previous literature [14,48,118]. Future work could involve the solution of a 2D axisymmetric or 3D HDE, since thermocouple radial, axial, and azimuthal positions were well-known throughout the combustor, and most tests contained up to 50 temperature channels measuring at different locations. Unfortunately, the constant Jacobian matrix method would not work in these cases, therefore the solution would likely require a model with significantly lower degrees of freedom. A secondary objective of accounting for thermal contact resistance between the thermocouple and the copper sample chamber would also be useful. Lastly, a model of the chamber liner and carbon contact resistances along with carbon depths (see Sections 4.2) and thermophysical properties (see Section 4.4) would allow for direct calculation of interior surface temperatures from exterior thermocouple data.

6.1.2 Deposit Depth

Initial inspection of the carbonaceous deposits revealed a two-layer structure, where the upper layer was porous and soot-like while the lower layer was dense and tenacious. Only the dense layer was present at axial locations within approximately 5 mm (0.20 inch) of the fuel-film injector, after which the deposits transitioned towards the two-layer structure with more soot-like carbon in the upper layer. An optical profilometer and scanning electron microscope were used to measure total and dense layer deposit thickness respectively as a function of axial distance from the fuel-film injector. SEM images showed clear signs of soot-like agglomerates in the porous layer, whereas the dense layer was smooth.

Both porous and dense deposit thicknesses increased monotonically with distance from the fuel-film injector, typically transitioning from dense to porous deposits at 5 to 15 mm (0.20 to 0.59 inch) downstream of the fuel-film injector. For the baseline fuel-film flow rate, the deposits transitioned back to the denser structure and rapidly dropped to less than 5 μm (200 μinch) depth at 60 to 70 mm (2.36 to 2.76 inch) downstream of the fuel-film injector. The main cause of deposit thickness independence from film mass flow rate is likely related to the constant film saturation temperature, similar to previous experimentalist's defining the liquid film length by the sudden rise in measured wall temperature past the liquid's saturation temperature. Repeatability between tests was confirmed for both low and high fuel-film flow rates, except in the case where a nozzle converging-section geometry change may have affected deposits over 35 mm (1.38 inch) downstream of the fuel-film injector. Fuel-film flow rate, bipropellant test time, fuel composition, chamber liner material, and initial metal surface roughness were varied to determine their effect on the total deposit depth.

Increasing the fuel-film flow rate by 40% did not appreciably increase deposit depths in the fuel-film injector near field, but did extend the region of dense and porous deposits past the chamber liner sample length, likely due to the constant saturation temperature boundary condition with varying fuel-film mass flow rate. Both layer depths increased nearly linearly with bipropellant run time at all axial positions except those within 10 mm (0.39 inch) of the fuel-film injector, where deposit depths were lowest.

Changing the main and film injector fuel from RP-2 to JP-8 resulted in more dense and porous carbon closer to the injector, a higher deposition rate when transitioning to porous carbon, and a sudden drop in deposit depth closer to the injector. The higher aromatic and olefin content of JP-8 likely caused these results. Scanning electron microscopy images showed no signs of filamentous carbon, suggesting that the differences in deposition were not caused by catalytic reactions due to higher JP-8 sulfur content.

Changing the chamber liner material from copper to stainless steel and Inconel resulted in higher wall temperatures, thicker porous deposits, and thinner dense deposits. The thinner dense deposits can be explained by higher wall temperatures, and therefore less condensation of heavy PAHs, whereas the thicker porous deposits can be explained by much higher soot volume fractions near the wall, despite the lower thermophoretic velocity towards the wall. The stainless steel and Inconel deposit depths were nearly identical, likely due to the similar thermal conductivity, density,

and specific heat of the two metals when compared with copper. Higher porous carbon surface roughness was observed for the Inconel test when compared with stainless steel, potentially due to a higher wall temperature caused by a lower thermal expansion coefficient.

Surface roughness of the virgin sample tube may have affected deposition rate when the deposit layer thickness was smaller than the initial metal surface roughness, which occurred near the fuel-film injector where deposit rates were lowest. Initial metal surface roughness seemed to have no effect on the deposits farther from the fuel-film injector. These conclusions are of particular interest to additively manufactured parts, where surface roughness can be orders of magnitude higher than traditionally machined parts.

Deposit thermal resistance is proportional to thickness; therefore, its measurement was directly related to objective one. SEM micrographs revealed deposit layer structure and physical characteristics related to objective two. Lastly, micrographs of the porous layer suggested a thermophoretic mechanism for deposition, as related to objective three.

6.1.3 Chemical Characterization

The dense and porous layers were characterized using GCMS, Raman spectroscopy, and XPS to better determine the mechanism by which they were deposited. Samples were examined in their undisturbed state where possible.

GCMS was used to identify compounds in porous and dense carbon collected from a baseline test sample. The dense layer had considerable amounts of heavy PAHs in the 200-350 g/cm³ molecular weight range, most of which were not present in the porous layer sample. Even the PAHs that were evident in the porous sample were present in trace quantities compared to those in the dense layer. This dichotomy in layer composition leads me to believe that physical condensation of heavy PAHs is a considerable mechanism for dense layer deposition. The heavier PAHs likely diffuse through the porous layer in a gaseous state, since most of the porous layer was at too high of a temperature for condensation to occur. Those PAHs that were able to reach the cooler wall would then condense, forming the dense layer that was always found beneath the porous layer. While a quantitative analysis was not completed in this work, it would be the next logical step because quantitation could determine the extractable content and composition of the dense layer.

Raman spectroscopy was used to measure planar coherence length and other structural order trends with axial distance from the fuel-film injector. Dense and porous layer structural order indicators were constant and increased with axial distance, respectively. The constant dense layer order is consistent with its proposed condensation deposition mechanism, which is directly tied to the spatially constant wall temperature of the heat sink cooled combustor. The decrease in porous layer structural order suggests a decrease in soot formation temperature with axial distance. Peak ratios and FWHM structural parameters gave opposite results for the porous layer, although the former can be taken as a more trustworthy indicator.

XPS measured changes in surface composition and hybridization. Carbon-to-oxygen ratio increased with axial distance, and was likely driven by the transition from dense to porous layer. This result matched an ESCA study by Saito et al. [25] on similarly formed deposits. The C 1s and O 1s spectra confirmed the increase in carbon-to-oxygen ratio. The C 1s spectrum also contained evidence of a PAH satellite site only evident in copper (cool wall), near-injector regions. The O 1s spectrum showed a transition from C=O to C-O bonded oxygen with axial distance. Lastly, the C KLL Auger peak from the survey spectra indicated a preponderance of sp^2 hybridized carbon compared to sp^3 .

Overall, all three of these analysis techniques independently point towards mechanisms of heavy PAH condensation in the dense layer and thermophoretic diffusion of soot agglomerates in the porous layer, thus partially satisfying objective three.

6.1.4 Thermophysical Properties

Measurement of deposit density, specific heat, thermal conductivity (or diffusivity), and emissivity are important for quantifying deposits' insulating effect as related to objective one.

Averaged across three different samples, porous layer apparent density was measured as 1910 kg/m^3 , while porous and dense layer envelope densities were 216 and 1460 kg/m^3 respectively. The dense layer envelope density likely would have been similar to that of the porous layer, that is, close to the typical engineering graphite density. Radial air gaps in the dense layer likely accounted for the difference between apparent and envelope density. The fluffy, agglomerate soot of the porous layer had an envelope density half an order of magnitude lower than the dense layer.

Difficulties were encountered while measuring specific heat, although I would not expect significant differences between graphite and carbonaceous deposit specific heats, especially based on specific heat measurements of soot in literature [106].

Thermal conductivity was successfully measured for bulk samples, similar in structure to the dense layer, from a fuel-rich gas generator environment. The Task 1 combustor samples were too thin for most measurement techniques, although many were attempted. Thermal conductivities from 0.2 to 1.1 W/m-K, depending on the sample, were measured for the gas generator samples with relative uncertainties of approximately 10%.

An infrared microscope with heated stage was used to measure surface emissivity of the carbon deposits at 40°C. Azimuthal injector asymmetries were visible in the near-injector region of the samples. The emissivity rapidly increased from 0.2 to 0.65 within the first 6 mm (0.24 inch) of the film injector, after which it remained constant.

6.2 Task 4 Combustor

The fuel-film oxygen-kerosene carbonaceous deposit combustor, or FFOKCDC for short, was designed to fix the shortcomings of the Task 1 combustor. Qualification testing revealed inadequate mixing in the inverted shear coaxial injector, an unproven design that was chosen to meet a CFD validation requirement for the combustor. While the startup sequence was proven feasible in multiple hardware configurations at multiple run conditions, the main injector will need a small redesign towards a radial fuel injection into an oxygen cross flow, at the cost of breaking axisymmetry in the combustor.

APPENDIX A. TASK 1 COMBUSTOR TEST MATRIX

Full test matrix for Task 1 combustor where bolded entries indicate a condition that varied from the baseline. A surface roughness of 50–50 indicates a sample tube chamber liner that had 50% of its interior artificially roughened, as shown in Figure 3.2. An asterisk (*) indicates a 4-6-4 test that fired monopropellant mode both before and after bipropellant mode. A dagger (†) indicates a test before which null point calorimeter thermocouples (TCs) were reinstalled. The “blend” entry for test 50 in the fuel column was a mixture of a proprietary hydrocarbon and RP-2 in 10:90 mass proportions. A nozzle geometry change occurred starting with test 47, as indicated by the (‡) symbol.

Test Number	Test Date	Fuel	Biprop Time (s)	Biprop Pressure (MPa)	Core Mixture Ratio	Total Mixture Ratio	Sample Material	Sample Surface Roughness	Number of TCs Installed
29	02/06/2018	RP-2	15	1.4	2.96	2.96	C101	Fine	0
34	04/13/2018	RP-2	6	2.99	7.62	2.67	C101	Fine	0
35	05/08/2018	RP-2	6	4.70	7.43	2.89	C101	Fine	0
36	05/08/2018	RP-2	6	4.66	7.43	2.89	C101	Fine	0
38	06/18/2018	JP-8	6	4.71	7.36	3.46	C101	Fine	0
39	06/18/2018	RP-2	6	4.74	7.43	3.50	C101	Fine	0
40	06/18/2018	RP-2	15	4.83	7.44	2.89	C101	Fine	0
41	07/30/2018	RP-2	6	4.50	7.37	4.80	C101	Fine	0
42	07/31/2018	RP-2	6	4.63	4.60	3.00	C101	Fine	0
43	07/31/2018	RP-2	6	4.64	7.37	2.87	C101	Fine	0
44	07/30/2018	RP-2	6	4.59	7.40	3.48	C101	Fine	0
45	09/12/2018	JP-8	6	4.63	4.60	3.00	C101	Fine	0
46	09/12/2018	JP-8	15	4.32	7.36	3.46	C101	50–50	0
47‡	09/27/2018	RP-2	6	4.41	7.35	4.79	C101	50–50	0
48	09/27/2018	RP-2	6	4.10	7.39	4.81	C101	Rough	0
49	10/03/2018	RP-2	6	3.67	7.38	4.81	C101	50–50	0
50	10/04/2018	Blend	6	3.50	7.35	4.79	C101	50–50	0

51	10/05/2018	RP-2	1	4.29	7.38	4.81	C101	50-50	0
52	10/05/2018	RP-2	6	4.29	7.39	4.81	S304	50-50	0
53	02/15/2019	RP-2	6	4.59	7.50	3.53	C101	50-50	25 [†]
54	02/22/2019	RP-2	6	4.58	7.51	3.53	C101	50-50	50 [†]
55	02/22/2019	RP-2	6	4.63	7.5	3.53	S304	50-50	50
56	03/13/2019	RP-2	6	4.58	7.48	3.52	N066	50-50	50 [†]
57	03/13/2019	RP-2	6	4.62	7.48	3.52	S304	50-50	50
58	03/13/2019	RP-2	6	4.63	7.47	3.52	N066	50-50	50
59	04/10/2019	RP-2	11	4.19	7.48	3.52	S304	50-50	50
60	04/17/2019	RP-2	6*	4.56	7.35	3.46	N066	50-50	50
61	04/17/2019	RP-2	6*	4.52	7.35	3.46	S304	50-50	50
62	04/17/2019	RP-2	6*	4.65	7.40	3.50	C101	50-50	50
63	04/29/2019	RP-2	10	4.58	7.36	3.47	N066	50-50	50
64	04/29/2019	RP-2	0.5	4.58	7.36	3.47	S304	50-50	50

APPENDIX B. TASK 1 HEAT FLUX ANALYSIS CODE

```
function [qdot_pp, tspan] = process_test_hf_optimize(tcs, freq)
%PROCESS_TEST_HF_OPTIMIZE Calculates the heat flux based on thermocouples.
% PARAMETERS
%   tcs (struct array): Array of thermocouples with data to include in the
%   heat flux calculation.
%   name (char array): Thermocouple name which indicates position.
%   data (double array): Thermocouple raw data in Celsius.
%   depth (double): Thermocouple depth into the copper heat sink sample
%   chamber, measured from the outer surface (meters).
%   N_t (int): Number of TC data points to process for heat flux
%   calculations.
%   T_init (double):
%   data_smoothed (double array): Thermocouple raw data smoothed with a
%   moving mean algorithm in Celsius.
%   dT (double array): Difference between adjacent thermocouple raw
%   data points using a two point centered differencing stencil in
%   Celsius.
%   dT_smoothed (double array): dT data smoothed with a movin mean
%   algorithm in Celsius.
%   freq (int): DAQ data measurement frequency for all channels.
%
% RETURNS
%   qdot_pp (double array): Estimated heat flux at each thermocouple data
%   point.
%   tspan (double array): Time array x-axis for qdot_pp.

% Global plot and debug variables for data visualization and debugging.
global PLOT;
global DEBUG;
PLOT = 0;
DEBUG = 0;

%% PDE parameters
% Determine the copper properties from:
% http://www-ferp.ucsd.edu/LIB/PROPS/PANOS/cu.html
dens = 8933;
spec_heat = @(T) 316.21 + 0.3177 * T - 3.4936e-4 * T.^2 + 1.661e-7 * T.^3;
therm_cond = @(T) 420.75 - 6.8493e-2 * T;

% Define the cylindrical radius mesh
r_inn = 1.261 / 2 * 0.0254;
r_out = 1.490 * 0.0254;
N_r = 15;
rmesh = linspace(r_inn, r_out, N_r);
```

```

% Find the maximum TC data array length to determine the time mesh size.
% TEMP: Set all TC N_t to the lowest TC N_t because otherwise there is a
% huge spike in heat flux where one TC's data drops out. Other potential
% fixes would involve completely removing the "bad TC" and comparing heat
% flux with it up to its stop point and without it for the full range.
N_t = tcs(1).N_t;
for i = 1:length(tcs)
    N_t = min(N_t, tcs(i).N_t);
end
for i = 1:length(tcs)
    tcs(i).N_t = N_t;
end

% Define the time mesh
t_start = 0;
t_end = (N_t - 1) / freq;
tspan = linspace(t_start, t_end, N_t);

%% TC zero adjustment
% Find the average initial temperature
t_init = 0.15; % All times before this are nearly constant temperature
T_init = 0; % Temperature average across all TCs
for i = 1:length(tcs)
    tcs(i).T_init = mean(tcs(i).data(1:round(t_init*freq)));
    T_init = T_init + tcs(i).T_init;
end
T_init = T_init / length(tcs);

% Adjust the individual TC data up/down based on the overall average such
% that all TCs have the same average temperature (up until t_init). Note
% that this procedure accounts for TC hardware offsets. Additionally, no
% data is lost because tcs(i).T_init is left unchanged.
if PLOT > 1
    figure();
    xlabel('Time (s)');
    ylabel('Temp (K)');
    title('TC offsets averaged out');
    hold on;
end
for i = 1:length(tcs)
    tcs(i).data = tcs(i).data + (T_init - tcs(i).T_init);
    if PLOT > 1
        plot(tspan(1:tcs(i).N_t), tcs(i).data(1:tcs(i).N_t));
    end
end
end

```

```

%% Heat flux guess
% Make the guess based on the time derivative of temperature.
qdot_pp_guess = nan(N_t, length(tcs));
for i = 1:length(tcs)
    % Smooth the TC data so that taking the derivative is more accurate.
    tcs(i).data_smoothed = smoothdata(tcs(i).data, 'movmean', 100);

    % Take the top half of the derivative using a two point centered
    % stencil from the two measurements next to the current time. Use a
    % guard point on the left that assumes an adiabatic Neumann BC.
    tcs(i).dT = tcs(i).data_smoothed(2:tcs(i).N_t+1) ...
        - [tcs(i).data_smoothed(1); tcs(i).data_smoothed(1:tcs(i).N_t-1)];

    % Smooth the derivative data.
    tcs(i).dT_smoothed = smoothdata(tcs(i).dT, 'movmean', 100);

    % Add all TC derivatives together for a first guess at heat flux.
    qdot_pp_guess(1:tcs(i).N_t, i) = tcs(i).dT_smoothed;
end

% Get the initial guess closer to the correct order of magnitude.
magic_constant = 8960 * 385 * (r_out^2 - r_inn^2) * freq / (2 * r_inn);
qdot_pp_guess = nanmean(qdot_pp_guess, 2) * magic_constant;

% Save the TC data in a convenient matrix for comparing to the model.
tc_data = [tcs.data];

% Iterate until the average thermocouple difference is smaller than a set
% tolerance.
tc_diff_avg = 0;
tc_diff_avg_tolerance = 1e0;
j = 1;
while j == 1 || abs(tc_diff_avg(j-1)) > tc_diff_avg_tolerance
    % Re-solve the PDE to get model temperatures.
    pdesol = process_test_hf_pde_solver(dens, spec_heat, therm_cond, ...
        T_init, qdot_pp_guess(:, j), rmesh, tspan);
    [~, T_mod(j, :, :)] = process_test_hf_calc_phi(pdesol, tcs, rmesh,
tspan);

    % Find the average TC difference (L1 norm).
    for i = 1:length(tcs)
        tc_diff_avg_arr(j, :, i) = tc_data(1:tcs(i).N_t, i) ...
            - T_mod(j, 1:tcs(i).N_t, i)';
    end
    tc_diff_avg(j) = mean2(squeeze(tc_diff_avg_arr(j, :, :)));

    % Adjust the heat flux guess with a power relation.
    qdot_pp_guess(:, j+1) = qdot_pp_guess(:, j) * 1.01^tc_diff_avg(j);

    % Iterate the loop counter.
    j = j + 1;
end

```

```

% Save the heat flux.
qdot_pp = qdot_pp_guess(:, j-1);

% Plot the heat fluxes and the temperature profile.
if PLOT > 1
    % Plot the TCs w/ models.
    process_test_hf_calc_phi(pdesol, tcs, rmesh, tspan);

    % Plot the heat fluxes
    yyaxis right;
    plot(tspan, qdot_pp_guess, '-.');
    ylabel('Heat Flux (W/m^2)');
    hLegend = findobj('Type', 'Legend');
    leg_string = hLegend.String;
    leg_string{end} = 'Heat Flux';
    legend(leg_string, 'Location', 'best');
end

% Final plot of the heat fluxes and the temperature profile.
if PLOT > 0
    % Plot the TCs w/ models.
    PLOT = 2;
    process_test_hf_calc_phi(pdesol, tcs, rmesh, tspan);

    % Plot the heat fluxes
    yyaxis right;
    plot(tspan, qdot_pp, '-.');
    ylabel('Heat Flux (W/m^2)');
    hLegend = findobj('Type', 'Legend');
    leg_string = hLegend.String;
    leg_string{end} = 'Heat Flux';
    legend(leg_string, 'Location', 'best');
end

function [pdesol] = process_test_hf_pde_solver(dens, spec_heat, ...
    therm_cond, T_init, q_inn, rmesh, tspan)
%PROCESS_TEST_HF_PDE_SOLVER Solves a transient, 1D heat transfer PDE.
% PARAMETERS
% dens (double): Copper (C10100) heat sink sample chamber density
% spec_heat (function): Temperature-dependent specific heat of C10100.
% therm_cond (function): Temperature-dependent thermal conductivity of
% C10100.
% T_init (double): Initial copper block temperature as determined from
% thermocouple data in Celsius.
% q_inn (double array): Estimate of heat flux data vs. time.
% rmesh (double array): Radial position axis.
% tspan (double array): Time axis.
%
% RETURNS
% pdesol (2D double matrix): PDE solution on the tspan, rmesh axes.

```

```

% Cylindrical coordinates
m = 1;

% Solve the PDE
pdesol = pdepe(m, @hf_pdefun, @hf_icfun, @hf_bcfun, rmesh, tspan);

%% PDE coefficients function
function [c, f, s] = hf_pdefun(r, t, T, dTdr)
% Returns PDE coefficients for the heat conduction problem
%  $c(r, t, T, dTdr) = 1/r \frac{d}{dr}(r f(r, t, T, dTdr))$ 
%  $+ s(r, t, T, dTdr)$ 

% Time derivative coefficient contains density and specific heat
c = dens * spec_heat(T);

% Flux term contains thermal conductivity and derivative
f = therm_cond(T) * dTdr;

% No source term
s = 0;

end

%% PDE initial conditions function
function [T] = hf_icfun(r)
% Returns the initial conditions as a function of r

% Assign the average initial temperature to all spatial points in r
T = T_init;

end

%% PDE boundary condition function
function [pl, ql, pr, qr] = hf_bcfun(r1, T1, rr, Tr, t)
% Assigns boundary conditions to the PDE of the form:
%  $p(r, t, T) + q(r, t) f(r, t, T, dTdr) = 0$ 
% for both the left and right sides of the domain for all t. Note that
% the boundary conditions is expressed in terms of the flux which is
% defined in hf_pdefun.m.

%  $r = r_{inn}$  with a heat flux boundary condition
pl = interp1(tspan, q_inn, t);
ql = 1;

%  $r = r_{out}$  with an adiabatic boundary condition
pr = 0;
qr = 1;

end
end

```

APPENDIX C. TASK 1 PROFILOMETER ANALYSIS CODE

```
function d_prof = process_profilometer(reprocess, dates, samples, d)
%PROCESS_PROFILOMETER Processes profilometer raw data into deposit heights.
% PARAMETERS
%   reprocess (boolean): Specifies whether or not to reprocess the user
%   data directly from the SDF file and to prompt the user to draw new
%   regions of interest. Defaults to false.
%   dates (cell array of char arrays): List of dates to process data from.
%   Defaults to processing data from every date.
%   samples (2D cell array of char arrays): List of samples to process data
%   from for each date, where the first index is for the date.

% Add the programs path for Tyler Voskuilen's uncertainty analysis class
% and Phil's Zygo SDF reader function.
addpath('F:\Programs');

% Add the path to a circle fitting program by:
% V. Pratt, "Direct least-squares fitting of algebraic surfaces",
%   Computer Graphics, Vol. 21, pages 145-152 (1987).
addpath('F:\Programs\CircleFitByPratt');

% Profilometer data folder location.
folder_data = 'F:\piper\Coking\phaseII\task1\Data';
folder_profilometer = [folder_data, '\Profilometer'];

% Profilometer data analysis file where results are stored.
file_analysis = [folder_profilometer, '\data.mat'];

% Load or create a variable for saving data in a MATLAB structure.
if ~exist('d', 'var')
    d = struct();
    if exist(file_analysis, 'file') == 2
        load(file_analysis, 'd_prof');
        if exist('d_prof', 'var')
            d = d_prof;
        end
    end
end

% Don't ask the user to draw regions of interest unless asked to.
if ~exist('reprocess', 'var')
    reprocess = false;
end

% Let the user specify a list of dates.
if ~exist('dates', 'var')
    dates = {};
end
```

```

% Let the user specify a list of samples.
if ~exist('samples', 'var')
    samples = {};
elseif length(dates) ~= size(samples, 1)
    warning('Samples length of %i does not match dates length of %i', ...
        size(samples, 1), length(dates));
    samples = {};
end

% Sample length constant to correct for measurements on the bottom halves.
L_sample = 2.9 * 0.0254;
L_sample_short = 1.9 * 0.0254;

% Function for a circle that can be fit to data slices.
fn_circle = @(b, x) b(2) - sqrt(b(3)^2 - (x - b(1)).^2);
r_zero = 1.173 * 0.0254 / 2;

% Load the test info Excel file sheet-by-sheet after checking for its
% existence. This file contains information about the axial locations of
% the profilometer measurements for each sample and test date.
data_info_file = [folder_profilometer, '\Profilometer Locations.xlsx'];
if ~isfile(data_info_file)
    error('No test data file exists at "%s"', data_info_file);
end
[~, sheets] = xlsfinfo(data_info_file);
for i = 1:length(sheets)
    % The sheet name should also match the test date.
    d(i).date = sheets{i};

    % Don't process this data if the dates cell array is specified and this
    % date is not in that cell array.
    if ~isempty(dates) && ~any(strcmp(dates, d(i).date))
        continue;
    elseif ~isempty(samples)
        i_date = find(strcmp(dates, d(i).date));
    end

    % Create a field called samples that is also a structure if it does not
    % already exist from loading a previous analysis data file.
    if ~isfield(d(i), 'samples') || isempty(d(i).samples)
        d(i).samples = struct();
    end

    % Open the Excel file sheet corresponding to the date at index i.
    [~, ~, site_info_raw] = xlsread(data_info_file, sheets{i});

    % Loop through each sample/site combination and process SDF data.
    % NOTE: The sites must be in order since the x position increment for
    % each site is incremented based on the previous site's position.
    j = 2; % Excel file row counter.
    last_sample_name = ''; % Used to check for a row with a new sample.
    i_sam = 0; % Counter that increases for each new sample.
    i_ROI = 1; % Counter for total number of data locations.

```

```

while j <= size(site_info_raw, 1)
    % Extract the Excel data into local variables.
    sample_name = site_info_raw{j, 1};
    zero_loc = site_info_raw{j, 2};
    site = site_info_raw{j, 3};
    z_obj = site_info_raw{j, 4} * 1e-3; % In meters.
    dy_site = site_info_raw{j, 5} * 0.0019809 / 2 / 7; % In meters.
    signal_thresh = site_info_raw{j, 6};
    scan_length = site_info_raw{j, 7};
    scan_pos = site_info_raw{j, 8};
    site_loc = site_info_raw{j, 9};
    skip = site_info_raw{j, 10};

    % Check if the sample name changed. If it did, then increment the
    % sample counter which is used to index the returned data variable.
    if ~strcmp(sample_name, last_sample_name)
        % Increment the sample counter and reset the ROI counter.
        i_sam = i_sam + 1;
        i_ROI = 1;

        % Save the sample name.
        d(i).samples(i_sam).name = sample_name;

        % Add the sites struct if it doesn't already exist.
        if ~isfield(d(i).samples(i_sam), 'sites')
            d(i).samples(i_sam).sites = struct();
        end

        % Save the sample name.
        d(i).samples(i_sam).name = sample_name;

        % Prepare sample variables for reprocessing.
        if reprocess && (isempty(samples) ...
            || any(strcmp(samples{i_date, :}, sample_name)))
            % Save the old data before reprocessing.
            d(i).samples(i_sam).y_mean_old = ...
                d(i).samples(i_sam).y_mean;
            d(i).samples(i_sam).dz_mean_old = ...
                d(i).samples(i_sam).dz_mean;
            d(i).samples(i_sam).dz_std_old = ...
                d(i).samples(i_sam).dz_std;

            % Clear the output arrays so that they can be reformed.
            d(i).samples(i_sam).y_mean = [];
            d(i).samples(i_sam).dz_mean = [];
            d(i).samples(i_sam).dz_std = [];
        end
    end

    % Skip this sample if it is not in the sample list.
    if ~isempty(samples) && ~any(strcmp(samples{i_date, :}, sample_name))
        last_sample_name = sample_name;
        j = j + 1;
        continue
    end
end

```

```

% Save the site data in the output data variable.
d(i).samples(i_sam).sites(site).z_obj = z_obj;
d(i).samples(i_sam).sites(site).dy_site = dy_site;
d(i).samples(i_sam).sites(site).signal_thresh = signal_thresh;
d(i).samples(i_sam).sites(site).scan_length = scan_length;
d(i).samples(i_sam).sites(site).scan_pos = scan_pos;
d(i).samples(i_sam).sites(site).site_loc = site_loc;

% Skip processing of this sample if specified in the data file.
% This is typically done when the scratch in the carbon surface is
% not sufficiently wide, is too diagonal, or is too messy.
if skip == 1
    last_sample_name = sample_name;
    j = j + 1;
    continue;
end

% Create a variable for the sample folder. The Zygo software has
% post-processing capabilities for surface roughness data. Assumes
% that the axial component of the sample is lined up with the X
% axis.
file_sample = sprintf('%s\\%s\\%s\\Site%i.sdf', ...
    folder_profilometer, d(i).date, sample_name, site);
if 2 ~= exist(file_sample, 'file')
    warning(['Folder "', file_sample, '" does not exist.']);
    last_sample_name = sample_name;
    j = j + 1;
    continue;
end

% Load the raw SDF file in SI units.
if ~isfield(d(i).samples(i_sam).sites(site), 'z_data_raw') ...
    || isempty(d(i).samples(i_sam).sites(site).z_data_raw)
    [x_data, y_data, z_data] = sdf_reader(file_sample, 1);
    d(i).samples(i_sam).sites(site).x_data_raw = x_data;
    d(i).samples(i_sam).sites(site).y_data_raw = y_data;
    d(i).samples(i_sam).sites(site).z_data_raw = z_data;
else
    x_data = d(i).samples(i_sam).sites(site).x_data_raw;
    y_data = d(i).samples(i_sam).sites(site).y_data_raw;
    z_data = d(i).samples(i_sam).sites(site).z_data_raw;
end

% Process the bottom or top datasets in a special manner since they
% do not have a razor blade cut.
if dy_site == 0
    last_sample_name = sample_name;
    j = j + 1;
    continue;
end

% Translate the data according to the profilometer stage X movement
% and the lens focal point Z movement between samples.
if ~isnan(z_obj)
    z_data = z_data + z_obj;
end

```

```

% Subtract off half of y_data range since sample zero is in
% the middle of the profilometer domain.
y_data = y_data - (max(y_data) - min(y_data)) / 2;

% Translate the Y position data based on if the sample axial top is
% facing 'closer' or 'further' from the operator of the optical
% profilometer while in use.
if strcmp(zero_loc, 'closer')
    y_data = -y_data ...
        + sum([d(i).samples(i_sam).sites(1:site).dy_site]);
elseif strcmp(zero_loc, 'further')
    y_data = y_data ...
        + sum([d(i).samples(i_sam).sites(1:site).dy_site]);
else
    warning('Zero location of "%s" does not compute.', zero_loc);
end

% Transform y_data based on sample type (upper lor lower).
if sample_name(end) == 'b' || sample_name(end) == 'l'
    % Subtract off y_data from the sample length for lower samples.
    if strcmp(d(i).samples(i_sam).name, 'T36_ii_b')
        y_data = L_sample_short - y_data;
    else
        y_data = L_sample - y_data;
    end
elseif sample_name(end) == 'u'
    % Flip y_data for the upper samples.
    y_data = flip(y_data);
else
    warning(['If sample "%s" is neither lower or upper, ' ...
        'what is it?'], sample_name);
end

% Add the 1/16" step at the fuel-film injector.
y_data = y_data + 1/16 * 0.0254;

% Save the adjusted data.
d(i).samples(i_sam).sites(site).x_data = x_data;
d(i).samples(i_sam).sites(site).y_data = y_data;
d(i).samples(i_sam).sites(site).z_data = z_data;

% Only prompt the user if the field does not exist or if the user
% asks to be prompted in the parameters.
if ~isfield(d(i).samples(i_sam).sites(site), 'ij_rect') ...
    || isempty(d(i).samples(i_sam).sites(site).ij_rect) ...
    || reprocess
    % Create a figure that fits the entire screen.
    figure('units', 'normalized', 'outerposition', [0 0 1 1]);

    % Plot the current sample depths in the upper left.
    if isfield(d(i).samples(i_sam), 'y_mean_old') ...
        && ~isempty(d(i).samples(i_sam).y_mean_old)
        % Select the top left plot location.
        subplot(2, 3, 1);
        hold on;
    end
end

```

```

% Plot the old data.
errorbar(d(i).samples(i_sam).y_mean_old * 1e3, ...
        d(i).samples(i_sam).dz_mean_old * 1e6, ...
        d(i).samples(i_sam).dz_std_old * 1e6, 'ok');

% Plot the current site in a different color.
errorbar(d(i).samples(i_sam) ...
        .y_mean_old(i_ROI:(i_ROI+1)) * 1e3, ...
        d(i).samples(i_sam) ...
        .dz_mean_old(i_ROI:(i_ROI+1)) * 1e6, ...
        d(i).samples(i_sam) ...
        .dz_std_old(i_ROI:(i_ROI+1)) * 1e6, 'or');

% Plot the new data.
if ~isempty(d(i).samples(i_sam).y_mean)
    errorbar(d(i).samples(i_sam).y_mean * 1e3, ...
            d(i).samples(i_sam).dz_mean * 1e6, ...
            d(i).samples(i_sam).dz_std * 1e6, 'xb');
    legend('Old depths', 'Current site', 'New depths');
else
    legend('Old depths', 'Current site');
end

% Annotate the plot.
xlabel('Axial distance (mm)');
ylabel('Total carbon depth (\mum)');
end

% Plot the linear fit based on sample curvature.
if isfield(d(i).samples(i_sam).sites(site), ...
        'fits_MATLAB_params') && ~isempty(d(i) ...
        .samples(i_sam).sites(site).fits_MATLAB_params)
    % Select the bottom left plot location.
    subplot(2, 3, 4);

    % Plot the circle fit Y coefficients, and the linear fit.
    plot(d(i).samples(i_sam).sites(site).y_domain, ...
        (d(i).samples(i_sam).sites(site) ...
        .fits_MATLAB_params(:, 2) - ...
        d(i).samples(i_sam).sites(site) ...
        .fits_MATLAB_params(:, 3)) * 1e6, 'ok');
    hold on;
    plot(d(i).samples(i_sam).sites(site).y_domain, ...
        polyval(d(i).samples(i_sam).sites(site).fit_b_line, ...
        d(i).samples(i_sam).sites(site).y_domain) * 1e6, 'k');

    % Annotate the plot.
    xlabel('Y index');
    ylabel('Y min offset (\mum)');
    legend('Circle fit data', 'Linear fit to data');
end

```

```

% Show a filled contour map of the data, with indices on the X
% and Y axes.
subplot(2, 3, [2:3, 5:6]);
contourf(1:length(x_data), y_data * 1000, ...
    (z_data - nanmean(nanmean(z_data))) * 1e6);
colorbar();
ylabel('Y (mm)');
yyaxis right;
contourf(z_data);
xlabel('X index');
ylabel('Y index');
zlabel('Height (\mum)');
title(sprintf('Date: %s, Sample: %s, Site: %i', d(i).date, ...
    sample_name, site), 'Interpreter', 'none');

% Plot the old rectangles if they exist.
if isfield(d(i).samples(i_sam).sites(site), 'ij_rect') ...
    && ~isempty(d(i).samples(i_sam).sites(site).ij_rect)
    % Save the old ROIs at the current site.
    d(i).samples(i_sam).sites(site).ij_rect_old = ...
        d(i).samples(i_sam).sites(site).ij_rect;
    d(i).samples(i_sam).sites(site).ij_rect = [];

    % Iterate through each ROI and plot it.
    hold on;
    for k = 1:size(d(i).samples(i_sam).sites(site) ...
        .ij_rect_old, 1)
        rectangle('Position', d(i).samples(i_sam) ...
            .sites(site).ij_rect_old(k, :), 'EdgeColor', 'r');
    end
end

% Prompt the user for three rectangles.
ij_rect = nan(3, 4);
for k = 1:size(ij_rect, 1)
    % Prompt the user for a rectangle and wait for them to
    % adjust the boundaries. Double click to submit.
    h_rect = imrect();
    wait(h_rect);

    % If the user closes the image without adding rectangles,
    % then they want to keep their old ROIs.
    if isempty(h_rect) || ~h_rect.isValid()
        ij_rect = d(i).samples(i_sam).sites(site).ij_rect_old;
        d(i).samples(i_sam).sites(site).ij_rect = ij_rect;
        break;
    end

    % Save the position in the rectangle.
    ij_rect(k, :) = h_rect.getPosition();
end
close();

% Save ij_rect in the output data variable.
d(i).samples(i_sam).sites(site).ij_rect = ij_rect;

```

```

else
    ij_rect = d(i).samples(i_sam).sites(site).ij_rect;
end

% Process the rectangle coordinates into integers.
i_x_rect = max(1, round(ij_rect(:, 1)));
i_y_rect = round(ij_rect(:, 2));
len_x_rect = round(ij_rect(:, 3));
len_y_rect = round(ij_rect(:, 4));
x_span_metal = i_x_rect(1):(i_x_rect(1)+len_x_rect(1)-1);

% Fit circles to each 1D axial slice of the data in order to
% normalize for the cylindrical geometry.
fits_MATLAB = cell(len_y_rect(1), 1);
fits_MATLAB_params = nan(len_y_rect(1), 3);
fits_MATLAB_SE = nan(len_y_rect(1), 3);
y_domain = i_y_rect(1):(i_y_rect(1)+len_y_rect(1));
for k = y_domain
    % Gather this slice's data into a compatible format.
    fit_input = [x_data(x_span_metal)', z_data(k, x_span_metal)'];

    % Clean the input of any NaN entries.
    i_fit_input = ~isnan(fit_input(:, 2));
    fit_input_clean = fit_input(i_fit_input, :);

    % Only fit if there are at least 3 points.
    if size(fit_input_clean, 1) < 3
        continue;
    end

    % Index that starts at 1 and ends at len_y_rect.
    k_fit = k - i_y_rect(1) + 1;

    % Generate a iteration zero for nonlinear fitter.
    [y_min, i_y_min] = min(fit_input_clean(:, 2));
    fit_zero = [fit_input_clean(i_y_min, 1), y_min + r_zero, ...
        r_zero];

    % Use the Pratt fit as a starting point for MATLAB's nonlinear
    % curve fitting tool, which calculates parameter uncertainty.
    fits_MATLAB{k_fit} = fitnlm(fit_input_clean(:, 1), ...
        fit_input_clean(:, 2), fn_circle, fit_zero);
    fits_MATLAB_params(k_fit, :) = ...
        fits_MATLAB{k_fit}.Coefficients.Estimate';
    fits_MATLAB_SE(k_fit, :) = ...
        fits_MATLAB{k_fit}.Coefficients.SE';
end

% Calculate the mean of the x offset and radius.
a_mean = mean(fits_MATLAB_params(:, 1));
r_mean = mean(fits_MATLAB_params(:, 3));

```

```

% Fit a line to the y offset to determine the tilt of the sample.
% TODO: Switch to robust linear fit.
y_to_min = fits_MATLAB_params(:, 2) - fits_MATLAB_params(:, 3);
fit_b_line = polyfit(y_domain', y_to_min, 1);
fit_b_line_rob = flip(robustfit(y_domain', y_to_min))';

% Flatten the z data based on the mean of the x offset parameter
% and the linear curve fit of the y_to_min parameter. Good luck
% propagating error you fucking idiot.
z_flat = nan(size(z_data));
for k = 1:length(y_data)
    y_to_min_fit(k) = polyval(fit_b_line_rob, k, 1);
    b_val = y_to_min_fit(k) + r_mean;
    z_correct(k, :) = fn_circle([a_mean, b_val, r_mean], x_data);
end
z_flat = z_data - z_correct;

% Save the fit data.
d(i).samples(i_sam).sites(site).y_domain = y_domain;
d(i).samples(i_sam).sites(site).fits_MATLAB_params ...
    = fits_MATLAB_params;
d(i).samples(i_sam).sites(site).r_mean = r_mean;
d(i).samples(i_sam).sites(site).a_mean = a_mean;
d(i).samples(i_sam).sites(site).fit_b_line = fit_b_line_rob;

% Find the means in the regions of interest.
for k = 1:size(ij_rect, 1)
    % Calculate various mean and std metrics in a structure that
    % will later be saved to the output variable.
    s = struct();
    s.xspan = i_x_rect(k):(i_x_rect(k)+len_x_rect(k));
    s.yspan = i_y_rect(k):(i_y_rect(k)+len_y_rect(k));
    s.z_flat_ROI = z_flat(s.yspan, s.xspan);
    s.z_flat_ROI_mean_x = nanmean(s.z_flat_ROI, 1);
    s.z_flat_ROI_mean_y = nanmean(s.z_flat_ROI, 2);
    s.z_flat_ROI_mean = nanmean(s.z_flat_ROI(:));
    s.z_flat_ROI_std = nanstd(s.z_flat_ROI(:));
    s.y_mean = interp1(1:length(y_data), y_data, mean(s.yspan));

    % Determine if this ROI is the metal surface or carbon.
    if k > 1
        % Determine the mean and standard deviation of the depth
        % difference with the metal surface ROI.
        s.dz_mean = s.z_flat_ROI_mean - d(i).samples(i_sam)...
            .sites(site).ROIs(1).z_flat_ROI_mean;
        s.dz_std = s.z_flat_ROI_std;

        % Save the data in sample-scope arrays that can be
        % accessed more quickly than digging in the trenches of
        % the sites/ROIs of each sample.
        d(i).samples(i_sam).y_mean(i_ROI) = s.y_mean;
        d(i).samples(i_sam).dz_mean(i_ROI) = s.dz_mean;
        d(i).samples(i_sam).dz_std(i_ROI) = s.dz_std;
        i_ROI = i_ROI + 1;
    end
end

```

```

else
    % This is the metal surface ROI. The mean is, of course, 0
    % since we are defining it that way. The
    % standard deviation is the Z depth standard deviation.
    s.dz_mean = 0;
    s.dz_std = s.z_flat_ROI_std;
end

    % Save the ROI structure in the output data variable.
    d(i).samples(i_sam).sites(site).ROIs(k) = s;
end

    % Save the sample name to check with the next row.
    last_sample_name = sample_name;

    % Iterate the Excel file row counter to move on to the next site.
    j = j + 1; % Counter for current row in Excel spreadsheet.
end
end

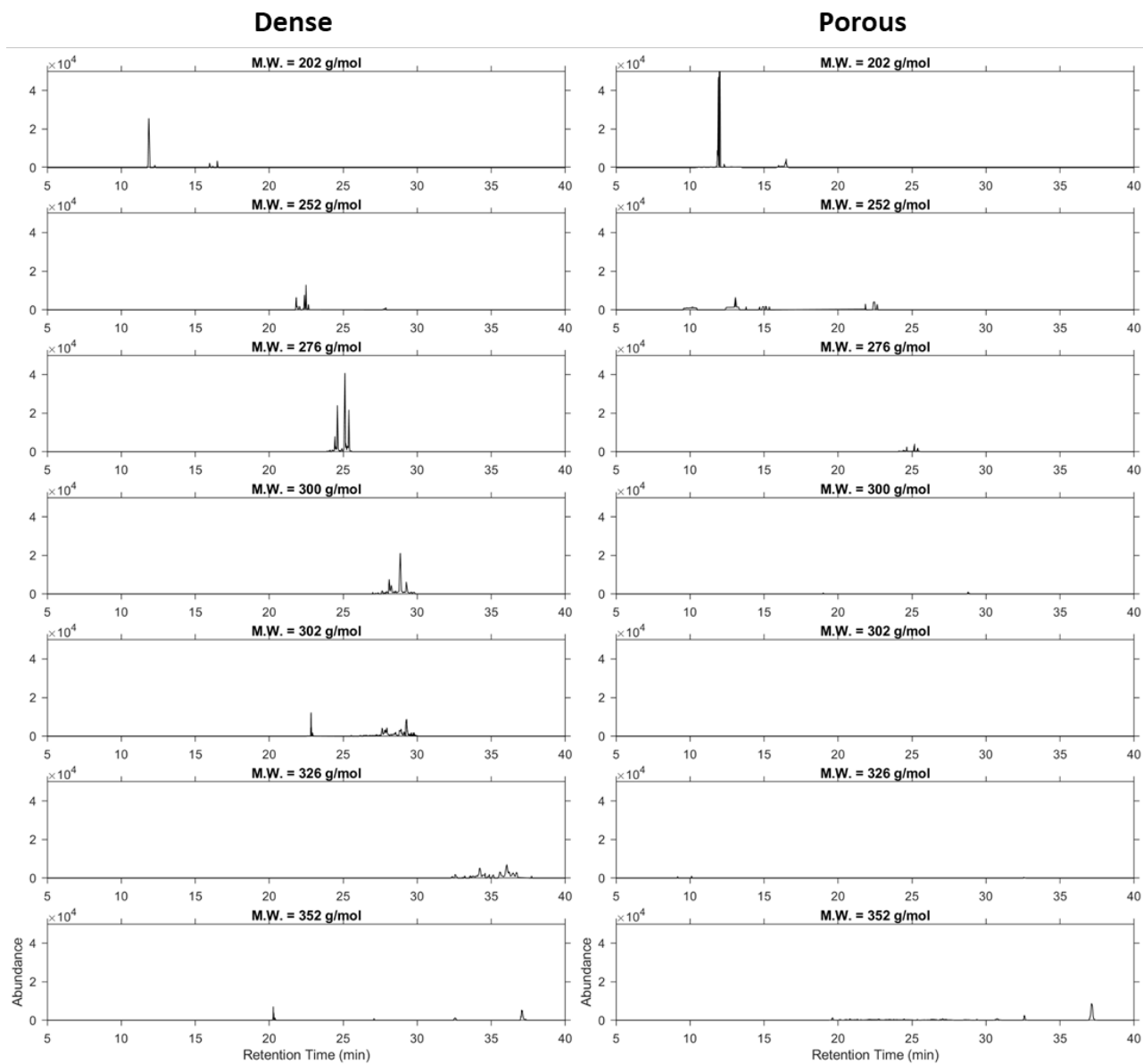
% Create profilometer map to get from sample names to struct locations.
d_map = containers.Map();
for i = 1:length(d)
    for j = 1:length(d(i).samples)
        if ~isKey(d_map, d(i).samples(j).name)
            d_map(d(i).samples(j).name) = [];
        end
        d_map(d(i).samples(j).name) = [d_map(d(i).samples(j).name); ...
            [i, j]];
    end
end

% Save the data in a version 7.3 file because the d_prof variable is larger
% than 2 GB.
if ~isempty(d)
    d_prof = d;
    d_prof_map = d_map;
    save(file_analysis, 'd_prof', 'd_prof_map', '-v7.3');
end

end

```

APPENDIX D. TASK 1 EXTRACTED ION SPECTRA



APPENDIX E. TASK 1 RAMAN SPECTROSCOPY ANALYSIS CODE

```
function [d_raman, errs, P_fits] = process_raman(f_terms, dates)
%PROCESS_RAMAN Processes Raman spectroscopy raw data.
% PARAMETERS
%   f_terms (boolean array): List describing which deconvolution curve to
%   use, 0 for Gaussian and 1 for Lorentzian.
%   dates (cell array of char arrays): List of dates to process data from.
%   Defaults to processing data from every date.

% Load baseline fitting code.
addpath('F:\Programs\baseline');

% Sample length for locating bottom sample Y positions.
L_sample = 2.9 * 0.0254;

% 0 for Gaussian, 1 for Lorentzian.
N = length(f_terms);
f_ram = @(a, x) 0;
f_ram_terms = {};
for i = 1:N
    j = (i - 1) * 3 + 1;
    if f_terms(i) % Lorentzian
        f_ram_terms{i} = @(a, x) a(j) ./ (1 + ((a(j+1) - x) / (a(j+2) / 2)).^2);
    else % Gaussian
        f_ram_terms{i} = @(a, x) a(j) * exp(-(x - a(j+1)) ./ a(j+2)).^2);
    end
    f_ram = @(a, x) f_ram(a, x) + f_ram_terms{i}(a, x);
end

% Raman curve fitting parameters.
% Raman carbon component order: G, D, A, D2, D'
P_ub = [1e5, 1600, Inf, 1e5, 1375, Inf, 1e5, 1525, Inf, 1e5, 1250, ...
        Inf, 1e5, 1630, Inf];
P_lb = [0, 1571, 0, 0, 1343, 0, 0, 1475, 35, 0, 1127, 0, 0, 1595, 0];
P_0 = [1000, 1585, 10, 1000, 1360, 10, 1000, 1500, 10, 1000, 1180, 10, ...
        1000, 1610, 10];
M = length(f_terms);
P_ub = P_ub(1:(3*M));
P_lb = P_lb(1:(3*M));
P_0 = P_0(1:(3*M));
[~, order_check] = sortrows(reshape(P_0, [3, M])', 2);
check_array = 1:M;
for k = 1:M
    order(k) = find(order_check' == check_array(k));
end
options = optimset('Display', 'off');

% Raman spectroscopy data folder location.
folder_data = 'F:\piper\Coking\phaseII\task1\Data';
folder_raman = [folder_data, '\Raman Spectroscopy'];
```

```

% Raman spectroscopy data analysis file where results are stored.
file_analysis = [folder_raman, '\data.mat'];

% Load or create a variable for saving data in a MATLAB structure.
d = struct();
if exist(file_analysis, 'file') == 2
    load(file_analysis, 'd_raman');
    if exist('d_raman', 'var')
        d = d_raman;
    end
end

% Let the user specify a list of dates.
if ~exist('dates', 'var')
    dates = {};
end

% Load the test info Excel file sheet-by-sheet after checking for its
% existence. This file contains information about the axial locations of
% the Raman spectroscopy measurements for each sample and test date.
data_info_file = [folder_raman, '\Raman Locations.xlsx'];
if ~isfile(data_info_file)
    error('No test data file exists at "%s"', data_info_file);
end
[~, sheets] = xlsfinfo(data_info_file);
i_site = 1;
for i = 1:length(sheets)
    % The sheet name should also match the test date.
    d(i).date = sheets{i};

    % Don't process this data if the dates cell array is specified and this
    % date is not in that cell array.
    if ~isempty(dates) && ~any(strcmp(dates, d(i).date))
        continue;
    end

    % Create a field called samples that is also a structure if it does not
    % already exist from loading a previous analysis data file.
    if ~isfield(d(i), 'samples') || isempty(d(i).samples)
        d(i).samples = struct();
    end

    % Open the Excel file sheet corresponding to the date at index i.
    [~, ~, site_info_raw] = xlsread(data_info_file, sheets{i});

    % Loop through each sample/site combination and process spectra data.
    j = 2; % Excel file row counter.
    last_sample_name = ''; % Used to check for a row with a new sample.
    i_sample = 0; % Counter that increases for each new sample.
    k = 1;
    while j <= size(site_info_raw, 1)
        % Extract the Excel data into local variables.
        sample_name = site_info_raw{j, 1};
        site = site_info_raw{j, 2};
        site_type = site_info_raw{j, 3};
    end
end

```

```

y_abs = site_info_raw{j, 4} * 1e-3; % In meters.
y_zero = site_info_raw{j, 5} * 1e-3; % In meters.
skip = site_info_raw{j, 6};

% Check if the sample name changed. If it did, then increment the
% sample counter which is used to index the returned data variable.
if ~strcmp(sample_name, last_sample_name)
    % Increment the sample counter and reset the ROI counter.
    i_sample = i_sample + 1;

    % Save the sample name.
    d(i).samples(i_sample).name = sample_name;

    % Add the sites struct if it doesn't already exist.
    d(i).samples(i_sample).sites = struct();

    % Save the sample name.
    d(i).samples(i_sample).name = sample_name;

    %
    k = 1;
end

% Determine if sample is upper or lower to get relative y.
% TODO: Check directionality.
if endsWith(sample_name, 'u')
    y = y_abs - y_zero;
elseif endsWith(sample_name, 'b')
    y = L_sample - (y_zero - y_abs);
end

% Save the site data in the output data variable.
d(i).samples(i_sample).sites(k).site = site;
d(i).samples(i_sample).sites(k).type = site_type;
d(i).samples(i_sample).sites(k).y_abs = y_abs;
d(i).samples(i_sample).sites(k).y_zero = y_zero;
d(i).samples(i_sample).sites(k).y = y;
d(i).samples(i_sample).sites(k).skip = skip;

% Create a variable for the sample file.
file_sample = sprintf('%s\\%s\\%s\\Site%s.txt', ...
    folder_raman, d(i).date, sample_name, num2str(site));
if 2 ~= exist(file_sample, 'file')
    warning(['File "', file_sample, '" does not exist.']);
    last_sample_name = sample_name;
    j = j + 1;
    continue;
end

```

```

% Skip processing of this sample if specified in the data file.
% This is typically done when the scratch in the carbon surface is
% not sufficiently wide, is too diagonal, or is too messy.
if skip == 1
    last_sample_name = sample_name;
    j = j + 1;
    continue;
end

% Load the raw TXT spectrum file.
raw_spectrum = dlmread(file_sample);
WN = raw_spectrum(:, 1);
I = raw_spectrum(:, 2);

% Calculate the derivative of I WRT WN.
% Uses central differencing with dI/dWN = 0 guard points.
Is = smoothdata(I, 'gaussian', 40);
dIsdWN = ([Is(2:end); Is(end)] - [Is(1); Is(1:end-1)]) ...
    ./ ([WN(2:end); WN(end)] - [WN(1); WN(1:end-1)]);

% Linear background fit.
WN_low = 800;
WN_high = 2000;
i_l = find(WN > WN_low, 1);
i_r = find(WN > WN_high, 1);
bg_poly = polyfit(WN(i_l), WN(i_r), [I(i_l), I(i_r)], 1);

% Correct the intensities.
WN_nobg = WN(i_l:i_r);
I_nobg = I(i_l:i_r) - polyval(bg_poly, WN(i_l:i_r));

% Calculate the intensity ratio without fitting/deconvolution.
i_mid = find(WN_nobg > 1495, 1);
[I_max_low, i_max_low] = max(I_nobg(1:i_mid));
[I_max_high, i_max_high] = max(I_nobg(i_mid:end));
WN_max_low = WN_nobg(i_max_low);
WN_max_high = WN_nobg(i_mid + i_max_high);
I_ratio = I_max_low / I_max_high;
L_a = 43.75 / I_ratio;

% Fit the data with 2 Gaussians.
[f_gauss2, G_gauss2] = fit(WN(i_l:i_r), I_nobg, ...
    ['gauss', num2str(length(f_terms))]);
P_fit_g(i_site, :) = coeffvalues(f_gauss2);
errs_g(i_site, :) = G_gauss2.sse;

% Second fit.
m = 1;
sorted = false;
P_0 = P_fit_g(i_site, :);
while ~sorted && m < 5
    [P_fit, errs(i_site)] = lsqcurvefit(f_ram, P_0, ...
        WN(i_l:i_r), I_nobg, P_lb, P_ub, options);
    P_fit_shape = reshape(P_fit, [3, M]);
    [P_fit_shape_sorted, order_check2] = sortrows(P_fit_shape, 2);

```

```

        P_0 = reshape(P_fit_shape_sorted(order, :)', [1, 3*M]);
        sorted = all(order_check == order_check2);
        m = m + 1;
    end
    P_fits(i_site, :) = P_fit;

    % Calculate peak areas.
    P_As = [];
    for m = 1:N
        if f_terms(m)
            C = 1.57;
        else
            C = 1.0645;
        end
        P_A(m) = C * P_fit(3*(m-1)+1) * P_fit(3*(m-1)+3);
    end

    % Calculate peak area ratios.
    A_ratio = P_A(2) / P_A(1);
    AD2_AG = P_A(5) / P_A(1);
    R2 = P_A(2) / (P_A(1) + P_A(2) + P_A(5));
    AD1_per = P_A(2) / (P_A(1) + P_A(2));

    % Save a variable for the site type.
    if strcmp(site_type, 'thin')
        C_type = 1;
    elseif strcmp(site_type, 'thick')
        C_type = 2;
    else % Transition
        C_type = 3;
    end

    % Save to the data variable.
    d(i).samples(i_sample).sites(k).C_type = C_type;
    d(i).samples(i_sample).sites(k).WN = WN;
    d(i).samples(i_sample).sites(k).I = I;
    d(i).samples(i_sample).sites(k).i_l = i_l;
    d(i).samples(i_sample).sites(k).i_r = i_r;
    d(i).samples(i_sample).sites(k).WN_nobg = WN_nobg;
    d(i).samples(i_sample).sites(k).I_nobg = I_nobg;
    d(i).samples(i_sample).sites(k).I_max_low = I_max_low;
    d(i).samples(i_sample).sites(k).I_max_high = I_max_high;
    d(i).samples(i_sample).sites(k).WN_max_low = WN_max_low;
    d(i).samples(i_sample).sites(k).WN_max_high = WN_max_high;
    d(i).samples(i_sample).sites(k).bg_poly = bg_poly;
    d(i).samples(i_sample).sites(k).I_ratio = I_ratio;
    d(i).samples(i_sample).sites(k).A_ratio = A_ratio;
    d(i).samples(i_sample).sites(k).L_a = L_a;
    d(i).samples(i_sample).sites(k).L_a = L_a;
    d(i).samples(i_sample).sites(k).f_ram = f_ram;
    d(i).samples(i_sample).sites(k).f_ram_terms = f_ram_terms;
    d(i).samples(i_sample).sites(k).P_fit = P_fit;
    d(i).samples(i_sample).sites(k).P_fit_errs = errs(i_site);
    d(i).samples(i_sample).sites(k).R2 = R2;
    d(i).samples(i_sample).sites(k).AD2_AG = AD2_AG;
    d(i).samples(i_sample).sites(k).AD1_per = AD1_per;

```

```

    % Save the sample name to check with the next row.
    last_sample_name = sample_name;

    % Iterate the Excel file row counter to move on to the next site.
    j = j + 1; % Counter for current row in Excel spreadsheet.
    k = k + 1; % Counter for the current site number of this sample.
    i_site = i_site + 1; % Counter for total number of sites, in all.
end
end

% Create the Raman map.
d_map = containers.Map();
for i = 1:length(d)
    for j = 1:length(d(i).samples)
        % Get name, site, and depths into smaller variable names.
        name = d(i).samples(j).name(1:end-2);
        y = [d(i).samples(j).sites.y]';
        I_ratio = [d(i).samples(j).sites.I_ratio]';
        L_a = [d(i).samples(j).sites.L_a]';
        WN_low = [d(i).samples(j).sites.WN_max_low]';
        WN_high = [d(i).samples(j).sites.WN_max_high]';
        C_type = [d(i).samples(j).sites.C_type]';
        P_fit = [d(i).samples(j).sites.P_fit];
        P_fit = reshape(P_fit, N*3, length(P_fit)/(N*3));
        R2 = [d(i).samples(j).sites.R2]';
        AD2_AG = [d(i).samples(j).sites.AD2_AG]';
        AD1_per = [d(i).samples(j).sites.AD1_per]';

        % Create the map key if it doesn't exist.
        if isempty(find(cellfun(@(s) ~isempty(strfind(name, s)), ...
            keys(d_map))))
            d_map(name) = [];
        end

        % Add the data to the map.
        d_map(name) = [d_map(name); [y, I_ratio, L_a, WN_low, WN_high, ...
            C_type, P_fit, R2, AD2_AG, AD1_per]];
    end
end

% Save the data.
if ~isempty(d)
    d_raman = d;
    d_raman_map = d_map;
    save(file_analysis, 'd_raman', 'd_raman_map');
end

```

APPENDIX F. TASK 4 CONDITION TABLES

Low contraction ratio (3.4), low pressure arrangement (325 psia). This table is repeated from Section 5.2 for completeness.

State	Double Ignition	Igniter Off	O ₂ Ramp	H ₂ +Fuel	Nominal
$\dot{m}_{O_2,ign}$ (g/s)	10	10	-	-	-
$\dot{m}_{H_2,ign}$ (g/s)	0.13	-	-	-	-
$\dot{m}_{O_2,main}$ (g/s)	-	-	75	75	75
$\dot{m}_{H_2,main}$ (g/s)	1.88	1.88	1.88	1.88	-
$\dot{m}_{fu,main}$ (g/s)	-	-	-	31.9	31.9
$\dot{m}_{fu,film}$ (g/s)	-	-	-	24.5	24.5
$\dot{m}_{H_2O,film}$ (g/s)	28	28	28	28	28
P_{ign} (psia)	178	-	-	-	-
P_{main} (psia)	81	80	179	341	321
O/F_{ign}	75	∞	∞	∞	∞
O/F_{main}	4.98	5.33	40.0	2.22	2.35
Time (s)	up to 2	0.5	2	0.5	up to 40

Low contraction ratio (3.4), medium pressure arrangement (650 psia).

State	Double Ignition	Igniter Off	O ₂ Ramp	H ₂ +Fuel	Nominal
$\dot{m}_{O_2,ign}$ (g/s)	10	10	-	-	-
$\dot{m}_{H_2,ign}$ (g/s)	0.13	-	-	-	-
$\dot{m}_{O_2,main}$ (g/s)	-	-	150	150	150
$\dot{m}_{H_2,main}$ (g/s)	3.75	3.75	3.75	3.75	-
$\dot{m}_{fu,main}$ (g/s)	-	-	-	61.5	61.5
$\dot{m}_{fu,film}$ (g/s)	-	-	-	24.5	24.5
$\dot{m}_{H_2O,film}$ (g/s)	28	28	28	28	28
P_{ign} (psia)	178	-	-	-	-
P_{main} (psia)	88	87	349	680	639
O/F_{ign}	75	∞	∞	∞	∞
O/F_{main}	2.58	2.67	40.0	2.30	2.44
Time (s)	up to 2	0.5	2	0.5	up to 40

Low contraction ratio (3.4), high pressure arrangement (1300 psia).

State	Double Ignition	Igniter Off	O ₂ Ramp	H ₂ +Fuel	Nominal
$\dot{m}_{O_2,ign}$ (g/s)	10	10	-	-	-
$\dot{m}_{H_2,ign}$ (g/s)	0.13	-	-	-	-
$\dot{m}_{O_2,main}$ (g/s)	-	-	300	300	300
$\dot{m}_{H_2,main}$ (g/s)	7.5	7.5	7.5	7.5	-
$\dot{m}_{fu,main}$ (g/s)	-	-	-	118	118
$\dot{m}_{fu,film}$ (g/s)	-	-	-	24.5	24.5
$\dot{m}_{H_2O,film}$ (g/s)	28	28	28	28	28
P_{ign} (psia)	178	-	-	-	-
P_{main} (psia)	100	99	686	1355	1268
O/F_{ign}	75	∞	∞	∞	∞
O/F_{main}	1.31	1.33	40.0	2.39	2.54
Time (s)	up to 2	0.5	2	0.5	up to 40

High contraction ratio (6.8), low pressure arrangement (650 psia).

State	Double Ignition	Igniter Off	O ₂ Ramp	H ₂ +Fuel	Nominal
$\dot{m}_{O_2,ign}$ (g/s)	10	10	-	-	-
$\dot{m}_{H_2,ign}$ (g/s)	0.13	-	-	-	-
$\dot{m}_{O_2,main}$ (g/s)	-	-	75	75	75
$\dot{m}_{H_2,main}$ (g/s)	1.88	1.88	1.88	1.88	-
$\dot{m}_{fu,main}$ (g/s)	-	-	-	30.7	30.7
$\dot{m}_{fu,film}$ (g/s)	-	-	-	24.5	24.5
$\dot{m}_{H_2O,film}$ (g/s)	28	28	28	28	28
P_{ign} (psia)	349	-	-	-	-
P_{main} (psia)	162	161	357	680	639
O/F_{ign}	75	∞	∞	∞	∞
O/F_{main}	4.98	5.33	40.0	2.30	2.44
Time (s)	up to 2	0.5	2	0.5	up to 40

High contraction ratio (6.8), medium pressure arrangement (1300 psia).

State	Double Ignition	Igniter Off	O ₂ Ramp	H ₂ +Fuel	Nominal
$\dot{m}_{O_2,ign}$ (g/s)	10	10	-	-	-
$\dot{m}_{H_2,ign}$ (g/s)	0.13	-	-	-	-
$\dot{m}_{O_2,main}$ (g/s)	-	-	150	150	150
$\dot{m}_{H_2,main}$ (g/s)	3.75	3.75	3.75	3.75	-
$\dot{m}_{fu,main}$ (g/s)	-	-	-	59.1	59.1
$\dot{m}_{fu,film}$ (g/s)	-	-	-	24.5	24.5
$\dot{m}_{H_2O,film}$ (g/s)	28	28	28	28	28
P_{ign} (psia)	349	-	-	-	-
P_{main} (psia)	176	175	699	1355	1268
O/F_{ign}	75	∞	∞	∞	∞
O/F_{main}	2.58	2.67	40.0	2.39	2.54
Time (s)	up to 2	0.5	2	0.5	up to 40

High contraction ratio (6.8), high pressure arrangement (2600 psia).

State	Double Ignition	Igniter Off	O ₂ Ramp	H ₂ +Fuel	Nominal
$\dot{m}_{O_2,ign}$ (g/s)	10	10	-	-	-
$\dot{m}_{H_2,ign}$ (g/s)	0.13	-	-	-	-
$\dot{m}_{O_2,main}$ (g/s)	-	-	300	300	300
$\dot{m}_{H_2,main}$ (g/s)	7.5	7.5	7.5	7.5	-
$\dot{m}_{fu,main}$ (g/s)	-	-	-	114	114
$\dot{m}_{fu,film}$ (g/s)	-	-	-	24.5	24.5
$\dot{m}_{H_2O,film}$ (g/s)	28	28	28	28	28
P_{ign} (psia)	349	-	-	-	-
P_{main} (psia)	199	199	1372	2699	2521
O/F_{ign}	75	∞	∞	∞	∞
O/F_{main}	1.31	1.33	40.0	2.48	2.64
Time (s)	up to 2	0.5	2	0.5	up to 40

APPENDIX G. TASK 4 COMBUSTOR AUTOSEQUENCE

A conservative and proven autosequence for the Task 4 combustor is shown below. The timings could be tightened up based on qualification testing, but more testing would be required to validate new timings. “Open” and “close” refer to the state of run valves and ramping refers to linearly increasing electronic regulator pressure as a function of time. The “Cool H₂O” run valve is in fact two different run valves, one upstream and one downstream of the combustor. The downstream valve is opened at the beginning of the test and the upstream valve is closed at the end to prevent water hammer in the main combustor coolant channels, which was demonstrated to consistently unseat o-rings if allowed to happen.

Time (s)	Ign O ₂	Ign H ₂	Main O ₂	Main H ₂	Main Fu	Film Fu	Film H ₂ O	Cool H ₂ O	Spark	Ign O ₂ Purge	Ign H ₂ Purge	Ign O ₂ Purge	Main Fu Purge	Film Fu Purge
0							open	open		open	open	open	open	open
1.5	open													
2									on					
2.5		open		open										
3.5		close							off					
4.5-5.5			ramp up											
4.75	close													
6.5					open	open								
7.5				close										
9.5					close	close								
10.5			close				close							
11								close						

APPENDIX H. TASK 4 COMBUSTOR QUALIFICATION TEST MATRICES

Measured igniter conditions are shown in the table below, as well as general comments about each given test. Igniter pressure was measured directly by a pressure transducer whereas igniter mixture ratio (O/F) and mass flow rate ($\dot{m}$) were measured by a pressure transducer upstream of a sonic orifice with an assumed discharge coefficient of 0.6. Dashes (-) indicate when a given field is not applicable to a given test. For instance, the igniter was not used during cold flow tests 2.1 and 2.2.

Test Num	Test Date	Igniter Pressure (psia)	Igniter O/F	Igniter $\dot{m}$ (g/s)	Ignition	Comments
1.1	04/24/20	89	88	4.7	yes	
1.2	04/24/20	97	70	4.7	yes	
1.3	04/24/20	151	92	9.6	yes	
1.4	04/24/20	166	71	9.6	yes	
1.5	04/24/20	165	72	9.6	yes	
2.1	04/28/20	-	-	-	-	Kerosene-N ₂ cold flow
2.2	04/28/20	-	-	-	-	Kerosene-N ₂ cold flow
3.1	04/29/20	120	67	4.7	yes	
3.2	04/29/20	119	73	4.7	yes	
3.3	04/29/20	118	75	4.7	yes	
3.4	04/29/20	119	75	4.7	yes	
3.5	04/29/20	119	76	4.7	yes	
3.6	04/29/20	119	76	4.7	yes	
4.1	05/12/20	114	68	4.7	yes	
4.2	05/12/20	114	72	4.7	yes	
4.3	05/12/20	112	75	4.7	yes	
4.4	05/12/20	113	75	4.7	yes	
4.5	05/12/20	113	75	4.7	yes	
4.6	05/12/20	213	69	9.7	yes	Coolant jacket failure during O ₂ ramp

5.1	05/13/20	216	69	9.6	yes	
5.2	05/13/20	213	70	9.5	yes	O ₂ ramp test only, no kerosene in this attempt
5.3	05/13/20	210	70	9.4	yes	Incorrect underpressure redline trips, thus cutting test short
5.4	05/13/20	202	67	9.0	yes	O ₂ bottle low
6.1	05/15/20	219	71	9.7	yes	Double ignition only to check heat transfer
6.2	05/15/20	218	72	9.7	yes	
6.3	05/15/20	-	-	-	-	Incorrect coolant pressurization order causes failure pre-test
7.1	05/15/20	380	81	9.8	yes	Smaller nozzles for double pressure
7.2	05/15/20	243	78	9.8	no	Ablated igniter set screw too far from spark rod
7.3	05/15/20	243	78	9.8	no	Sanity check of 7.2 failure; same failure occurs
7.4	05/15/20	381	78	9.7	yes	
7.5	05/15/20	379	78	9.7	yes	

Combustor conditions are shown at the following states: double ignition, igniter off, O₂ ramp, kerosene-H₂ transition, and nominal operation (kerosene-O₂). Pressures and mixture ratios for the kerosene-H₂ transition are omitted for brevity. The “Flame Held at State Transitions” column refers to the following states: double ignition, O₂ ramp, and nominal operation.

Test Num	Chamber Pressure (psia)				Chamber Mixture Ratio				Flame Held at State Transitions	Chamber Installed	Comments on $\dot{m}$ with respect to Nominal Values
	Double Ignition	Igniter Off	O ₂ Ramp	Nominal	Double Ignition	Igniter Off	O ₂ Ramp	Nominal	Y: yes N: no		
2.1	-	-	-	15	-	-	-	1.56	-, -, -	no	N ₂ as O ₂ main, low N ₂ bottle pressure
2.2	-	-	-	15	-	-	-	1.40	-, -, -	no	N ₂ as O ₂ main, low N ₂ bottle pressure
3.1	15	15	-	-	2.70	2.78	-	-	Y, -, -	no	
3.2	15	15	15	-	2.72	2.78	40.8	-	Y, N, -	no	
3.3	15	15	15	-	2.71	2.79	18.7	-	Y, Y, -	no	O ₂ main half
3.4	15	15	15	15	2.70	2.79	19.1	0.91	Y, Y, N	no	O ₂ main half
3.5	15	15	15	15	2.70	2.79	18.4	1.89	Y, Y, N	no	O ₂ main half, kero main half
3.6	15	15	15	15	2.70	2.78	19.2	2.49	Y, Y, Y	no	O ₂ main half, kero main 0.4x
4.1	19	-	-	-	2.73	-	-	-	N, -, -	short	
4.2	15	-	-	-	2.74	-	-	-	N, -, -	short	
4.3	35	32	35	-	2.73	2.83	41.2	-	Y, N, -	short	
4.4	30	32	25	-	2.73	2.83	20.0	-	Y, N, -	short	O ₂ main half
4.5	31	33	19	-	2.74	2.83	4.8	-	Y, N, -	short	O ₂ main reduced significantly
4.6	50	60	107	-	5.34	5.77	21.0	-	Y, Y, -	short	O ₂ main half, coolant failure
5.1	58	54	40	-	5.87	6.37	47.2	-	Y, N, -	short	
5.2	58	54	88	-	5.85	6.32	29.7	-	Y, Y, -	short	O ₂ main ramp from half from now on
5.3	58	53	90	-	5.77	6.21	31.6	-	Y, Y, -	short	
5.4	56	52	90	152	5.56	5.95	30.7	2.42	Y, Y, Y	short	
6.1	61	-	-	-	5.51	-	-	-	Y, -, -	long	Lower coolant mass flow (6.1-7.5)
6.2	64	62	110	211	5.53	5.89	29.1	2.40	Y, Y, Y	long	
6.3	-	-	-	-	-	-	-	-	-, -, -	long	
7.1	133	132	94	-	6.00	6.35	-	-	Y, N, -	long	
7.2	-	-	-	-	-	-	-	-	-, -, -	long	No ignition
7.3	-	-	-	-	-	-	-	-	-, -, -	long	No ignition
7.4	131	131	83	-	5.91	6.29	24.0	-	Y, N, -	long	
7.5	123	123	177	417	5.92	6.29	24.2	2.48	Y, Y, Y	long	H ₂ O film half

Calorimetry heat flux results from chambered qualification testing. Test series four and five used a single calorimeter chamber and nozzle, whereas tests six and seven used two calorimeter chambers and a nozzle. Test series one through three are omitted since they were chamberless tests.

Test Num	Calorimeter 1 (Upper) Heat Flux (MW/m ²)				Calorimeter 2 (Lower) Heat Flux (MW/m ²)				Nozzle Heat Flux (MW/m ²)				Comments on Heat Flux
	Double Ignition	Igniter Off	O ₂ Ramp	Nominal	Double Ignition	Igniter Off	O ₂ Ramp	Nominal	Double Ignition	Igniter Off	O ₂ Ramp	Nominal	
4.1	-	-	-	-	-	-	-	-	-	-	-	-	No double ignition
4.2	-	-	-	-	-	-	-	-	-	-	-	-	
4.3	1.64	1.16	-	-	-	-	-	-	6.99	8.41	-	-	Coolant failure in O ₂ ramp Open H ₂ O film before ign
4.4	1.18	1.40	-	-	-	-	-	-	6.95	9.18	-	-	
4.5	0.81	0.97	-	-	-	-	-	-	7.66	8.66	-	-	
4.6	1.73	1.88	2.23	-	-	-	-	-	6.70	7.71	4.96	-	
5.1	1.81	1.58	-	-	-	-	-	-	0.50	1.36	-	-	
5.2	2.10	1.89	1.39	-	-	-	-	-	2.44	3.01	4.61	-	
5.3	1.89	1.64	1.13	-	-	-	-	-	3.36	3.67	5.45	-	
5.4	2.15	1.85	1.46	1.15	-	-	-	-	5.88	6.03	7.26	6.06	
6.1	2.00	1.67	-	-	3.27	2.79	-	-	9.97	9.23	-	-	Coolant failure before test
6.2	2.24	2.14	1.56	2.06	3.46	3.47	5.69	4.17	9.15	8.97	8.55	9.07	
6.3	-	-	-	-	-	-	-	-	-	-	-	-	
7.1	2.09	3.01	-	-	2.55	3.00	-	-	1.32	2.78	-	-	No ignition
7.2	-	-	-	-	-	-	-	-	-	-	-	-	
7.3	-	-	-	-	-	-	-	-	-	-	-	-	No ignition
7.4	2.09	2.92	-	-	2.64	3.12	-	-	4.64	5.70	-	-	
7.5	2.18	3.01	2.36	3.46	2.47	3.02	4.80	5.24	3.96	4.71	5.35	5.99	H ₂ O film half on nozzle

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