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ABSTRACT

This study is part of a larger effort to establish a science-based model to predict the emissions from gas turbine engine combustors using alternative fuels. In order to validate and improve the chemical mechanisms in the model, four binary fuel mixtures comprised of the hydrocarbon compounds representative of the classes compounds that are expected in alternative aviation fuels. In each fuel mixture, n-dodecane was the base component. The second component was m-xylene, methylcyclohexane, iso-octane, or n-heptane that were selected to represent the molecular structures of aromatic, cyclo-paraffin, iso-paraffin, and n-paraffin. The binary fuel mixture (25% m-xylene and 75% n-dodecane in liquid volume fraction) was also evaluated as a surrogate for JP-8.

A burner system was developed and built to produce co-flow laminar jet flames with liquid fuel mixtures. The experimental conditions for flames were set at three equivalence ratios (Φ) of the fuel jet—Φ=∞, Φ=6, and Φ=2—to simulate the soot-rich zones in gas turbine engine combustors. The combination of laser extinction and laser-induced incandescence (LII) was applied to obtain the spatial distributions of soot volume fraction quantitatively. “Small aromatics” and “large aromatics,” containing 1-2 aromatic rings and 3-4 aromatic rings respectively, were detected by laser-induced fluorescence (LIF). A special configuration of thermocouple probe was developed to obtain the temperature distributions in the soot-free regions of the flames. Experimental results indicated that the PAH and soot from all paraffin fuels are similar, but PAH and soot of the aromatic fuel were much larger than for the paraffin fuels. The amount of soot was found to be higher in aromatic flames than in paraffin flames by a factor of between 2-4. The maximum LIF signals from both small and large aromatics along centerline were found to
be approximately ten times higher in the aromatic fuel than in paraffin fuels. Similar results, especially soot volume fraction distributions, was found between JP-8 and the m-xylene/n-dodecane fuel.

The experimental results were compared in detail to simulation results provided by Dr. Katta of Innovative Scientific Solutions, Inc. Basic consistent distribution trends for each fuel mixture were established with the simulation results. Similar qualitative distributions of soot volume fraction and semi-quantitative LIF signals from aromatic species as well as temperature were found for flames burnt with all fuel mixtures, even though the simulation always displayed large areas of soot and aromatics existing regions. The maximum soot volume fraction along centerline in flames was estimated with values similar to experimental data for paraffin fuels. Several potential explanations were produced for the significant discrepancy of soot distributions in aromatic flames between the simulation and experimental data. Other simulation results, including the distributions of OH and rates of soot nucleation, soot surface growth, and soot oxidation were presented to gain insight into the reasons for the discrepancies between the simulations and the experiment.
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Chapter 1 Introduction

1.1 Background

The demand for energy has been increasing dramatically, especially in the last few decades. Among the various types of energy sources, liquid fossil fuel serves as the primary fuel source for transportation vehicles. It is expected that the average annual world consumption of liquid fossil fuels will soar to ~250 quadrillion Btu in 2030, compared to the consumption of ~50 quadrillion Btu in 1965 [1]. In the meantime, the emissions and pollutants caused by burning liquid fossil fuels are raising public concerns, due to their harmful effects on human beings and the environment.

Within the U.S., the Department of Defense (DOD) is among the largest consumers of fuels, with annual expenditures of billions of dollars, and is investing in many initiatives to reduce its fuel consumption and change its mix of energy sources. In FY2011, DOD consumption was approximately 117 million barrels of oil [2]. The Air Force, as the largest consumer, accounts for 53% of total DOD fuel use; in comparison, the Department of Navy uses 28% and the Army uses 18% [3]. The largest volume of DOD’s total fuel consumption comes from Gas Turbine Engines (GTEs), which are also the major source of pollutants, including carbon monoxide (CO), unburned hydrocarbons (UHC), oxides of nitrogen (NOx) and soot, produced at military airbases [4].

Two classes of emissions from GTEs burning liquid fuels are paid significant attention: polycyclic aromatic hydrocarbons (PAHs) and soot. Most of the PAHs produced within the combustor by thermal pyrolysis and oxidation are on the list of hazardous air pollutants (HAPs). The World Health Organization (WHO) has already added PAHs to its
list of priority pollutants in both air and water, since some of them are thought to be carcinogenic [5, 6].

Previous research has identified soot’s harmful effects on human health and the environment. Epidemiological research [7, 8] indicates that poor air quality is thought to increase the odds for lung cancer and other cardiopulmonary diseases. Specifically, fine particulate matter, whose diameter is equal to or smaller than 2.5μm (PM2.5), does great harm to human health since it can be breathed more deeply into the lungs [9]. Each year, nearly 600,000 kg of soot is emitted into the atmosphere by U.S. military aircrafts. Soot deposits have been found on the polar snow packs and ice sheets and contribute to the accelerated melting of the polar ice caps since the soot decreases reflecting of solar radiation back into space [10, 11]. In addition, soot can adversely affect gas turbine combustors as soot radiation can cause overheating and damage, which finally limits the combustor’s performance. Beyond this, excessive quantities of soot can erode the turbine blades, and soot deposited on the fuel nozzle can result in fuel-spray distortion and even blockage. These problems in engines are critical in military applications, where a fuel-rich primary combustion zone is needed since it enhances the engine’s high-altitude reignite ability. Soot in the exhaust of jet aircrafts also makes them more easily detected by the adversary [12]. From an academic perspective, the formation of PAHs and soot are intensely related: PAHs are generally considered as the precursors for soot.

Driven by the depletion of fuel sources and stricter environmental regulations, the combustion research community has been focusing on improving engine efficiency and emission performance, which are affected by the properties of the fuel. The work in this
dissertation is supported by a DOD project that aims to understand the effects of fuel on the emissions from GTEs.

1.2 Jet fuels and alternative fuels

When the Wright Brothers needed fuel for their first flight in 1903, they used standard motor gasoline. Then, in the 1940s, the inventors of jet-powered aircraft, Dr. Hans Von Ohain in Germany and Sir Frank Whittle in Great Britain, chose gasoline and “illuminating kerosene” respectively as fuels due to their availability.

Current jet fuel properties are primarily dictated by fuel system constraints, operational requirements and, ultimately, by availability. From the 1940s until today, in military use, jet propellant (JP) has been developed with various properties, from JP-1 to JP-8, while JET-A and JET-A1 are used in commercial civil use. In Table 1-1, several important characteristics are compared between several common jet fuels [13].

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<tr>
<td>Base</td>
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<tr>
<td>Flash Point (min) °C</td>
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<td>38</td>
<td>38</td>
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<tr>
<td>Flash Point (max) °C</td>
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<td>-46</td>
<td>-47</td>
<td>-40</td>
<td>-47</td>
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<td>AO,CI/LI, FSII</td>
<td>AO,CI/LI, FSII,SDA</td>
<td>None</td>
<td>None</td>
</tr>
</tbody>
</table>
Besides the fuel itself, fuel additives are used to modify the properties of jet fuel in order to satisfy some specific requirements. For example, JP-8 is essentially Jet A (Jet A-1) with a military additive package: corrosion inhibitor (CI) to prevent fuel pump failure; fuel system icing inhibitor (FSII) to prevent water in the fuel from freezing; and static dissipater additive (SDA) to prevent accidents due to static discharge during fueling operations [13].

The liquid fossil fuel will continue playing a key role in the transportation realm. It is anticipated that air traffic will continue to grow by around 5% annually in the next 20 years [14]. In this context of scarce energy resources, researchers are investigating possible alternative fuels to satisfy future demands. Within the realm of fossil fuels, liquid fuels derived from coal, natural gas and biomass are commonly considered to be significant sources of alternative fuels. Currently, the fuels produced via Fischer-Tropsch (F-T) synthesis [termed synthetic paraffinic kerosenes (SPKs)] are attractive, since they could be burnt cleaner than other alternative fuels.

Recent years have seen renewed interest in F-T technology, discovered by the Germans Fischer and Tropsch in 1925. Generally, the method first converts the sources to synthesis gas, i.e., carbon monoxide and hydrogen, and then this mixture is variously “reconstituted” by using different catalysts to produce hydrocarbons and oxygen-containing chemicals. Essentially, F-T technology is a catalytic process that converts synthesis gas (CO+H₂) into a mixture of hydrocarbons (synthetic fuel). The reactions can be regarded as hydrogenation of carbon monoxide and are expressed as follows [15]:

$$n \ CO + 2n \ H_2 \rightarrow -(CH_2)n - + n \ H_2O$$ (1.1)
Specifically, SASOL in South Africa has been producing liquid fuels from coal for about 30 years. Many oil companies such as Shell Oil, Chevron and ExxonMobil have been conducting research to build smaller plants. Usually, the SPK consists almost entirely of iso-paraffins and n-paraffins, although relatively small amounts of cyclo-paraffins are present in some fuels [16]. Unlike other alternative fuels, the composition of SPK does not depend on the feedstock, since it could be derived from coal, natural gas, and biomass. Consequently, the use of F-T synthesis is expected to increase fuel choice and flexibility for DOD.

In 2009, an ASTM specification was created to allow the use of alternative fuels derived from paraffinic kerosene fuels as blending feedstocks up to 50% by volume with petroleum derived fuels [17]. At present, the use of 50/50 blending mixture of SPK and JP-8 is certified by the entire fleet in U.S. Air Force [18].

There have been several programs, e.g., Bulzan, et al. [19], and Miake-Lye [20], that compared emissions from engines fueled by petroleum-based fuels to the same engines fueled by several of the proposed alternative fuels and blends. These results indicated that the most significant effect of transitioning from JP-8 to alternative fuels was a change in soot emissions. It has also been observed that changes occur in emissions of specific hydrocarbon species, some of which are classified as Hazardous Air Pollutants (HAPs), and sometimes in CO. Generally, there are few or no observed changes in NO\textsubscript{x} emissions. Consequently, the main interests in emission performance from alternative fuels relate to soot and PAHs.
1.3 Soot formation

Even though it has been investigated extensively over many years, only very broad features of the soot formation processes have been established. Now, many researchers accept that soot formation and oxidation in combustion systems can be divided into four processes, including: soot precursor formation, soot particle inception, soot growth and soot oxidation [21-23], each of which is discussed below. The summary of soot information is shown in Figure 1-1 [24]:

![Figure 1-1 Basic steps from fuel break-up to soot](image)

1.3.1 Soot precursor formation

Among the four steps, soot precursor formation and its nucleation and growth are poorly understood and difficult to model [25]. During the research history of the soot inception process, many investigators have spent much effort to find the “bridge” to the first particle. These bridges involve polyacetylenes proposed by K. H. Homann and H. G. Wagner [26], ionic species proposed by Calcote [27], acetylene [6, 28, 29], ethylene [30,
31], 1,3-butadiene [32, 33] and their associated radicals. The major accepted opinion at present, supported by numerous experimental and modeling studies, is that soot particles form via polycyclic aromatic hydrocarbons (PAHs) [34, 35]. The two most cited reactions leading to cyclization (i.e., ring formation) are shown below: (reactions 1.2 and 1.3)

\[
\begin{align*}
n - C_4H_3 + C_2H_2 & \rightarrow C_6H_5 \quad (1.2) \\
n - C_4H_5 + C_2H_2 & \rightarrow C_6H_6 + H \quad (1.3)
\end{align*}
\]

\(C_6H_6\) is benzene and \(C_6H_5\) is phenyl. Reaction 1.2 plays a key role in the formation of the first aromatic ring on the basis of detailed kinetic simulations of shock-tube acetylene pyrolysis [36], and reaction 1.3, suggested by Bittner and Howard [37], is of significance at lower temperature [34, 38]. These two reactions were dismissed by Miller and Melius [39], who suggested that the concentrations of \(n\)-C_4H_3 and \(n\)-C_4H_5 are not sufficiently high; as a result, these compounds transform rapidly to their corresponding resonantly stabilized isomers, \(\text{iso-C}_4\text{H}_3\) and \(\text{iso-C}_4\text{H}_5\). This resulted in the identification of an odd-carbon-atom pathway via the combination of propargyl radicals (reactions 1.4 and 1.5) proposed by Miller and Melius, along with others [40].

\[
\begin{align*}
C_3H_3 + C_3H_3 & \rightarrow C_6H_6 \quad (1.4) \\
C_3H_3 + C_3H_3 & \rightarrow C_6H_5 + H \quad (1.5)
\end{align*}
\]

\(C_6H_6\) is benzene and \(C_6H_5\) is phenyl. Apart from these reactions, considering the knowledge from quantum chemical calculations, one odd-carbon-atom pathway has been suggested, as below: (reactions 1.6 and 1.7) [41, 42].

\[
C_5H_5 + CH_3 \rightarrow \text{benzene} + H + H \quad (1.6)
\]
Finally, another possibility for the initial ring formation is the reaction between propargyl and acetylene to form a cyclopentadienyl radical (reaction 1.8). This reaction combines the benefits of the two reactant types discussed above: a highly stable radical, propargyl, and the most abundant “building block” [41, 42].

\[
C_3H_3 + C_2H_2 \rightarrow c - C_5H_5 \quad (1.8)
\]

This propargyl-acetylene reaction could be a possible explanation for an experimentally observed enhancement in the production of soot in shock-heated mixtures of benzene and allene [38], as well as the reaction’s feasibility as verified by recent quantum Monte Carlo calculations [43]. Furthermore, by comparing the rate of reaction 1.8 with those of reactions 1.4 and 1.5, it is found by Frenklach et al. [44] that reaction 1.8 is thought to be faster than reactions 1.4 and 1.5 by a factor of two thousand, which implies that reaction 1.8 is probably playing a dominant role in the formation of the first aromatic ring.

Once the first ring is formed, the mechanism frequently used to explain the aromatics’ growth toward soot is HACA, introduced in Frenklach and Wang’s paper [45]. The term HACA is the abbreviation for “H-Abstraction-C2H2-Addition.” The HACA mechanism is a repetitive reaction sequence of two principle steps:

\[
A_i + H \rightarrow A_i^- + H_2 \quad (1.9)
\]

\[
A_i + C_2H_2 \rightarrow \text{products} \quad (1.10)
\]

\( A_i \) is an aromatic molecule with \( i \) peri-condensed rings, and \( A_i^- \) is its radical according to Frenklach’s usual notation for aromatics [38]. Reaction 1.9 indicates the abstraction of a hydrogen atom from the reacting hydrocarbon by a gaseous hydrogen atom,
followed by reaction 1.10, in which the addition of a gaseous acetylene molecule to the radical site forms soot products. The significance of reactions 1.9 and 1.10 was identified in a numerical modeling of detailed reaction kinetics of the growth of aromatics [44]. In reaction 1.9, through converting the molecule $A_i$ to a radical, the molecule obtained further growth. The majority of the experimental data indicate that gaseous H is the dominant abstraction species [36, 39, 44]. The key feature of the first step in the HACA mechanism is its reversibility both from the reverse reaction of reaction 1.9, reaction 1.11, and another reaction, 1.12.

$$A_i^- + H_2 \rightarrow A_i + H \quad (1.11)$$

$$A_i^- + H \rightarrow A_i \quad (1.12)$$

Pressure and molecular size are two possible factors that might affect the contributions of reaction 1.12 compared to that of reaction 1.11.

Actually, following the suggestion of Glassman [46], other species, especially acetylene, could contribute to aromatic growth. Frenklach found that acetylene could be helpful for in the growth of biphenyl, as shown in reaction 1.13 [38].

$$\text{C}_{2}H_2 + \text{C}_{6}H_5 \rightarrow \text{C}_{6}H_{4} + \text{H} \quad (1.13)$$

More details about other recent pathways for the growth of multiple aromatic rings can be found in the references [47].

At the time of aromatics’ growth, the aromatic radicals could be oxidized by O$_2$, primarily, and less significantly by OH. The HACA mechanism indicates that the effect of oxidization occurs at the very beginning of aromatics’ growth. However, since the growth
is governed by H atom production, while H atoms could consume oxygen, the aromatics might use up all the available oxygen when the growth is completed. This mechanism also explains the observation that soot inception usually occurs near the main combustion zone, where exist rich H and lean in O₂. Though the role of OH has been researched for a while [38, 48], its mechanism is not yet well understood.

1.3.2 Soot particle inception

Once the PAHs are formed in the process above, they continue to grow to eventually become the smallest identifiable soot particles with a certain diameter and mass, such as in the order of 1nm diameter and masses of 1000amu, as suggested by Ian M. Kennedy [49]. The soot particle inception in a flame is inherently a chemically-controlled phenomenon. The basic reason for this conclusion is that the thermodynamics alone is unable to describe the process since the soot is formed beyond regimes where it is thermodynamically stable relative to the oxides of carbon [49]. Frenklach pointed out initially that the condensation reactions of converting gas phase species to solid particles are purely chemical [36]. In order to expand this initial model, Frenklach took the collision of PAHs into consideration. Specifically, PAH dimers are formed due to smaller PAHs sticking to each other during the collision process. Then the PAH trimmers might be formed by the collisions of the PAH dimers and PAH or PAH dimers. Similarly, PAH tetramers and other larger particles could be produced by the collisions between the smaller particles. In addition, Frenklach suggested the adoption of PAH dimers to mark the emergence of the “solid” particle phase in practical measurement [36, 45].

Beyond these approaches, Violi and her colleagues adopted molecular dynamics simulations together with the well-tempered Metadynamics algorithm to investigate the
soot nucleation process. The results indicated that the stability of PAH dimers is influenced by factors including the mass and number of aromatic rings, molecular symmetry, and the presence of paraffin chains [50].

**1.3.3 Soot growth**

Soot growth is believed to occur via two mechanisms: surface growth and collisional coagulation. Basically, the former mechanism is a chemical process, while the latter is a physical process in nature [51].

Essentially, the surface growth by which the bulk of the solid-phase material is generated involves the attachment of gas-phase species to the surface of the particles and their incorporation into the particulate phase. Early in the 1980s, Haynes and Wagner employed first-order kinetics to describe the rate of appearance of soot by surface growth in laminar flames:

$$\frac{df_v}{dt} = -K_{sg}(f_v - f_v^\infty)$$

where \(f_v\) is the total amount of soot formed, and the typical values of \(K_{sg}\) range between 30 to 500 s\(^{-1}\) [52]. It was thought that the surface growth rate should be proportional to the soot surface area and typical hydrocarbon concentration, especially the concentration of acetylene, which is the principal gaseous species that reacts on the particle surfaces [52-54]. However, experimental results sometimes show that the rate does not depend either on soot surface area or acetylene concentration [55]. Even so, this empirical rate law is often used in simple models.
Frenklach and coworkers have produced a large and impressive body of research work based upon the HACA mechanism, which is also used in the formation of PAHs. Table 2 shows the HACA mechanism, including only the irreversible addition of acetylene (reactions 1a, 1b, 2, 3a, 3b) [45, 56]. The absence of the reversible addition of acetylene might cause insufficient dependence on temperature [45]. At the same time, the inclusion of reversible addition of acetylene (reactions 4a, 4b and 5 in Table 2) was kept by Colket and Hall in their models, though it might lead to over-prediction of thermal decomposition of surface intermediates with temperature [57].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$k_0$ ($cm^3/mol/s$)</th>
<th>$E_A$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a $C_{soot,t}H + H \leftrightarrow C_{soot,t}^0 + H_2$</td>
<td>$1.2 \times 10^{14}$</td>
<td>21.8</td>
</tr>
<tr>
<td>1b $C_{soot,t}H + OH \leftrightarrow C_{soot,t}^0 + H_2O$</td>
<td>$1.0 \times 10^{12}$</td>
<td>54.2</td>
</tr>
<tr>
<td>2 $C_{soot,t} + H \leftrightarrow C_{soot,t}H$</td>
<td>$1.0 \times 10^{13}$</td>
<td></td>
</tr>
<tr>
<td>3a $C_{soot,t}^0 + C_2H_2 \leftrightarrow C_{soot,t}^0 + C_{soot,t}C_2H_2$</td>
<td>$1.0 \times 10^{13}$</td>
<td></td>
</tr>
<tr>
<td>3b $C_{soot,t}C_2H_2 \leftrightarrow C_{soot,t+1}H + H$</td>
<td>$1.0 \times 10^{10}$</td>
<td></td>
</tr>
<tr>
<td>4a $C_{soot,t}^0 + O_2 \leftrightarrow C_{soot,t-1} + 2CO$</td>
<td>$2.5 \times 10^{12}$</td>
<td></td>
</tr>
<tr>
<td>4b $C_{soot,t}C_2H_2 + O_2 \leftrightarrow C_{soot,t}^0 + 2CHO$</td>
<td>$2.5 \times 10^{12}$</td>
<td></td>
</tr>
<tr>
<td>5 $C_{soot,t}H + OH \leftrightarrow C_{soot,t}^0 + CH + CHO$</td>
<td>$7 \times 10^{13}$</td>
<td></td>
</tr>
</tbody>
</table>

The acetylene-driven HACA model is consistent with the analysis of Harris and Weiner [58]. Their experimental observations indicate that the surface growth rate declines with the extent of particle growth, a phenomenon termed soot surface aging [54, 58]. The decrease in either H atom concentration or the equilibrium in the gas phase is considered
to be the reason for this declination [45-47]. Specifically, the H concentration decrease reduces the kinetic driving force, while the super equilibrium degree reduces the particle surface activity due to the formation of surface defects. Generally, surface growth results in an increase in the amount of soot, while the number of particles remains unchanged [48].

The other simultaneous process of soot growth is coagulation, in which particles collide and coalesce, thereby decreasing the number of particles while the amount of soot remains constant. In 1981, Haynes and Wagner observed soot under an electron microscope and found that soot is initially spherical and then grows to form straight or branched chains, as seen in Figure 1-2. The spherical soot is marked by the white circles, and the bright spots are shadows of the particles in the chains [48]. Hence, soot coagulation is usually classified as coalescent growth and agglomeration into fractal aggregates. Normally, when the soot is spherical, the particles collide and coalesce completely to form new spherical soot. The phenomenology is borrowed from the field of aerosol dynamics and is described by Smoluchowski master equations with the collision coefficients dependent on the sizes of colliding particles [55]. Furthermore, the soot particles in coagulation are observed to agglomerate at some point to form chains by sticking to each other. The experimental data in numerous flames indicate that the agglomeration process usually takes place when the soot particles are “mature” or of a certain “age,” and the range of agglomeration fractal dimension is between 1.7-1.9 [35, 59]. However, the transition from spherical to fractal growth is not well understood.
1.3.4 Soot oxidation

All the above processes are about the formation and growth of soot; in the meantime, there exists a parallel process to reduce soot, which is called soot oxidation. Finally, the eventual emission of soot from any combustion device will depend on the balance between the processes of formation and oxidation.

In fact, soot oxidation occurs during the entire combustion period. During the process of PAHs’ formation and growth, the PAHs could be oxidized by O$_2$, mainly, while oxidation by OH is less important or at least poorly understood. These results are supported by experimental observation and deductions based on numerical simulations, in which the decreasing concentration of O$_2$ in a fuel-rich environment is observed [44, 60]. Lee et al.
point out that other oxygenated species, such as O atoms, H₂O and CO₂, may be important under some conditions [61]. Emission of soot from a flame depends on whether the soot, once formed, has sufficient time to be burnt in the presence of oxidizing species to form gaseous products such as CO and CO₂. Obviously, if the ratio of soot oxidation length to the flame height exceeds about one, the soot oxidation is quenched before completion and the flame smokes [45].

1.4 Literature review

Future research and development on improving engines’ combustion efficiency and emission performance depends highly on computational work. However, normal jet fuels such as Jet A and JP-8, or even SPKs, are complex mixtures of hundreds of chemical components. The capability of existing computational combustion models for predicting engine emissions depends on the availability of elementary reactions. Consequently, it is impractical to create a detailed chemical kinetic model containing all of a fuel’s individual components because of the lack of data such as thermodynamic parameters, chemical reaction pathways, and kinetic rate constants. A feasible approach to simulate a real fuel is to design a surrogate that contains several chemical species and behaves similarly to some key features of the real fuel, such as the burning velocity, volatility, the cetane number, etc.

During recent decades, many researchers have been filling in the blanks of detailed mechanisms for various components via experimental and computational work. Starting in the late 1980s, Wood et al. [62] designed a 14-compound mixture as a JP-4 surrogate to match JP-4’s chemical structures and distillation curves. In 2002, a 6-component surrogate (30% n-dodecane, 20% tetradecane, 20% methylcyclohexane, 15% m-xylene, 10% iso-
octane, 5% tetralin in molar fractions) designed by Smooke, Gomez and Ranzi et al. was studied both experimentally and computationally in diffusion flames [63]. The sooting behavior, together with some physical characteristics, including density and distillation curve, were matched to JP-8 [63]. Seshadri et al. investigated a 3-component mixture (30% n-dodecane, 20% tetradecane, 20% methylcyclohexane in liquid volume) in laminar non-premixed flames to capture the sooting behavior of JP-8 [64]. A simpler binary-component surrogate (80% n-decane and 20% 1,2,4-trimethylbenzene by weight fraction) developed in Aachen was capable of accurately reproducing the ignition and extinction behavior of kerosenes [65]. Brief summaries of research work on jet fuel surrogates were given by Hanson [66], Dagaut [67], and Farrell et al. [68]. With respect to sooting tendency, more recently, A.G. Mouis and her colleagues compared the results between experiments and simulation for the effects of m-xylene on aromatics and soot in laminar ethylene flames in the pressure range from 1 to 5 atm [69].

In the realm of soot formation research, numerous factors, including the fuel’s molecular structure, environmental pressure, the diluents, and the additives, were investigated in laminar flames.

In the 1980s, Olson, Pickens, Calcote, Manos and Glassman et al. investigated the effects of molecular structure on soot formation and developed an understanding of the consequence of the soot tendency:

Acetylene < alkenes < isoalkanes < n-alkanes < alkylbenzenes < naphthalenes

with their understanding quantified and examined for validity by using TSI ranges, i.e., 0< 26-65<61-70<34-76<83-91<100 for the various structures listed above [46, 70].
Street and Thomas found that the critical equivalence ratio for soot formation increased by about 3-5% per 100K as the temperature of the unburned gas mixture in Bunsen flames was increased [70]. Normally, the soot volume fraction and local temperature are highly related, which was verified by Santoro [71], Faeth et al. [72] in their experiments via laser extinction and laser scattering.

A number of studies have been conducted on the effect of pressure on soot formation, especially the soot volume fraction in laminar flames [73, 74]. Maah, Miller, Flower, and Bowman et al. all found that the rate of soot oxidation increases with higher pressure, which leads to a lower soot volume fraction [75-77]. Quantitatively, the integrated soot volume fraction along the radial flame path is proportional to $P^n$, where $n$ is from 1.1 to 1.3. Lee and Na [78] found that the maximum soot volume fraction is proportional to $P^{1.26}$ in laminar ethylene flames in pressure range 1~4 atm.

More recently, the soot tendencies in laminar diffusion flames of n-heptane were investigated by Zhou [79], and the integral soot volume fractions show power law dependence on pressures, being proportional to $p^n$, with $n$ being 3.4±0.3 in the pressure range of 1.0 to 3.0 bar. In addition, Zhou selected two typical molecular structures, namely linear and saturated cyclic hydrocarbons (n-hexane ($C_{16}H_{14}$) and cyclohexane ($C_6H_{12}$)) and their oxygenated forms, to investigate the effects of molecular structure on soot in the pressure range from 1.5 to 2.0 bar [80].
1.5 Research program

1.5.1 Motivation

The DOD established goals for transitioning from petroleum-derived JP-8 fuel to synthetic-derived alternative JP-8, which will consist of blends of petroleum JP-8 and synthetic fuels and fully synthetic fuels. A joint university, industry, and Air Force program was established to investigate the fundamental science relevant to control the emissions from military GTEs burning alternative fuels. The main objectives of this program are to:

(1) establish a science base needed to develop accurate models for total UHC, HAPs, soot, and CO and NO\textsubscript{x} emissions from military gas turbine engines burning alternative fuels and

(2) establish a science-based methodology for selecting practical alternative fuels that minimize emissions.

Figure 1-3 shows the overall technical approach for the project: the bottom row lists all the experimental work, while the top row displays the corresponding simulation work. Increasing complexities of the experiments and models are shown in the figure as increasing from reactors where chemical kinetics dominate to real devices where kinetics, diffusion, turbulence and bulk mixing are all involved.
1.5.2 Research objectives and approach

Specifically, the research group at The Pennsylvania State University is responsible for the experimental work for the production of emission species within laminar jet flames and from a model gas turbine combustor. Corresponding simulation work on the flames is being carried out by Dr. Katta in Innovative Scientific Solutions, Inc. Joint comparison of the model and experiments allows the chemical kinetic mechanisms and soot formation models to be evaluated.

The main research questions addressed in this dissertation are as follows:

1. What are the effects of fuel molecular structure on PAHs and soot in laminar jet flames for non-premixed and partially premixed fuel jets?
2. What is the models’ performance compared to the experimental work?
In addition, the research investigated how well a simply binary surrogate could reproduce the sooting behavior of JP-8.

The overall experimental approach applied in this research included:

1. Design of the experimental test matrix included the fuels and flame conditions conducive for implementing the laser-based diagnostic measurements;
2. Quantitative measurements of two-dimensional soot volume fraction in the flames by the application of laser-induced incandescence and laser extinction;
3. Qualitative measurements of distribution of PAHs in flames via laser-induced fluorescence;

The successive chapters of the dissertation are organized as follows:

Chapter 2 provides theoretical descriptions of the measuring techniques: laser extinction; laser-induced incandescence; laser-induced fluorescence; and temperature measurement.

In Chapter 3, the experimental work is described, including the fuel matrix design, the selection of the flames’ conditions, the burner system, the implementation of laser diagnostics, and the micro thermocouples.

The experimental and simulation results in the laminar flames are shown and analyzed in Chapter 4, followed by comparisons and discussion.

Finally, Chapter 5 summarizes all the conclusions and indicates potential directions for future work.
Chapter 2 Experimental Methods

The applications of laser diagnostics have been proven to be efficient in the investigation of soot formation processes in flames, due to their higher sensitivity, faster response, and non-intrusive character comparing to soot sampling methods [81]. Within this research program, laser extinction and laser-induced incandescence (LII) were used to measure soot volume fraction distributions. Laser-induced fluorescence (LIF) was used to obtain the qualitative distributions of aromatic species. In addition, since temperature plays a key role in the combustion process, the temperature distribution in the soot-free regions was obtained by micro thermocouples. A brief introduction of these diagnostics is given in the following sections.

2.1 Laser Extinction

Laser extinction, or light-extinction techniques have been widely used to measure the soot volume fraction distributions in a variety of hydrocarbon flames, such as methane/air and ethane/air flames [82, 83]. Moreover, the combination of light scattering and laser extinction can provide researchers with the ability to obtain sizing information of soot particles [84].

The theory of laser-extinction technique applied to soot particles in flames was described by D’Alessio and co-workers in the 1970s [85-87] and was then first adopted by Wagner and his co-workers in the 1980s to measure the soot volume fractions in diffusion flames [88-90].
Basically, in the laser-extinction technique, part of the light going through a cloud of soot particles will be scattered and absorbed, as shown in Figure 2-1 [91]. According to the energy balance in equation 2.1:

\[ I_{\text{transmitted}} = I_{\text{incident}} - (I_{\text{absorbed}} + I_{\text{scattered}}) \] (2.1)

the term "\( I_{\text{absorbed}} + I_{\text{scattered}} \)" is the so-called “extinction.”

According to Lambert-Beer’s law, the transmitted laser intensity after passing through the particle cloud is indicated in equation 2.2.

\[ I = I_o \exp \left(- \int_0^L K_{\text{ext}} \, dl \right) \] (2.2)

\( I_o \) = intensity of incident laser (W/m²)

\( K_{\text{ext}} \) = extinction coefficient for a cloud of particles (1/m³)

\( L \) = length of path that laser beam follows through the particle cloud (m)

Based on the calculation using Mie’s solution to Maxwell’s equations with the appropriate boundary conditions defined by Van De Hulst [92]; Kerker [93], the extinction coefficient \( K_{\text{ext}} \) is dependent on the size, number, and properties of the particles in the cloud, as shown in equation 2.3.
\[ K_{\text{ext}} = \frac{\pi}{4} C_n \int_0^\infty Q_{\text{ext}} N(D) D^2 dD \]  

(2.3)

\[ C_n = \text{number density of soot particles (}D^{-3}\text{)} \]

\[ Q_{\text{ext}} = \text{extinction efficiency of a single soot particle with diameter } D \]

\[ D = \text{diameter of soot particle (}\mu\text{m)} \]

\[ N(D) = \text{normalized soot particle size distribution function} \]

There is no exact expression for \( Q_{\text{ext}} \), which is a complex function of the size and refractive index of the soot particle. However, the value of \( Q_{\text{ext}} \) can be calculated under various approximations. The most common approximation is Rayleigh scattering, applied when the scattering parameter \( x = \pi D / \lambda \), where \( \lambda \) is the wavelength of light used, is small.

Typically, soot particles are smaller than 60nm of diameters, with roughly spherical shapes. In most experiments using laser extinction, visible wavelength lasers are used because of experimental simplicity. For visible light, the value of \( \pi D / \lambda \) is much smaller than 1. According to the Rayleigh scattering approximation, the extinction efficiency is:

\[ Q_{\text{ext}} = Q_{\text{absorption}} + Q_{\text{scattering}} = 4x\text{Im} \left( \frac{\tilde{m}^2 - 1}{\tilde{m}^2 + 2} \right) + \frac{8}{3} x^4 \text{Re} \left( \frac{\tilde{m}^2 - 1}{\tilde{m}^2 + 2} \right) \]  

(2.4)

where \( \tilde{m} \) is the complex refractive index.

The scattering efficiency can be neglected when the scattering parameter \( x \) is much smaller than 1. So equation 2.4 can be reduced to equation 2.5.

\[ Q_{\text{ext}} = Q_{\text{absorption}} = 4x\text{Im} \left( \frac{\tilde{m}^2 - 1}{\tilde{m}^2 + 2} \right) \]  

(2.5)

Combining equations 2.2, 2.3, and 2.5, equation 2.2 becomes equation 2.6.

\[ I = I_0 \exp \left( -\pi^2 \frac{L}{\lambda} \text{Im} \left( \frac{\tilde{m}^2 - 1}{\tilde{m}^2 + 2} \right) C_n \int_0^\infty N(D) D^2 dD \right) \]  

(2.6)
The soot volume fraction $f_v$ is related to the number density of soot particles, as shown in equation 2.7.

$$f_v = \frac{\pi}{6} C_n \int_0^\infty N(D)D^3dD = -\frac{2}{3L} \frac{D_{32}}{Q_m} \ln \left(\frac{l}{j_0}\right) \quad (2.7)$$

$D_{32}$ is known as the volume/surface mean diameter, or Sauter mean diameter, and $Q_m$ is the mean extinction efficiency for a soot particle cloud. The other parameters, L and $\ln \left(\frac{l}{j_0}\right)$, are measured in the experiments. Kontani and Gotoh carried out a detailed analysis on $Q_m$ and $Q(D_{32})$ and concluded that the difference between them is less than 5% [94]. So equation 2.7 reduces to equation 2.8.

$$f_v = -\frac{\lambda}{6\pi \cdot L \cdot \text{Im}\left(\frac{\tilde{m}}{m^2+1}\right)} \ln \left(\frac{l}{j_0}\right) \quad (2.8)$$

Now the only unknown parameter in the equation is the imaginary part of the complex refractive index function. This could be considered as the major source of uncertainty since it is dependent on not only the soot properties but also the light wavelength, as reported by Chang and Charalampopoulos [95]. Dalzell and Sarofim chose $\tilde{m} = 1.57 - 0.56i$ in their work [96], and then Olson et al. [97] and Lee, Tien [98] used the values of $\tilde{m} = 1.93 - 0.52i$ for a 514.5nm wavelength and $\tilde{m} = 1.89 - 0.48i$ for a 632.8nm wavelength for the wick burner study. Chang and Charalampopoulos experimentally measured the variation of refractive index with wavelength, as shown in Table 2-1 [95].
Table 2-1 Soot Index for various wavelengths.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Refractive Index ($\bar{m}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>337</td>
<td>1.48-0.77i</td>
</tr>
<tr>
<td>532</td>
<td>1.75-0.61i</td>
</tr>
<tr>
<td>633</td>
<td>1.80-0.58i</td>
</tr>
<tr>
<td>810</td>
<td>1.85-0.57i</td>
</tr>
<tr>
<td>1064</td>
<td>1.91-0.59i</td>
</tr>
</tbody>
</table>

In order to maintain consistency with previous experimental results from our research group, in this dissertation $\bar{m} = 1.57 - 0.56i$ is used for laminar flames.

Since the obtained values of $ln \left( \frac{I}{I_0} \right)$ are the integrated values of the local extinction coefficient along the optical path through the flames, some conversion methods are needed to yield the local values of soot volume fractions. Within this research program, Fourier inversion [99], which assumes the flame to be symmetric, was adopted. Previously, three-point Abel technique [100] was used; however, the results obtained from Abel technique were producing more noises and fluctuations in the radial distributions of soot volume fraction. Consequently, Fourier inversion was selected due to its better performance than three-point Abel technique.

2.2 Laser-Induced Incandescence (LII)

Laser-induced incandescence has become a preferred technique in soot concentration measurement, due to its simple implementation. In addition, LII can provide a two-dimensional contour of soot concentration distribution, compared to laser extinction, which provides only point measurement. For spatially non-uniform soot particle fields, LII is able to provide a much better approach to measure the soot volume fractions, at least
qualitatively. With proper calibrations, the LII technique can produce quantitative measurements with high spatial and temporal resolutions.

2.2.1 Theory basis

Essentially, LII is generated when the soot particles are irradiated with an intense laser light. A high-energy laser pulse heats the soot particles up to the point of vaporization (~4000K). Then the energy is transferred from the soot particles in the form of thermal radiation, the intensity of which is directly related to the total volume of soot particles in the measuring probe volume.

The theoretical basis regarding the potential of LII for measuring quantitative soot volume fraction was first investigated by Melton [101] and Dasch [102-104]. Fundamentally, the LII signals are the result of a complex thermo-optical phenomenon, depending on particle size, temperature (particle and ambient environment), laser energy intensity, incident laser intensity profile, etc. The following introduction presents a computational model based on the work of Hofeldt [105], in which more details can be found.

The energy balance equation 2.9 describes the heat transfer between the particle and its surroundings, as well as the interaction of the particle with the incident laser radiation.

\[
m_s \frac{d(c_s T_s)}{dt} - \frac{H_v}{M_v} \frac{dm_s}{dt} = q C_{abs} - h A_s (T_s - T_\infty) - \int_0^\infty 4C_{abs} E_{b,\lambda}(T_s) d\lambda + \int_0^\infty 4C_{abs} E_{b,\lambda}(T_w) d\lambda
\]

where \(m_s\) is the mass of a particle; \(c_s\) is the specific heat of the particle; \(T_s\) is the particle temperature; \(T_\infty\) is the gas temperature; \(H_v\) is the enthalpy of vaporization; \(M_v\) is
the molecular weight of the vapor; \( q \) is the laser excitation intensity; \( C_{abs} \) is the particle absorption cross section; \( h \) is the convective coefficient; \( A_s \) is the surface area of the particle; \( E_{b,\lambda} \) is the blackbody spectral irradiance; \( \lambda \) is the wavelength; and \( T_w \) is the temperature of the radiant surroundings.

The terms on the left-hand side are: (1) the rate of increase of energy stored in the particle; (2) the loss in particle energy due to vaporization. The terms on the right-hand side are: (1) the rate of energy absorption from the laser pulse; (2) the collisional cooling rate in terms of convection; (3) radiative emission; (4) radiative absorption. Radiative absorption is usually neglected, unless there are significant contributions from the surroundings.

By assuming a constant or average value for \( c_s \) and neglecting radiation from the surroundings, equation 2.9 can be written as equation 2.10:

\[
\frac{dT_s}{dt} = \frac{l_t A_{abs}}{c_s} - \frac{6h(T_s-T_\infty)}{\rho_s c_s D_s} - \frac{6N_v M_v}{\rho_s c_s D_s N_{AV}} - \frac{3}{2\rho_s c_s D_s} \int_0^\infty Q_{abs} E_{b,\lambda}(T_s) d\lambda \tag{2.10}
\]

For a stationary particle surface in which only vapor diffusion is considered as a transport process, the continuity equation is:

\[
\frac{dm_s}{dt} = - \frac{N_v \pi D_s^2 M_v}{N_{AV}} \tag{2.11}
\]

The mass of particles changes, as shown in equation 2.12, if the spherical particles are of a constant density:

\[
\frac{dm_s}{dt} = \frac{\pi}{2} \rho_s D_s^2 \frac{dD_s}{dt} \tag{2.12}
\]
where \(A_{\text{abs}}\) is the mass specific absorption cross-section; \(\rho_s\) is the mass density of the particle; \(D_s\) is the equivalent diameter of the particle; \(N_v\) is the molecular diffusion flux; \(N_{AV}\) is the Avogadro’s number; and \(Q_{\text{abs}}\) is the absorption efficiency.

With some assumptions and manipulations, the collected LII signal can be related to the soot volume fraction, shown in equation 2.13:

\[
S = V_{mv} \frac{\Omega}{4\pi} \int_0^\tau m_s(t)W(t) \int_0^\infty g(D_s) \int_0^\infty G_r(\lambda)A_{\text{abs}}(\lambda, D_s)E_{\text{b,}\lambda}(T_s) d\lambda dD_s dt
\]  

(2.13)

where \(V_{mv}\) is the probe volume; \(\Omega\) is the solid angle; \(\tau\) is the time for LII signals being collected; \(W(t)\) is the signal windowing function; \(g(D_s)\) is the normalized volume weighted distribution function, \(g(D_s) = f(D_s)(D_s/D_{30})^3\); \(f(D_s)\) is the normalized size distribution function; \(D_{30}\) is the diameter of average particles, \(D_{30} = \int D_s^3 f(D_s) dD_s\); and \(G_r(\lambda)\) is the relative wavelength response function for the detector plus optics.

Besides the soot volume fraction, equation 2.13 relates the LII signal intensities to the soot size information as well. Melton [101] concluded that the LII signal is proportional to \(D_s^x\), where \(x = 3 + 0.154\lambda^{-1}\). Consequently, by selecting a longer incident laser light wavelength, the value of \(x\) gets closer to 3.

### 2.2.2 Experimental considerations

The following factors are crucial in making LII measurements: (1) laser excitation energy and wavelength; (2) laser intensity profile; (3) spectral detection region; (4) detection gate width and timing.

The excitation energy is usually provided by a pulsed laser with \(\sim 10\) ns duration. Previous research has shown that soot particles begin to vaporize at a laser fluence of \(\sim 0.2\)
J/cm² at 532 nm (or 0.4J/cm² at 1064 nm) [106]. Below this threshold value, the soot particles are absorbing the energy from the laser to raise their temperature. Well above the value, the LII signal exhibits a “plateau” region, which indicates that the signal value becomes relatively independent of incident laser energy, as shown in Figure 2-2 [106]. This curve was obtained for a Gaussian intensity profile over a wide range of incident laser fluence values, up to maximum of 10 J/cm². It indicates the rapid rise in the LII signal as the laser fluence increases until the threshold value (0.2 J/ cm²), followed by a “plateau” region. This curve trend is commonly found in other research work; however, the laser fluence varies somewhat. For example, Ni et al. limited their study for a Gaussian intensity profile up to 0.35 J/ cm² [107, 108].

![Figure 2-2 Laser fluence dependence of LII signals measured in steady laminar diffusion flames [106]. Data were collected at 20mm height in an ethylene/air flame for detection gate durations of 19 ns (+) and 85 ns (○), both gates opening coincident with the arrival of a ∼5 ns laser pulse. Data were also shown for a methane/air flame at 50mm with a 85 ns gate (●). Raw signals for each condition have been normalized to a value of 1.0 at a fluence of 0.6 J/cm². The solid line shown is the least-squares power-law fit of the methane data for fluences greater than 0.03 J/ cm².](image)
The selection of the excitation laser wavelength is not critical, as long as the soot particles exhibit sufficient absorption. The general selection of wavelength aims to reduce the potential interferences that can accompany the laser excitation process, such as laser-induced fluorescence from other species. In most cases of the soot formation process, a very likely source of interference is LIF signals from polycyclic aromatic hydrocarbons (PAHs). For example, the PAHs could be excited by the 266 nm and 532 nm wavelength excitation lasers; however, they would not be excited by a 1064 nm wavelength laser. Consequently, the use of a 1064 nm laser line is often selected to avoid this source of interference. However, the implementation of a 1064 nm wavelength laser line will cause experimental challenges, due to its invisibility.

Another equally important factor is the laser intensity profile. For Gaussian shape profiles, the LII signal often exhibits the behavior evident in Figure 2-2. In contrast, for a “top hat” or rectangular profile, Vander Wal and Jensen [109] showed that the LII signal achieved a plateau region between ~0.2J/cm² and 0.4J/cm² and then decreased as laser fluence increased. Similarly, Ni et al. [108] and Witze et al. and Vander Wall, et al [110], have reported that when using uniform profiles with increasing laser fluence, the LII signal achieves maximum value and then decreases to a plateau at higher fluences, as shown in Figure 2-3. Due to availability considerations, most two-dimensional LII measurements are made using Gaussian energy intensity profile laser sheets.
The spectral detection region can be very wide, given the blackbody nature of the incandescence. In fact, the background and laser-induced interferences are given greater considerations than the spectral responses. C$_2$ emissions, generated by the laser heating processes, can introduce interferences in the wavelength region between ~420 nm and 620 nm. The use of narrowband filters that have peak transmission wavelengths at ≤ 450 nm was verified to be effective in reducing C$_2$ emission interferences [106]. The other potential interference: LIF signals produced by PAHs are usually spectrally red-shifted compared to the excitation laser. Unless UV laser sources are selected to excite the LII signals, the approaches aiming to reduce the C$_2$ emission interference typically address the PAHs’ LIF interference as well. The most effective way to reduce both C$_2$ and PAHs interference simultaneously is to use a 1064 nm excitation source.

A typical temporal LII signal trend is shown in Figure 2-4, obtained by Ni, et al. The LII signals increased rapidly to their peak values in ~10 ns, and then decreased until
zero by several hundred nanoseconds. Researchers have used two time-resolved measurements for gated detection of LII based on this temporal behavior: (1) prompt gating; (2) delayed gating. The former approach involves collecting the LII signals at the start of the laser pulse, with a time period of ~10-50 ns. The major advantage of prompt gating is its ability to minimize the effects of particle-size differences; the major disadvantage is its possible interference from PAHs’ LIF signals, which increase to their peak values similarly to LII signals, as will be discussed later in this chapter. Consequently, the delayed gating method has been recommended to discriminate against interferences from vaporized species or species that fluoresce from the excitation laser, since the fluorescence decay times are much shorter than the LII signal’s. However, since the cooling rates vary with the particle sizes, this approach essentially disproportionally weights larger particle sizes as either the gate delay time or gate width increases.

![Figure 2-4 Temporal profile of an LII signal obtained in the ethane/air laminar diffusion flame. Data were obtained at heights of 10 mm and 30 mm above the fuel tube exit and at radial locations corresponding to the peak soot volume fraction for these heights [109].](image-url)
### 2.2.3 LII calibration

Most LII calibrations have been performed by comparing the LII signals to laser extinction measurements, the traditional *in situ* diagnostic for soot concentrations, as discussed above. However, the following factors in laser extinction measurement can affect the calibration of LII:

1. The laser extinction technique relies on the assumption that the soot particles are within the Rayleigh size limit with respect to the incident light source. However, laser scattering measurement indicates that the soot particle size varies within the flames [71].

2. The selection of refractive index ($\bar{m}$). Different indexes available in the literature can lead to substantially different quantitative results, as much as a factor of two.

3. Usually, the laser extinction measurement is applied in a diffusion laminar flame, together with a tomographic conversion technique. Either 3-point Abel or Fourier conversion can cause uncertainties and errors in the final results.

Besides laser extinction, the LII calibrations can be achieved by other methods including cavity ringdown and gravimetric techniques [111].

### 2.3 Laser-Induced Fluorescence (LIF)

As described in Chapter 1, current models of the formation of soot particles assume that soot nuclei are formed from PAHs. Therefore, investigations of PAHs are important to understand the mechanism of soot formation. Laser-Induced Fluorescence (LIF) is one
of the most powerful tools for direct measurement of the distribution of PAHs in a flame. Moreover, LIF can also be used to detect the presence of chemical radicals such as OH, CH, NO, CH₂, and CN [112-115]. The principle of the LIF technique is detection of the spontaneous emission of radiation from atoms or molecules, the electrons of which have been excited to higher energy levels, from a source such as a laser. Thus, the intensity of an LIF signal can be correlated to the population of the excited state or broadly to the concentration of a particular species in the flame.

2.3.1 Theory Basis

For mathematical simplicity, the two-level model of laser-induced fluorescence is used to illustrate the basic concepts with the following mathematical derivations [111]. In Figure 2-5, the rate constants for the optical and collisional processes connecting the upper and lower levels are shown. \( b_{12} \) and \( b_{21} \) are, respectively, the rate constants for absorption and stimulated emission and are related to the Einstein coefficient for stimulated emission or absorption \( B \), through the relation in equation 2.14.

\[
b = \frac{B l_{\nu}}{c} \quad (2.14)
\]

\( l_{\nu} \) is the incident laser irradiance per unit frequency interval \((W/cm^2 \cdot sec^{-1})\) and \( c \) is the speed of light.

![Simple two-energy-level diagram for LIF modeling](image-url)
$A_{21}$ is the spontaneous emission rate constant given by the Einstein coefficient $A$, $W_{2i}$ is the photoionization rate constant, $Q$ represents the collisional quenching rate constant, and $P$ is the predissociation rate constant. The rate equations for the temporal derivatives of the state population densities, denoted by $N$, are as follows:

\[
\frac{dN_1}{dt} = \dot{N}_1 = -N_1 b_{12} + N_2 (b_{21} + A_{21} + Q_{21}) \tag{2.15}
\]

\[
\frac{dN_2}{dt} = \dot{N}_2 = N_1 b_{12} - N_2 (b_{21} + A_{21} + Q_{21} + P + W_{2i}) \tag{2.16}
\]

In these equations, $\dot{N}_i$ are the rates of population change; the product terms on the right hand side are also rates: e.g., $N_2 b_{21}, N_2 Q_{21}$, etc.

If predissociation and photoionization are negligible, adding equation (2.15) and equation (2.16) results in:

\[
\frac{dN_1}{dt} + \frac{dN_2}{dt} = \frac{d}{dt}(N_1 + N_2) = 0 \tag{2.17}
\]

Hence, $N_1 + N_2 = \textit{constant} = N_{10}$, where the zero superscript identifies the level population prior to laser excitation. Strictly speaking, equation (2.14) should be expressed:

\[
b = \frac{B}{c} \int_{\nu} I_{\nu}(\nu) g(\nu) d\nu \tag{2.18}
\]

$I_{\nu}(\nu)$ is the laser lineshape and $g(\nu)$ is the absorption lineshape, depending on whether the absorption transition is in the Doppler-broadened, collision-broadened, or Voigt regime, respectively. Following Partridge and Laurendeau, the laser lineshape may be written as:

\[
I_{\nu}(\nu) = I_{\nu0} L(\nu) \tag{2.19}
\]
where the laser spectral distribution function $L(\nu)$ is normalized such that

$$\int_{\nu} L(\nu) d\nu = \Delta \nu_L,$$

where $\Delta \nu_L$ is the laser profile FWHH. $I^0_{\nu}$ is termed as the normalized spectral irradiance and is related to the irradiance $I$ as follows:

$$l \equiv \int_{\nu} I_{\nu}(\nu) d\nu = \int_{\nu} I^0_{\nu} L(\nu) d\nu = I^0_{\nu} \Delta \nu_L \quad (2.20)$$

hence, inserting equation 2.19 into equation 2.18 results in

$$b = \frac{B}{c} I^0_{\nu} \int_{\nu} L(\nu) g(\nu) d\nu \quad (2.21)$$

Assuming the laser frequency, $\nu_0$, is centered on the absorption feature and that $\Delta \nu_L$ is sufficiently broad that $L(\nu)$ varies negligibly over the absorption lineshape, then equation (2.21) may be written

$$b = \frac{B}{c} I^0_{\nu} \int_{\nu} L(\nu) g(\nu) d\nu = \frac{B}{c} I^0_{\nu} L(\nu_0) = \frac{B}{c} I_{\nu}(\nu_0) \quad (2.22)$$

where $I_{\nu}(\nu_0)$ is the laser spectral irradiance on line center.

Equation 2.21 can be solved by eliminating $N_1$ using $N_1 + N_2 = N^0_1$ and integrating

$$N_2(t) = \frac{b_{12} N^0_1}{r} (1 - e^{-rt}) \quad (2.23)$$

where $r = b_{12} + b_{21} + A_{21} + Q_{21}$ and $N_2(t = 0) = 0$ has been assumed as the initial condition.

For values of $rt \ll 1$, the upper level population initially builds up linearly with time,

$$N_2(t) = b_{12} N^0_1 t,$$

then begins to roll over, and reaches a steady state value of $N_2 = \frac{b_{12} N^0_1}{r}$ for values of $rt > 1$. Once the steady state is achieved,
\[ N_2 = N_1^0 \frac{b_{12}}{b_{12} + b_{21}} \frac{1}{1 + \frac{A_{21} + Q_{21}}{B_{12} + B_{21}}} \]  

(2.24)

The fluorescence signal power, \( F \), is proportional to \( N_2 A_{21} \), specifically expressed as

\[ F = h\nu N_2 A_{21} \frac{\Omega}{4\pi} \ell A = h\nu \frac{\Omega}{4\pi} N_1^0 \frac{B_{12}}{B_{12} + B_{21}} \frac{A_{21}}{1 + \frac{I_{sat}^\nu}{I_{sat}}^\nu} \]  

(2.25)

\( h \) = Planck’s constant

\( \nu \) = the frequency of the emitted fluorescence

\( \Omega \) = the collection solid angle

\( A \) = the focal area of the laser beam

\( \ell \) = the axial extent along the beam from which the fluorescence is observed

\( I_{sat}^\nu \) = the saturation spectral irradiance defined as \( I_{sat}^\nu = \frac{(A_{21} + Q_{21})c}{B_{12} + B_{21}} \)

The final equation 2.25 relates the fluorescence signal to the initial population of the specific rotational level excited, which, in turn, is related to the total species population throughout the Boltzmann expression. A similar two-level model description is introduced by Daily and Piepmeier in their review of LIF [117, 118]. The analysis of the two-level model can be extended to three- and four-level models. In reality, the analysis becomes more complex for real molecules due to multiple rotational and vibrational energy levels.

### 2.3.2 Experimental Considerations

Several factors need to be considered when LIF is applied to measure the PAHs’ concentration, including the wavelength and energy of incident light, wavelength of the PAHs’ radiation, and the gate setup for data collection, etc.
For the selection of incident light wavelength, it is known that most PAHs have strong absorption bands in the UV range (200nm to 300nm), which is widely adopted by researchers for excitation of LIF [116]. To excite LIF from large PAHs of more aromatic rings, excitations can be moved from the UV range to the visible range. Usually, large PAHs have been detected with argon lasers upon excitations at 460, 488, and 514nm [119-121].

Generally, since the difference of energy level between the molecular ground state and the electronic excitation state decreases with an increase of the molecular mass size of PAHs, the fluorescence wavelength shifts toward longer wavelengths when the molecular size of PAHs increases. The relationship between the size and maximum emission wavelength of PAHs was studied by Zizak and his co-workers see Figure 2-6 [122].

![Figure 2-6 The size of PAHs and their spectral properties](image-url)
Usually, the LIF signal is collected by the ICCD camera or the PMT, which must be “gated” to remain open to the signal during a specific time period. Figure 2-7 shows the typical temporally resolved emission scans [123, 124].

![Figure 2-7 Temporally resolved emission scans using 266-nm excitation light at a detected wavelength of 450nm at 6mm above the burner [123].](image)

When PAHs are studied in sooting flames, laser induced incandescence from the soot can interfere with the LIF. Normally, the duration of the LIF signal is tens of nanoseconds, while the LII signal approaches its peak nearly together with the LIF signal and decays for several hundred nanoseconds. In order to distinguish the LII and LIF signals, two means are usually adopted: (1) reduce the laser intensity below the threshold for LII; or (2) select the duration of the gate later than the LIF signal. In the second option, the LII signal collection starts immediately when the LIF signal ends. A typical gate setup used within the program for both LII and LIF is shown in Figure 2-8.
2.3.3 Calibration of LIF

Many parameters are needed to determine the number density from a fluorescence power measurement. These include the fluorescence wavelength, the radiative decay rate, the collection solid angle, the sample volume, and the light collection efficiency. Though the values of these parameters could be obtained in various ways, a great deal of effort is needed to do so.

A more practical way to calibrate an LIF signal from radicals such as OH, CH, and NO is usually performed under well-known conditions in well-described flames, such as...
the McKenna burner, where the absolute concentration of the investigated molecule can be calculated or can be measured by another technique such as line of sight absorption spectroscopy [125, 126]. For the LIF signals from PAHs, PAH can be condensed and separated by dichloromethane extraction and filtration. The identification and quantitative measurement of these PAH can then be completed by gas-chromatography mass spectrometry, as performed by Ciajolo et al. [127].

2.4 Temperature measurement

Temperature is a key parameter in the combustion process, because of the strong dependence of some reaction rates on temperature. Thus, temperature distribution information is very important to validate and calibrate simulation models.

There are many methods for measuring temperature distribution in a flame environment, such as CARS [128], TFP (Thin Filament Pyrometry) [129], and 2-Color technique [130]. In this dissertation, the widely used thermocouple method was selected to measure temperature. Since the temperatures in flames are usually so high, the energy loss from the thermocouple cannot be ignored. In principle, the thermocouple within the flames is experiencing four types of heat transfer:

1. Convection between the gases and the thermocouple. This is desirable since it is the objective of a thermocouple measurement to determine the local gas temperature.
2. Radiant heat transfer between the thermocouple and its surroundings. This can cause a difference between the thermocouple measurement result and the actual local gas temperature.
Conduction along the thermocouple wires. This can result in significant heat loss from the thermocouple junction. Usually, researchers use sufficiently long and thin thermocouple wires to minimize such heat loss [131].

Coating was not considered in the flame environment, since it could not survive in the high-temperature regions.

Surface-induced catalytic reactions. These effects on thermocouple measurements in combustion process are poorly understood, both in terms of the magnitude of these effects and the factors affecting them. Heitor and Moreira explained catalytic reactions as the effects of radical recombination on the surfaces of the thermocouple wire and bead [131]. Many non-catalytic surface coatings have been considered as possible solutions to eliminate the catalytic effects, including silica (Kaskan, 1957), BeO/Y₂O₃ ceramic (Kent, 1970), and alumina-based ceramic (Burton et al., 1992). However, these coatings affected the radiant, convective, and conductive heat transfer as well, which caused other problems.

McEnally and his colleagues have thoroughly investigated temperature measurement via thermocouple [132]. McEnally compared the performance of different types of thermocouples consisting of various thermocouple wire and bead size [133]. Experimentally, a typical temporal thermocouple measurement in the sooting zone is shown in Figure 2-9 [132], obtained by McEnally. t=0 in the horizontal axis indicates the moment at which the thermocouple bead arrived in the measuring position.

The thermocouple bead temperature trend can be divided into three stages:

1. Transient-response stage, in which the temperature increased to its peak value, lasts ~0.2 s. The initial temperature was ~1500K at t=0, instead of 300K, since the bead
was already heated during the process of rapid insertion. The upper right profile is
the expanded view of the first two seconds of the curve. The dotted line in the inset
is an approximate extrapolation of the bead temperature data to t=0 moment. Within
this stage, the temporal characteristic is mostly determined by the thermal
properties of the thermocouple bead.

(2) Variable-emissivity stage. In the soot-free regions, the thermocouple’s maximum
readout should be constant, as the former stage is over. However, in the regions of
the flame with soot, the temperature decreases continually as soot deposits on the
bead, leading to increased emissivity and diameter. The variable-emissivity stage
happens first and ends at the moment that the emissivity of the thermocouple bead
is equal to that of the soot. In this curve, the stage ends around 5s; however, it will
vary with different locations where the local soot concentrations are changing.

(3) The variable-diameter stage occupies all of the t > 5s time period, in which the
temperature decreases more gradually compared to the former stages. It was verified
experimentally by McEnally that the decrease of temperature is due to the increase
of thermocouple bead diameter, as a consequence of the soot depositing on it. The
dividing point between stages (2) and (3) is indicated by the relatively sharp slope
change at t = 5s.
Figure 2-9 A thermocouple bead temperature history measured near the centerline, 50 mm above the fuel tube opening in an ethylene/air co-flowing flame. [132]
Chapter 3 Experimental Approach

This chapter describes the fuels used in the present study and the selection of the flame conditions, including fuel flow rates, equivalence ratios, and fuel dilutions. This discussion is followed by a description of the experimental set-up of all diagnostics for soot concentration measurements (laser extinction and laser-induced incandescence), aromatic species distribution measurements (laser-induced fluorescence), measurements of temperature in soot-free regions, and the simulation approach developed by Katta in ISSI.

3.1 Fuel matrix and flame conditions

Normally, real aviation fuel components fall into four molecular classes: normal paraffins, iso-paraffins, cyclo-paraffins, and aromatics. The fuel matrix in Table 3-1 (a) was designed to investigate the fuel molecules’ effects on soot and aromatic species formation in flames. The set of four fuel binary mixtures was designed so that includes each of the four chemical classes. The first designed mixture was the mixture of 75% n-dodecane and 25% m-xylene (liquid volume fraction). The selection of 25% volume fraction was derived from the ASTM requirement [134], in which 25% is the maximum volume fraction of aromatics permitted under JP-8 specifications. An important consideration in the selection of m-xylene as the aromatic compound for the study was the availability of a chemical kinetic model from an earlier research project [135].

In the other three fuel mixtures, m-xylene was replaced by iso-octane, methylcyclohexane, and n-heptane, with volume fractions shown in Table 3-1(a). The volume fraction of these three hydrocarbons was set such that the total number of carbon atoms from the second component in the binary mixture, e.g., n-heptane, was held constant.
at the same value as that for the m-xylene fuel. The composition in this set simulates the presence of light hydrocarbons in jet fuel and is consistent with the fuel specifications for the 10% distillation fraction, which must occur at a maximum temperature of 205°C. The boiling temperature of n-dodecane is highest among this fuel set, while the other components have similar lower boiling points.

An addition to the fuels in the test matrix for the overall program, four other fuels shown in Table 3-1 (b) were also used in the program: pure n-dodecane served as another basic reference fuel for the four fuel mixtures shown in Table 3-1 (a). JP-8 was used to evaluate the surrogate performance of m-X mixture; and pure iso-octane and SPK were designed to understand the performance of SPK and its surrogate fuel. Detailed information on JP-8 and SPK can be found in Appendix A.

<p>| Table 3-1 selected properties of fuel mixtures used within program. (a) |</p>
<table>
<thead>
<tr>
<th>name</th>
<th>component</th>
<th>volume fraction (%)(^a)</th>
<th>mass fraction (%)(^b)</th>
<th>hydrogen content (%)(^c)</th>
<th>H/C ratio</th>
<th>density (g/ml)(^d)</th>
<th>heat of combustion (MJ/kg)(^e)</th>
<th>flash point (°C)(^f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-X</td>
<td>m-xylene</td>
<td>25.0</td>
<td>27.7</td>
<td>13.8</td>
<td>1.90</td>
<td>0.778</td>
<td>43.0</td>
<td>44</td>
</tr>
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<td></td>
<td>n-dodecane</td>
<td>75.0</td>
<td>72.3</td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCH</td>
<td>methylcyclohexane</td>
<td>28.4</td>
<td>28.9</td>
<td>15.1</td>
<td>2.12</td>
<td>0.758</td>
<td>42.9</td>
<td>&lt; 5</td>
</tr>
<tr>
<td></td>
<td>n-dodecane</td>
<td>71.6</td>
<td>71.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>i-C(_8)</td>
<td>iso-octane</td>
<td>30.6</td>
<td>28.9</td>
<td>15.5</td>
<td>2.19</td>
<td>0.737</td>
<td>43.3</td>
<td>&lt; 5</td>
</tr>
<tr>
<td></td>
<td>n-dodecane</td>
<td>69.4</td>
<td>71.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(_7)</td>
<td>n-heptane</td>
<td>31.3</td>
<td>29.2</td>
<td>15.6</td>
<td>2.20</td>
<td>0.734</td>
<td>43.4</td>
<td>&lt; 5</td>
</tr>
<tr>
<td></td>
<td>n-dodecane</td>
<td>68.7</td>
<td>70.8</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
The fuel mixtures listed in Table 3-1 were used to in nitrogen diluted, co-flow, axisymmetric laminar diffusion and partially premixed flames. The flow rates of fuel mixtures were determined based on the nearly constant carbon flow rate (~0.011 mole/min), shown in Table 3-2 (a) and Table 3-2 (b).

The non-premixed (equivalence ratio $\Phi=\infty$) and partially premixed ($\Phi=6$ and $\Phi=2$) flames were used in order to simulate the fuel-rich conditions in the primary zone in the GTE’s combustor. The flow rate of 0.2 L/min dilution nitrogen was selected as a compromise between producing stable flames and suitable measuring species concentrations. For the flames fueled by m-X and JP-8, a higher flow rate of dilution nitrogen (0.48 L/min) was used to eliminate the soot emitting from the flames.
Table 3-2 Flame conditions for fuels in Table 3-1.

(a)

<table>
<thead>
<tr>
<th>Flame Name</th>
<th>Fuel</th>
<th>Fuel Flow Rate (ml/min)</th>
<th>Dilution Nitrogen Flow Rate(L/min)</th>
<th>Equivalence Ratio (Φ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C7-Φ=∞</td>
<td>C7</td>
<td>0.218</td>
<td>0.2</td>
<td>∞</td>
</tr>
<tr>
<td>C7-Φ=6</td>
<td>C7</td>
<td>0.218</td>
<td>0.2</td>
<td>6</td>
</tr>
<tr>
<td>C7-Φ=2</td>
<td>C7</td>
<td>0.218</td>
<td>0.2</td>
<td>2</td>
</tr>
<tr>
<td>i-C8-Φ=∞</td>
<td>i-C8</td>
<td>0.217</td>
<td>0.2</td>
<td>∞</td>
</tr>
<tr>
<td>i-C8-Φ=6</td>
<td>i-C8</td>
<td>0.217</td>
<td>0.2</td>
<td>6</td>
</tr>
<tr>
<td>i-C8-Φ=2</td>
<td>i-C8</td>
<td>0.217</td>
<td>0.2</td>
<td>2</td>
</tr>
<tr>
<td>MCH-Φ=∞</td>
<td>MCH</td>
<td>0.209</td>
<td>0.2</td>
<td>∞</td>
</tr>
<tr>
<td>MCH-Φ=6</td>
<td>MCH</td>
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<td>0.2</td>
<td>6</td>
</tr>
<tr>
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<td>0.209</td>
<td>0.2</td>
<td>2</td>
</tr>
<tr>
<td>m-X-Φ=∞-0.2N2</td>
<td>m-X</td>
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<td>∞</td>
</tr>
<tr>
<td>m-X-Φ=∞-0.48N2</td>
<td>m-X</td>
<td>0.48</td>
<td>0.48</td>
<td>∞</td>
</tr>
<tr>
<td>m-X-Φ=6-0.2N2</td>
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<td>0.200</td>
<td>0.2</td>
<td>6</td>
</tr>
<tr>
<td>m-X-Φ=6-0.48N2</td>
<td>m-X</td>
<td>0.200</td>
<td>0.2</td>
<td>6</td>
</tr>
<tr>
<td>m-X-Φ=2-0.2N2</td>
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<td>0.2</td>
<td>2</td>
</tr>
<tr>
<td>m-X-Φ=2-0.48N2</td>
<td>m-X</td>
<td>0.200</td>
<td>0.2</td>
<td>2</td>
</tr>
<tr>
<td>Flame Name</td>
<td>Fuel</td>
<td>Fuel Flow Rate (ml/min)</td>
<td>Dilution Nitrogen Flow Rate(L/min)</td>
<td>Equivalence Ratio (Φ)</td>
</tr>
<tr>
<td>--------------------</td>
<td>-------</td>
<td>-------------------------</td>
<td>-----------------------------------</td>
<td>-----------------------</td>
</tr>
<tr>
<td>JP-8·Φ=∞-0.2N₂</td>
<td>JP-8</td>
<td></td>
<td>0.2</td>
<td>∞</td>
</tr>
<tr>
<td>JP-8·Φ=∞-0.48N₂</td>
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<td>0.48</td>
<td>∞</td>
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<td>0.2</td>
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<td></td>
<td>0.48</td>
<td>6</td>
</tr>
<tr>
<td>JP-8·Φ=2-0.2N₂</td>
<td>JP-8</td>
<td></td>
<td>0.2</td>
<td>2</td>
</tr>
<tr>
<td>JP-8·Φ=2-0.48N₂</td>
<td>JP-8</td>
<td></td>
<td>0.48</td>
<td>2</td>
</tr>
<tr>
<td>SPK·Φ=∞</td>
<td>SPK</td>
<td></td>
<td></td>
<td>∞</td>
</tr>
<tr>
<td>SPK·Φ=6</td>
<td>SPK</td>
<td>0.208</td>
<td>0.2</td>
<td>6</td>
</tr>
<tr>
<td>SPK·Φ=2</td>
<td>SPK</td>
<td></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>C₁₂·Φ=∞</td>
<td>C₁₂</td>
<td></td>
<td>0.2</td>
<td>∞</td>
</tr>
<tr>
<td>C₁₂·Φ=6</td>
<td>C₁₂</td>
<td>0.211</td>
<td>0.2</td>
<td>6</td>
</tr>
<tr>
<td>C₁₂·Φ=2</td>
<td>C₁₂</td>
<td></td>
<td>0.2</td>
<td>2</td>
</tr>
<tr>
<td>Pure-i-C₈·Φ=∞</td>
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<td>∞</td>
</tr>
<tr>
<td>Pure-i-C₈·Φ=6</td>
<td>Pure i-C₈</td>
<td></td>
<td>0.2</td>
<td>6</td>
</tr>
<tr>
<td>Pure-i-C₈·Φ=2</td>
<td>Pure i-C₈</td>
<td></td>
<td>0.2</td>
<td>2</td>
</tr>
</tbody>
</table>
3.2 Burner System

The flames were obtained from the system shown in Figure 3-1. The liquid fuel stored in the Syringe D500 fuel pump was delivered through the 1/16” stainless steel tube to the mixing and vaporizing chamber, which is a 1/4” brass Swagelok tee filled with a small amount of fiberglass [136]. The tubing in the system was wrapped with heat tapes from one foot upstream of the mixing chamber to the end of the burner. Inside the mixing chamber, the liquid fuel vaporized by the heat conduction from these heat tapes was carried by the dilution nitrogen. An orifice of 100\(\mu\)m diameter was used to produce suitable pressure and residence time for vaporizing the liquid fuel mixture. Dilution nitrogen and premixing air were metered by a mass flow controller (Brooks Instrument), while the co-flow air was set by a flow meter to keep a constant flow rate of 4 ft\(^3\)/min. Four filters were installed in the system for the fuel, dilution nitrogen, mixture, and premixing air inlet. Additionally, K-type thermocouples were installed to monitor the temperatures in several locations, of which the two most important were between the mixing chamber and orifice (TC#2) and 5cm below the tip of the fuel tube (TC#5). Through adjusting the power supply for the heating tapes, the temperature was kept around 250°C along the pipe to prevent condensation of fuels.
The co-flow burner used in this study is based on the design of Santoro et al. [71], which has a central fuel jet (I.D = 11.1 mm) surrounded by a co-flowing air stream (I.D = 101.6 mm). The annular region for the co-flow air contains screens, glass beads, and a honeycomb, as shown in Figure 3-2, to produce a uniform exit velocity profile [69, 71]. The fuel and dilution nitrogen mixture tube extends 4 mm above the top surface of the annulus for air flow. Translation stages using step motors were used to move the burner in axial and radial directions.

Some minor modifications were applied on the burner in order to reduce the residence time for the fuel mixture and consequent reactions within the tubes. During the development of the modified burner, samples of the vapor mixture exiting the tube exit were collected for GC-FID analysis to check whether reaction was occurring in the fuel system. The results, as shown in Figure 3-3, indicate that the fraction of pyrolyzed or
reacted fuel mixture within the tubing system was negligible. Previous studies [137, 138] also verified that the oxidation and pyrolysis of fuels in this temperature range were negligible.

Figure 3-2 Schematic drawing for the burner.
Figure 3-3 A typical GC-FID result from a vapor sample from the tube exit. This figure was obtained for the i-C₈-Φ=6 flame.

Due to the significance of boundary conditions to the simulation work, the radial temperature distribution at the tube exit was measured. The temperature profile was measured when the flame was off using a K-type thermocouple. The radial velocity at the tube exit was measured with a hot wire anemometer at room temperature (20°C) and then corrected with the measured temperature distribution. Boundary temperature and velocity profiles are shown in Figure 3-4. The difference of boundary temperature and velocity is negligible for the test conditions used for the various fuel mixtures.
3.3 Laser Extinction

The laser extinction studies were carried out using a Coherent Innova 70 (2W), 514.5nm wavelength argon ion laser. The optical layout for the system is shown in Figure 3-5. The laser beam was chopped at 1000Hz (Stanford Research Systems, Model SR540), and a photodiode was used to continuously measure the intensity of the incident laser beam, which was recorded as $I_0$. A set of convex and concave lens was used to expand the laser beam diameter for incident laser energy measurement by the photodiode, to increase the sensing area of the photodiode. Due to the axi-symmetry of the flames, data collection was simplified by taking line-of-sight average absorption measurements through different locations of the flame. The transmitted light, called “$I$,” was measured by another photodiode together with an integrating sphere in order to eliminate “beam steering” interference. Both photodiodes were used within the range in which the signals were linear with respect
to the laser intensities. All the output signals from the photodiodes were processed through transimpedance and lock-in amplifiers to minimize interference from extraneous radiation, and data were collected by a National Instruments data acquisition system (NI-PCI-6110) with a sampling rate of 10Hz and 40 samples at each measuring point. The path-integrated laser-extinction measurements are inverted tomographically, using Fourier inversion, and cast as radial profiles of soot volume fraction in the flames [139]. The section of FORTRAN code for this inversion is attached in Appendix B. The value of $\tilde{m} = 1.57 - 0.56i$ was selected for comparison with previously published work [140]. Different selections of refractive indexes could result in different soot volume fractions by a factor of at most two.

![Figure 3-5 Optical arrangement for laser-extinction experiment. NDF=Neutral Density Filter.](image-url)
3.4 Laser Induced Incandescence

A pulsed Nd:YAG laser (Surelite, Continuum, 10Hz frequency and 7ns pulse duration) was used as the energy source in the LII setup, shown in Figure 3-6. The laser beam of 0.3mm diameter, operated at a 532nm wavelength, was expanded into a vertical sheet of 50mm length and 350µm width, via a fused silica cylindrical lens. The laser sheet was focused at the center of the flame using a 500mm focal length convex lens. Before data collection, it was verified, as shown in Figure 3-7, that the incident laser energy was set to ensure that the LII signals were in the “plateau” region, which indicated that the LII signal intensities were weakly dependent on the incident laser energy. The LII signals were collected by an ICCD installed perpendicularly to the laser sheet. In order to reduce effects of fluorescence, the LII radiation was focused on the ICCD using an f 2.8 105mm UV lens, fitted with a narrow-band interference filter centered at 430nm with 10nm FWHM. The ICCD was triggered by the laser pulse, with a 10ns gate delay and 100ns gate width. The ensemble-averaged LII signals were obtained from 300 measurements and the spatial resolution was 0.125mm/pixel. The LII signals were calibrated via laser extinction to get quantitative soot volume fraction distributions.

The uncertainties of LII measurements are mostly from the following aspects: (1) the variation of incident laser intensity could be ±10%; (2) the distribution of laser intensity is not uniform along the laser sheet; the basic shape of the profile is Gaussian type, while the peak values could be around two times higher than the lowest values; (3) the sensitivity of ICCD camera was considered as uniform, while no substantial methods were taken to verify in the measurements.
Figure 3-6 Layout of LII experiment.

Figure 3-7 LII signal's dependence on laser energy.
3.5 Laser-Induced Fluorescence

Laser-induced fluorescence was applied to obtain the spatial distribution of aromatic species in the flames. An Nd:YAG laser (Surelite, Continuum) with the fourth harmonic wavelength of 266nm operating at 10Hz was used as an excitation source. The optical arrangement for the LIF experiment is shown in Figure 3-8.

Both laser sheets and laser beams were used for excitation. The laser fluence was set at about a 10mJ/pulse for the laser sheet, while a 0.2mJ/pulse was used for the laser beam to avoid interference from LII signals. The LIF signals from the laser sheet were captured by the ICCD camera, with 200 images and a 35ns gate width, starting with the laser pulse. The LIF signal from the laser beam was collected by a PMT (Hamamatsu RS928) together with a Boxcar average (Stanford Research Systems, Model SR250) with a 35ns gate width, initiating at the laser pulse, and 100 samples per second with a collection time of 15 seconds. Before the ICCD camera and PMT, two sets of wavelength filters were employed: (1) WG320 and UG11 filters to transmit fluorescence ranging from 320 nm to 380nm, which corresponds to small aromatics (1 and 2 rings); (2) GG420 and BG12 filters to transmit fluorescence ranging from 420 nm to 480 nm, which corresponds to large aromatics (3 and 4 rings). Initially, the laser sheet was adopted; however, its detection sensitivity was insufficient to capture LIF signals for most partially premixed flames. Consequently, the laser beam was employed in the research program to capture the weak LIF signals. Since the signals were collected from a group of species, it is impractical at this time to calibrate the LIF signal with aromatic species concentration. Therefore, only qualitative concentration results of aromatics could be obtained.
LIF experiments are essentially qualitative; especially for the aromatics are sensitive to the environmental temperature. Similar to collecting LII signals, the grids of sensor on ICCD are not possessing the same sensitivities of LIF signals.

Figure 3-8 Optical arrangement for LIF experiment.

3.6 Temperature measurement

At first, the temperature measurement technique developed by McEnally was tried in these flames. However, the technique could not be implemented successfully due to equipment limitations. Figure 3-9 shows the temperature distribution at 5mm height above the tube exit in the C7-Φ=∞ flame. The curve with the legend “McEnally’s design” refers data collected based on McEnally’s method. The thermocouple wire diameter in this case was 125 micron, which is larger than those used by McEnally. Smaller thermocouples could not be used without breaking. The use of the larger thermocouples led to peak
temperatures that were much lower than in the simulation, while the temperature at the center was higher in experiments than in the simulation. It was suspected that the heat conduction from the flame to the thermocouple bead via the thermocouple wire was affecting the experimental result.

Therefore, an alternative method was developed. An uncoated R-type micro-thermocouple of 125\(\mu m\) wire diameter and 250 \(\mu m\) bead diameter was used. A small “loop” thermocouple design was developed, as shown in Figure 3-10, to reduce the effects of conduction across the thermocouple wire. In Figure 3-9, the curve with the legend “Loop TC” indicates much improvement with this method when compared to the simulation results.

Unfortunately, the back projection method commonly used to avoid soot depositing on thermocouples could not be applied in the loop design. The rapid movement of the

![Figure 3-9 Measuring temperature comparison obtained via different configurations.](image)
thermocouple required for the back projection method led to large uncertainty in the location of the thermocouple bead. Consequently, the temperature measurement could be achieved only in the soot-free regions. In this work, the measurements were taken along the centerline up to ~20mm height above the tube exit, and radially at 5mm height above the burner in the flames. Because of flame attached to the thermocouple in the Φ=2 flames, reliable temperature measurements could not be obtained.

The uncertainties of temperature measurement via thermocouple were due to two killers: fluctuations of flame; uncertainties from the radiation corrections. While keeping the thermocouple within the flames, the flames could fluctuate around ±1.5mm at most. Usually, the radiation correction of thermocouple could enhance the measured temperature by at most 50°C.

![Figure 3-10 Temperature measurement configuration.](image)
3.7 Model approach

A time-dependent, axisymmetric mathematical model known as UNICORN (UNsteady Ignition and COmbustion using ReactioNs) [141-144] was used by Dr. Vish Katta for the simulation of the laminar jet diffusion flames. A clustered mesh system was employed to trace the large gradients in flow variables near the flame surface. A semi-detailed chemical-kinetics model (CRECK-0810) developed by Ranzi et al. [145, 146], which consists of 206 species and 5652 reactions, was used. Thermo-physical properties such as enthalpy, viscosity, thermal conductivity, and binary molecular diffusion of all the species were calculated from the polynomial curve fits for the temperature range 300 - 5000K. Mixture viscosity and thermal conductivity were then estimated using the Wilke and Kee expressions, respectively. Molecular diffusion was assumed to be of the binary-diffusion type, and the diffusion velocity of a species was calculated using Fick's law and the effective-diffusion coefficient of that species in the mixture.

Soot in the flames was simulated assuming it to be gaseous species and through the solution of two conservation equations--one for the soot volume fraction and the other for the soot number density. These two terms were obtained using a comprehensive soot model constructed based on the simplified assumptions that (1) soot nucleation is a first-order function of acetylene concentration [147]; (2) soot growth occurs via the H-Abstraction-C2H2-Addition (HACA) mechanism of Frenklach and Wang [45]; (3) soot oxidation is due to the presence of O2, OH, O, CO2, and H2O [148, 149]; and (4) soot agglomeration results from binary collisions between soot particles in a free molecular regime [89, 150].

A simple radiation model for gaseous species, based on the optically thin-media assumption, was incorporated into the energy equation [151]. Only radiation from CH4,
CO, CO$_2$, and H$_2$O was considered in the present study. Radiation from soot was modeled assuming it as blackbody type [152].
Chapter 4 Results and Discussion

This chapter contains two topics: experimental results and comparisons to the simulation analysis. Experimentally, the fuel mixtures listed in Table 3-1 were investigated in laminar flames, using the techniques introduced in Chapter 3. Since the fuels, C_{12}, Pure-i-C_{8}, and SPK, were not part of the original program, the experimental results from these fuel mixtures are shown in the Appendix C as supplementary data.

In the first part of this chapter, the following measurement results are presented: visible flame appearances; soot volume fraction distributions; aromatic species distributions; and temperature distributions in soot-free regions. For each result, the fuel molecular structure effects are first analyzed, followed by a comparison between JP-8 and m-X, which was considered as a simple surrogate for JP-8. Most attention was paid to the fuel type effects and equivalence ratio effects.

Predicting the performance of the real fuels (JP-8 and SPK) was beyond the capacity of the simulation, so only the simple mixtures of pure components were studied computationally. In addition to the results shown in the second part of this chapter, the simulation results of C_{12} and Pure-i-C_{8} are shown in the Appendix D. Similar to the experimental results analysis, the predicted outcomes for laminar flames are displayed in order to evaluate the model and explore the results for further study.

3.3 Experimental results
3.3.1 Flames’ visible appearances

The visible appearances of the flames listed in Table 3-2 (a) are displayed in Figure 4-1. The pictures of the flames were obtained via a digital camera. In order to display the appearances of the flames clearly, different operating parameters were applied on the digital camera. The pictures of the flames are arranged according to their fuel types and equivalence ratios, as indicated by the legends above each picture. Figure 4-1 (a), Figure 4-1 (b), and Figure 4-1 (c) are for the flame conditions of $\Phi = \infty$, 6, and 2 respectively.

As shown in Figure 4-1, all the flames have closed tips except the m-X- $\Phi=\infty-0.2N_2$ flame, in which soot was escaping from the tip. For all the flames, a small gap of ~3mm was present between the bottom of the flame and the tube exit.

In the pictures of the flames, the bright orange and white regions indicate the existence of soot due to its radiation, while the blue regions represent the light emissions from species such as CH. For a given equivalence ratio, flames burnt with m-X fuel always have larger sooting regions, while other fuels have similar visible appearance. When air is added to the fuel jet, the soot regions shrink substantially. For example, premixing more air into the m-X- $\Phi=\infty-0.2N_2$ flame stopped it from smoking. The $\Phi=2$ flames were mostly blue with small orange tips, indicating a very small amount of soot produced. Interestingly, the $\Phi=2$ flames exhibit a “double flame” structure, which contains inner and outer blue flame boundaries, as shown in [153].
Figure 4-1 Visible appearances of flames for different fuel mixtures. (a) $\Phi=\infty$ conditions; (b) $\Phi=6$ conditions; (c) $\Phi=2$ conditions.
Figure 4-2 shows the comparison of the appearances between JP-8 and m-X flames. A higher flow rate of dilution nitrogen (0.48l/min) was used to avoid soot escaping from the tip of the m-X- Φ=∞ flame. The Φ=∞-0.2N₂ flames were both smoking for m-X and JP-8 fuels, as shown in Figure 4-2 (a) and Figure 4-2 (b), while the smoking phenomenon was stopped by increasing the dilution nitrogen flow rate to 0.48l/min. However, except for the smoking flames, the two different dilution nitrogen flow rates did not affect the flames’ appearances significantly.

![Figure 4-2 Visible appearances of flames burnt with (a) m-X mixture; (b) JP-8.](image-url)
The summary of flame heights is shown in Figure 4-3 and Figure 4-4. The flame height was defined as the length of the flame from the tube exit to the visible flame tip. Consequently, the heights for the smoking flames cannot be identified. In Figure 4-3, the flame heights were compared between different fuel types under $\Phi=\infty$, 6, and 2 conditions. At a given test condition, the m-X flames are always longer than flames of the paraffinic fuels, which tend to have similar flame heights. The measurement of flame heights has an uncertainty of ±1 mm due to the fluctuations and unsteadiness of the flames. By taking this uncertainty in height into consideration, the effects of fuel type on the flame heights for the fuels, except for m-X, are almost negligible. For all the fuels, as more air is premixed, the flame height decreased significantly, since the oxygen is chewing up precursors.

![Figure 4-3 Flame heights comparison for study of molecular structure effects.](image-url)
In Figure 4-4, m-X flames are shown to always be slightly longer than JP-8 flames, by at most 3.4mm. For the non-smoking flames, the variations caused by different dilution nitrogen flow rates were quite small.

Overall, by observing the flames’ appearances, it is safe to conclude that m-X flames are different from other flames, which are themselves quite similar, and m-X flames are similar to JP-8 flames.
3.3.2 Soot volume fraction distribution

As mentioned in Chapter 3, the soot volume fraction distribution was measured using the combination of LII and laser extinction. The two-dimensional qualitative LII measurement was calibrated by the quantitative laser extinction measurement. Figure 4-5 shows the principle of obtaining the LII calibration factor, which is equal to the ratio of LII signal counts to soot volume fraction (ppm). A radial distribution of soot volume fraction was obtained by both laser extinction and LII. A peak in soot volume fraction and a corresponding peak in LII counts occurs on each side of a flame. The calibration factor was then calculated based on these peak values according to the ratio of LII signals to peak soot volume fractions with unit ppm.

![Figure 4-5 LII calibration determination principle. The radial data was obtained 25mm above the tube exit in m-X-\( \Phi=\infty-0.2N_2 \) and JP-8-\( \Phi=\infty-0.2N_2 \) flames.](image-url)
Figure 4-6 indicates the dependence of LII calibration factors on the soot volume fractions. Generally, the calibration factors converge more as the soot volume fraction increases, while they are more scattered in the lower regions. For different groups of flames, two values of average calibration factors were determined: in Figure 4-6 (a), the value of 475 was selected; in Figure 4-6 (b), the value became 480. For convenience and consistency in this dissertation, the calibration factor of 480 ± 15 with a 95% confidence interval was set.
The two-dimensional distribution of soot volume fraction is shown in Figure 4-7 and Figure 4-8. Unfortunately, the soot concentrations in Φ=2 flames were below the detection ability, so the experimental results for soot concentrations in Φ=2 flames are not shown. In the laser extinction measurement, the minimum positive value of soot volume fraction was 0.1 ppm, while it was suspected that the detection limit in LII was close to 0.5 ppm due to the poor performance of the intensifier in ICCD. In order to display the distribution trends clearly, different ranges for soot volume fractions were used for each of the contour plots, as shown within the brackets above the plot.
Figure 4-7 2-D distribution of soot volume fraction for study of fuels’ molecular structure effects.
Figure 4-8 2-D distribution of soot volume fraction for study of JP-8 and its surrogate.
For the non-smoking flames, a common and typical trend could be found. Take the m-X-\(\Phi=6\)-0.2N\(_2\) flame for example, in which there was nearly no soot produced below 15mm height. Soot started to occur at annular regions in the range of 15mm to 23mm height. The peaks of soot concentrations moved towards the center of the flame, with increasing values, as shown in the 25mm to 35mm region. Finally, the soot regions became narrower and smaller areas due to soot oxidation. However, in the \(\Phi=\infty\) flames under 0.2L/min dilution nitrogen conditions, soot was emitting from the flame tips. Qualitatively, the measured soot distributions introduced above are consistent with previous research conclusions.

In Figure 4-7, compared with other fuels, m-X presents larger sooting regions and a higher amount of soot produced. The distributions of soot volume fraction are very similar in the MCH, i-C\(_8\), and C\(_7\) flames under given equivalence ratios. With more air premixed with the fuel jet, both the areas of the soot regions and the amount of soot produced decreased substantially, which is consistent with the trend shown in visible light images of the flames. However, by comparing the sooting regions in Figure 4-7 and Figure 4-1, it is observed that for non-aromatic flames, the sooting regions are smaller in LII images than in luminous pictures, especially for \(\Phi=6\) flames. It is believed that this discrepancy could be mostly caused by the poor detection ability of the LII measuring system, especially the ICCD. Specifically, the average calibration factor based on 300 accumulated images is 480 in this dissertation; however, the value was around 35,000 in previous research with 200 accumulations in earlier work in the lab [69]. A possible reason for this discrepancy might be the poor performance of the intensifier within the ICCD.
Figure 4-8 again indicates similar distributions of soot volume fraction between m-X and JP-8 flames. All the trends discussed above can also be found in Figure 4-8. However, by comparing Figure 4-8 and Figure 4-1, the soot existing regions are consistent in m-X and JP-8 flames, due to their higher concentrations of soot.

Figure 4-9 and Figure 4-10 depict the measured soot volume fraction (ppm) as a function of height above the tube exit (mm) on the centerline. Normally, the fuel types are indicated by different colors of the curves. The definition of soot concentration along the centerline in LII measurement was the average value of soot volume fractions within the width of three pixels. The 10-point moving average trend lines were applied to smooth the noise in the LII data. The variation in soot volume fraction occurring at ~60mm height above the tube exit were caused by the reflections from the edges of the optical windows. The overall shape of the soot profiles along the centerline in these flames is similar to that found in previous research [154]. However, in the smoking flames, the soot was not burnt out downstream; instead, the soot volume fraction increased. Except for the smoking m-X-Φ=∞-0.2N₂ flame, the locations where the soot volume fraction peaks are fairly consistent: 30mm ~ 35mm height above the tube exit.

With respect to the fuels’ molecular structure effects, m-X flames present the highest amount of soot produced, while the other flames show similar levels of soot. For both Φ=∞ and Φ=6 conditions, m-X flames present larger amounts of soot over a greater distance along the centerline. Take the Φ=6 flames for instance, the soot started to occur at around 17mm height above the tube exit in the m-X-Φ=6-0.2N₂ flame, and the soot volume fraction became zero at around 55mm. So measureable soot existed over a distance of approximately 40mm. However, this soot containing region on the centerline shrunk to
approximately 16 mm for the other flames, with measureable soot beginning at 24mm and ending at 40mm. Quantitatively, the peak values of soot volume fraction in m-X flames are higher than in other flames by a factor of ~ 2-4.

The premixing air reduced the soot volume fractions in all flames significantly, which could also be indicated by the range of vertical axis: 12 ppm for Φ=∞ flames and 7 ppm for Φ=6 flames. In addition, the distance in which the soot appeared became shorter in Φ=6 flames than in Φ=∞ flames.

Figure 4-10 illustrates how similar soot volume fraction distribution is between m-X and JP-8 flames. When the flow rate of dilution nitrogen changed from 0.2L/min to 0.48L/min, the initial location where the soot started to occur moved downstream by ~10mm while the soot-disappearing locations were almost unaffected. Quantitatively, the increasing amount of dilution nitrogen reduced the peak soot volume fractions by a factor of around 2.

An interesting finding in Figure 4-10 is the great consistency between m-X and JP-8 flames, especially for 0.2N₂ flames, in which the curves are almost overlapping. For 0.48N₂ flames, even though the curves are not overlapping, the fluctuations are still similar and repeatable.
Figure 4-9 Soot volume fraction distribution along the centerline for study of fuels' molecular structure effects. (a) $\Phi=\infty$ conditions; (b) $\Phi=6$ conditions.
Figure 4-10 Soot volume fraction distribution along the centerline for study of JP-8 and its surrogate. (a) $\Phi=\infty$ conditions; (b) $\Phi=6$ conditions.
Figure 4-11 shows the original calibrated LII signals for m-X and JP-8 flames. Generally, the noise or the fluctuations in the curves might be from the following sources:

1. the laser output energy’s difference at each pulse;
2. the fluctuations and unsteadiness of the flames during the measurement;
3. the variations of sensitivities of the pixels in the ICCD camera;
4. the variations of laser energy along the laser sheet due to the Gaussian profile of laser energy;

During the LII measurement, the laser’s output energy was monitored, which showed the energy variations in different pulses were within 10%. Though much effort was spent to reduce the problem of fluctuations, the flames still displayed some tiny unsteadiness. However, the above two types of uncertainties should be unrepeatable and only responsible for the noises in the signals. There is no evidence to identify whether the soot distribution is similar for m-X and JP-8 flames in the smoking zones. In addition, the LII results averaged three hundred accumulations of LII images; consequently, this data collection strategy should eliminate or at least reduce noises due to laser output energy or unsteadiness of the flames.

The ICCD camera was also tested with a white sheet of paper, which served as a uniform light source for the camera. The results did not indicate any potential variations along the ICCD that could lead to the significant fluctuations in the smoking regions of $\Phi=\infty-0.2N_2$ flames. The identification of these repeatable fluctuations needs further investigation.
3.3.3 Distribution of aromatic species

The aromatic species produced in the flames are usually considered as the precursors for soot and classified as hazardous air pollutants (HAPs) [155, 156]. As introduced in Chapter 3, two groups of aromatics were measured by LIF: “small aromatics” and “large aromatics,” which contain one and two aromatic rings and three and four aromatic rings, respectively.

Initially, LIF signals from aromatic species were measured using ICCD with a planar laser sheet to obtain the two-dimensional distribution in flames. However, for most flames, the LIF signals were too weak to be collected by the ICCD due to the low concentrations of aromatic species. Then the PMT was adopted to capture the LIF signals.

Figure 4-11 Raw calibrated LII signals data from m-X and JP-8 flames.
with a laser beam, although PMT could provide only point measurement, rather than two-dimensional contours. In the measurements, the voltage for the PMT was kept constant (1100V), while the sensitivity of the Boxcar averager was adjusted to different signal intensities.

Because the LIF signals collected in the present work are from many different aromatic species, it is impractical to obtain quantitative values of the concentrations of aromatics. In addition, the temperature and oxygen quenching can affect the LIF signals substantially. Hence, only qualitative experimental analysis is given in this study.

While considering the comparison of the concentration levels of small and large aromatics, the following considerations should be kept in mind: the transmittance curves for the different filter glasses are not uniform across the band pass filters and the quantum efficiency of the PMT is not uniform across the different wavelength regions. These variations were not corrected in the experimental results. Consequently, the ratio of small and large aromatics from the experiments was not exactly the same as the actual ratio. Detailed information about these filters and the PMT is presented in the Appendix E. Both radial and axial measurements were carried out in all flames for LIF. For some partially premixed Φ=2 flames, the LIF signal intensities were too weak to be detected.

3.3.3.1 Small aromatics

Due to the existence of m-Xylene, which is also a one-ring aromatic and fluoresces in the wavelength range of “small aromatics,” the m-X-Φ=∞-0.2N₂ flame has the strongest LIF signal intensity. Figure 4-12 shows the small aromatics’ LIF signal distribution in the m-X-Φ=∞-0.2N₂ flame. Figure 4-12 (a) was obtained by an ICCD, while Figure 4-12 (b)
was collected using the PMT. The resolution for the ICCD was 0.125mm/pixel, and the LIF signals were collected at 1mm, 3mm, 5mm, 10mm, 15mm, 20mm, 25mm, 30mm, 35mm, and 40mm height above the tube exit with 0.25mm in radial location, by the PMT. For all the other flames, including JP-8 and the other flames listed in the Appendix, the small aromatics’ LIF signals were normalized to the maximum value, which appears in the center of the tube exit in the m-X- Φ=∞-0.2N₂ flame.

![Figure 4-12 LIF images from small aromatics obtained by (a) ICCD; (b) PMT. Data was obtained from an m-X-Φ=∞-0.2N₂ flame.](image)

Similar to the soot volume fraction measurement, qualitative radial profiles of small and large aromatics’ LIF signals were obtained at various heights above the tube exit. Radial measurements were carried out from the beginning of the flame, moving downstream until the farthest point from the tube exit at which any signal was detected. Data were collected mostly with 5mm height intervals; however, since more details were needed near the tube exit, data at 1mm, 3mm, and 5mm above the tube were also collected. Due to the significant difference of the signal intensities for different flames, the figures
with LIF data are plotted with different scales. In this way, the aromatics’ distribution trends can be more clearly understood.

Figure 4-13 shows the typical distribution of small aromatics in flames for (a) aromatic fuel mixture and (b) paraffin fuel mixture. In Figure 4-13 (a), at the beginning of the m-X-Φ=∞-0.2N₂ flame, small aromatics’ LIF signals were of their highest values with the greatest width. Then both the magnitude and radial width of LIF signals decrease substantially downstream due to the consumption of m-xylene. As shown in Figure 4-13 (b), the small aromatics’ LIF signals display a trend similar to the distribution of soot: the small aromatics’ LIF signals occur at the annual region of the flame, then the peaks move towards the center with increasing values and finally decrease to zero downstream. This trend is common for all the paraffin fuels, including MCH, i-C₈, C₇, and C₁₂.

Ideally, there should exist only fuels, dilution nitrogen, and air (partially premixed conditions) coming out at the tube exit. Ignoring the quenching effects, the small aromatics’ LIF signals at the tube exit should depend on the concentrations of m-xylene alone in m-X flames. Since the temperatures at the tube exit were almost the same for all m-X flames, as shown later in this dissertation, the normalized concentrations of m-xylene for different m-X flames should be nearly equal to the normalized mole fractions.

Quantitatively, the peak signal value at the beginning of the m-X-Φ=∞-0.2N₂ flame corresponds to 0.043 (mole fraction) or 0.911 mole/m³ of m-xylene. However, this quantitative link might not be valid in all flame regions and all fuels, since other newly produced small aromatic species might contribute to the LIF signals. It is important to note that the scale of normalized small aromatics’ LIF signals changed from 1.0 to 0.1 for two
different flames in Figure 4-13. However, it is incorrect to claim that the concentration of small aromatics produced in the m-\(X-\Phi=\infty-0.2N_2\) flame is higher than that produced in the MCH-\(\Phi=6\) flame by a factor of \(\sim 10\). Many other factors including the cross sections of aromatics, the LIF signals’ dependence on temperature, and the quenching effects caused by oxygen are affecting the LIF signals significantly.

![Figure 4-13](image)

Figure 4-13 Typical radial distribution of normalized LIF signals from small aromatics in: (a) m-\(X-\Phi=\infty-0.2N_2\) flame; (b) MCH-\(\Phi=6\) flame.
In addition to the radial results, Figure 4-14 shows the normalized LIF signals from small aromatics along the centerline for all flames in Table 3-2 (a). Since the magnitude of the fluorescence signal in m-X flames is much higher than that of the other fuels, the results for the other fuels are shown in an inset in the right top corner of Figure 4-14 (b). For m-X flames, the small aromatics’ LIF signals peak at the beginning of the flames (0mm height above tube exit) and then decrease rapidly downstream as m-xylene was consumed by reactions or converted into large aromatics. Except for the m-X flames, the other paraffin flames showed quite similar distribution trends along the centerline: small aromatics start to occur at the low part of the flame and climb to peaks in the middle region, followed by the slow decay downstream, where the small aromatics were oxidized or/and converted into larger aromatics or/and soot.

Quantitatively, the peak values of small aromatics’ LIF signals are higher in m-X flames than in other flames by a factor of ~10 and ~20 under $\Phi=\infty$ and $\Phi=6$ conditions respectively. The uncertainty for m-X, MCH, and i-C$_8$ flames is within 5%, while for C$_7$ flames, the value could be approximately 10%. After taking this uncertainty into consideration, the small aromatics’ LIF signal intensities are equivalent between MCH, i-C$_8$, and C$_7$ fuels.

By observing the scale of vertical axis changes from 1.0 in Figure 4-14 (a) to 0.5 in Figure 4-14 (b), due to two factors: (1) dilution effect; (2) quenching effect caused by the oxygen existing in the premixing air. However, the quenching effect by oxygen could not be evaluated in the measurement.
Figure 4-14 Normalized LIF signals from small aromatics along centerline. (a) $\Phi=\infty$ flames; (b) $\Phi=6$ flames.
The small aromatics’ LIF signals along the centerline in m-X and JP-8 flames under 0.2 L/min and 0.48 L/min dilution nitrogen conditions are compared in Figure 4-15 and Figure 4-16 respectively. Very similar trends could be found in JP-8 flames, while the scale changed from 0~1 to 0~1.6. As indicated in the Appendix A, there exist a total of 18.7% (by weight) aromatics (1 and 2 rings) in JP-8. So, the small aromatics’ LIF signals also peak at the beginning of the flames. As the small aromatics were burnt or converted to larger aromatics, the signals decayed rapidly, as seen in m-X flames. Again, keep in mind that the LIF signals were essentially qualitative, so it is not valid to compare the signals across different fuels quantitatively. For example, the relatively stronger signals in JP-8 flames did not necessary mean there were higher concentrations or mole fractions of small aromatics in JP-8. The absolute values of LIF signals were also dependent on the cross sections, quenching effect, etc.

By comparing the scales in Figure 4-15 and Figure 4-16, it is observed that the initial peak values of small aromatics’ LIF signals decrease as a higher flow rate of dilution nitrogen was used. An interesting finding is the region circled in Figure 4-16 (a), where it is believed that the relatively flat region was the outcome of the balance between m-xylene consumption and the production of other small aromatics. This trend will also be shown in the simulation results discussed later. For fuel type effect, m-X flames always need longer distances along the centerline for small aromatics’ LIF signals to decay to zero.
Figure 4-15 Normalized LIF signals from small aromatics along centerline for 0.2N₂ conditions. (a) m-X flames; (b) JP-8 flames.
Figure 4-16 Normalized LIF signals from small aromatics along centerline for 0.48N₂ conditions. (a) m-X flames; (b) JP-8 flames.
3.3.3.2 Large aromatics

Besides small aromatics, measurements for large aromatics were also carried out. The LIF signals from large aromatics were around 50% of the signals from small aromatics. Consequently, experimental results were obtained using a PMT.

As expected, the m-X-Φ=∞-0.2N2 flame had the strongest large aromatics’ fluorescence signals because it has the highest concentration of m-xylene, and consequently, large aromatics will be produced at the highest concentration in this flame. This maximum value, which appears at 15mm height above the tube exit around the center in the m-X-Φ =∞-0.2N2 flame, was selected as the reference for normalization of all other large aromatics’ LIF signals from other flames. As noted earlier, due to the number of aromatic species contributing to the LIF signal and to quenching effects, the fluorescence signals could not be converted to quantitative concentrations.

In Figure 4-17, both m-X-Φ=6-0.2N2 and i-C8- Φ=∞ show similar qualitative trends, as discussed in Figure 4-13 (b): the peak occurs at the edge of the flames, and then moves towards the center and finally decreases until the tip of the flames.
Figure 4-17 Typical radial distribution of normalized LIF signals from large aromatics in: (a) m-X·Φ=6-0.2N₂ flame; (b) i-C₈·Φ=∞ flame.
The normalized LIF signals from large aromatics along the centerline in all flames are shown in Figure 4-18, for both $\Phi=\infty$ and $\Phi=6$ conditions. Qualitatively, the large aromatics occur earliest and disappear latest in m-X flames, while other flames of the other fuels perform quite similarly. The locations where the large aromatics’ LIF signals peak are slightly upstream in m-X flames, as expected, since the presence of a single-ring aromatic compound in the fuel accelerates the formation of multi-ring aromatic species. For all fuel mixtures, the spatial extent of the signal from large aromatics shrunk significantly as more air was premixed in the fuel jet.

Quantitatively, the peak values of large aromatics’ LIF signals are higher in m-X flames than in other fuels’ flames, by a factor of ~10, for both equivalence ratio conditions. Due to the lower signal to noise ratio compared to small aromatics LIF measurement, the uncertainty of large aromatics’ LIF measurement was 10%. Considering the uncertainty, it is observed that the large aromatics’ distributions along centerline are almost the same for MCH, i-C$_8$, and C$_7$ flames. The vertical axis scale was changed from 0-1.0 to 0-0.3 in Figure 4-18 (a) and (b) due to the reduction of large aromatics’ LIF signals as air was premixed into the fuel jet. This reduction of signal intensities could be due to both dilution and the quenching effect of premixing air.
Figure 4-18 Normalized LIF signals from large aromatics along centerline. (a) $\Phi=\infty$ flames; (b) $\Phi=6$ flames.
The distribution of large aromatics is compared between m-X and JP-8 flames, as shown in Figure 4-19. Trends similar to those discussed above could be observed in flames from both fuels. Specially, the signals started to occur and peak earlier in the flames, in which the original concentration if m-xylene within mixture is higher.

However, the quantitative comparison indicates that the normalized LIF signals from large aromatics are lower in JP-8 flames. For m-X flames, the large aromatics’ LIF signals became undetectable in m-X-Φ=2-0.2N₂ and m-X-Φ=2-0.48N₂ flames only; however, for JP-8 flames, contrary to expectations, the signals went below the detection limit in the JP-8- Φ=6-0.48N₂ flame. Again, the quantitative trends among flames were similar for JP-8 and m-X flames.

By observing the large aromatics’ initial LIF signals in JP-8 flames, the values are small but still not zero, especially for Φ=∞ conditions. It was suspected that some large aromatics should be on the list of JP-8 fuel’s components; however, JP-8’s detailed composition obtained via GC/MS analysis did not reveal any large aromatics. Consequently, some minor species, which could produce LIF signals within the large aromatics’ collection wavelength range, must remain in JP-8.
Figure 4-19 Normalized LIF signals from large aromatics along centerline. (a) m-X flames; (b) JP-8 flames.
3.3.3.3 Distribution of aromatics and soot

An interesting comparison is that of the small and large aromatics and soot along the centerline of the flames, as shown in Figure 4-20. The m-X- Φ=6-0.2N₂ flame and MCH- Φ=∞ flame are selected to represent the aromatic fuel mixture and paraffin fuel mixture respectively. In Figure 4-20 (a), the small aromatics occur at the beginning of the flame due to the existence of m-xylene within the fuel mixture. Following the small aromatics, large aromatics occur downstream and peak in the lower part of the flame, followed by the soot, which starts to occur and peak latest along the centerline. For the paraffin fuel flame shown in Figure 4-20 (b), without the interference of aromatics in the fuel mixture, the small aromatics appear earliest in the beginning of flame. Subsequent to the small aromatics, the large aromatics and soot start to occur and peak downstream in the flames. Another interesting finding of these profiles is that the inception of soot usually occurs near the peak of large aromatics’ LIF signals and increases significantly as the aromatic species are consumed.
3.3.4 Temperature distribution in soot-free regions

The temperature distribution, measured using a thermocouple, was corrected for radiation effects. The detailed correction calculations are shown in Appendix F, according to which the corrected temperatures are higher than measured results by 50 K at most. The uncertainty of the thermocouple bead position could be ±0.75mm due to the distortion by the thermocouple.

Due to the special configuration of the thermocouples used in this work, as mentioned in Chapter 3, the temperature distribution only in soot-free regions could be obtained. Figure 4-21 shows the typical radial distribution of corrected temperature at 5mm and 15mm height above the tube exit. For most flames, the soot starts to disturb the temperature measurement at ~20mm height. Specifically, for m-X flames under 0.2 L/min dilution nitrogen condition, soot was depositing at 15mm height above the tube exit. During
the radial measurement, in order to avoid the distortion of the flames by the thermocouple probe, only half (-10mm to 0mm) of the flame was measured, with the resolution of 0.25mm per step. In order to compare conveniently, the flames under Φ=∞ and Φ=6 conditions are shown in the left and right half respectively in each profile.

Qualitatively, all flames show similar parabolic trends for both heights: the temperature peaks at the edge of the flames (~±6 mm in radial location), while the temperatures are lowest in the center of the flame zones.

Figure 4-21 Typical radial distribution of temperature at (a) 5mm; (b) 15mm height above the tube exit in flames.
The quantitative comparison between all temperature curves indicates rare differences caused by the fuel types, equivalence ratios, and locations in the centerline of the flames, given the uncertainty of the temperature measurement. If any, the peak values of temperature are very slightly higher in $\Phi=6$ flames and are also slightly higher downstream in these flames (15mm height above the tube exit). At higher axial locations in the flames, the radial temperature gradient becomes smaller, since the centerline temperature increases. In detail, the temperatures of the center point increase by ~200K and ~400K for $\Phi=\infty$ and $\Phi=6$ flames respectively by moving from 5mm to 15mm height above the tube exit.

Figure 4-22 shows the radial temperature distribution comparison between m-X and JP-8 flames. Again, the $\Phi=2$ flames were not measured due to the severe distortion created by the thermocouple. A measurement was taken only at 5mm height above the tube exit in order to avoid the soot deposit problem. Two different equivalence ratios of flames are shown in Figure 4-22 (a) and (b): $\Phi=\infty$ and $\Phi=6$ respectively. The qualitative trends for $\Phi=\infty$ and $\Phi=6$ are almost identical with those previously discussed in Figure 4-21 and are consistent between m-X and JP-8 flames. Even quantitative comparison could not demonstrate any difference caused by the different fuel types and by different equivalence ratios. For the temperature at the center radial location, JP-8 flames consistently have lower values than the m-X flames, though the difference is still less than 50K. As more dilution nitrogen was mixed within the flames, the peak temperature values reduced by around 100K.
Figure 4-22 Radial distribution of temperature at 5mm height above the tube exit in m-X and JP-8 flames under conditions: (a) $\Phi=\infty$; (b) $\Phi=6$. 
Besides radial temperature distribution, the temperature along the centerline in all the flames was also obtained. In order to avoid the soot region, the axial measurement was carried out until the point (20~25 height above tube exit) where soot started to deposit on the thermocouple bead. The resolution for the axial temperature measurement was 1mm per step.

Figure 4-23 shows the fuel types’ effects on the axial temperature distribution. For all the flames under both equivalence ratios, the temperature increases rapidly downstream of the flames. Except for the m-X flames, the other three fuels’ flames (MCH, i-C₈, and C₇) display very similar trends both qualitatively and quantitatively, especially for the Φ=6 conditions. However, at the beginning of all flames, m-X flames show values very close to those of other flames; the temperature in m-X flames starts to be higher at around 5mm height above the tube exit. For Φ=6 conditions, the temperature along the centerline in the m-X- Φ=6 flame is higher than in the other flames by ~200K, while this value was ~100K in Φ=∞ flames. For a given fuel, the difference caused by equivalence ratios is not noticeable in Figure 4-23.
Similarly, Figure 4-24 displays the temperature along the centerline up to 20mm height in m-X and JP-8 flames. The overall trends are consistent with the discussions for Figure 4-23. For the equivalence ratio effect, the temperature in $\Phi=6$ flames was initially lower than in $\Phi=\infty$ flames, due the fact that the dilution effect dominated. However, $\Phi=6$ flames show higher temperature at downstream locations, especially in 0.2 L/min dilution nitrogen conditions: the “crossover” occurred at around 11-13mm height above the burner.

The temperature was always lower in 0.48 L/min dilution nitrogen flames than in 0.2 L/min dilution nitrogen flames, due to the dilution effect. However, differences of temperature distribution caused by fuel type are not evident in the data in Figure 4-24.
Figure 4.24 Temperature distribution along centerline in soot-free regions in (a) m-X and (b) JP-8 flames.
3.4 Simulation performance

The simulation of the laminar flames burnt with m-X, MCH, i-C₈, and C₇ fuels was completed by Dr. Katta of ISSI. Corresponding to the experimental results shown in section 4.1, the computational outcomes including the shape of the flames, soot volume fraction distributions, aromatic species distributions, and temperature distributions are presented and discussed below.

3.4.1 Flame shape

Usually, the distributions of OH and CH [157] are used to identify the shape of the flames, since they mostly appear in the stoichiometric region of diffusion flames. Apart from this, the maximum temperature distribution has also selected to represent the stoichiometric line [158], especially in the less sooty flames (< 1 ppm). Due to the amount of soot produced in the flames in this study, the distribution of OH mole fraction, rather than maximum temperature, was selected to identify the flames’ shapes, as shown in Figure 4-25. The results are grouped according to different equivalence ratios—Φ=∞, Φ=6, and Φ=2—and the same scale for OH mole fraction was used.

Generally, the shapes of OH distributions in all flames appear at the outer edge of the flames and are also typical of the shapes found in previous research work in co-flow laminar jet flames. There is no apparent effect of fuel type on the distribution of OH. However, two changes of OH contours are observed with more air premixed: (1) the thickness of the OH region increases; (2) the location where OH starts to occur in the centerline moves upstream.
Figure 4.25 Computational distribution of OH radical’s mole fraction in flames. (a) $\Phi=\infty$ conditions; (b) $\Phi=6$ conditions; (c) $\Phi=\infty$ conditions.
Quantitatively, the maximum mole fraction of OH is increases in magnitude and moves closer to the tube exit, as more air is added into the fuel jet. The observations discussed above can be explained by the fact that less oxygen would be needed via diffusion from co-flow air, since some oxygen is already available from the premixing air within the mixture coming out of the tube exit.

The OH mole fraction contours in m-X flames at the two different nitrogen dilution ratios are shown in Figure 4-26. Similar trends are also observed with respect to the equivalence ratio effect at the two dilution ratios. However, the addition of added dilution nitrogen stretched the contours slightly.

Overall, the qualitative shape of OH contours is within the visible flame regions, as shown in Figure 4-1 and Figure 4-2. However, comparisons between Figure 4-1, Figure 4-2 (a), Figure 4-25, and Figure 4-26 show that the OH contours are similar to the visible edges of flames, especially for paraffin flames. Consequently, the flame shapes defined by OH contours were estimated larger than in measurements.
Similar to the flame heights comparison in Figure 4-3 and Figure 4-4, it was intended to compare the flame heights between the computations and experiments. However, the definition of visible flame heights in the measurements is not applicable for the computational results, except for m-X flames. As discussed later in this chapter, in the rest of the flames burnt with MCH, i-C₈, and C₇, the soot volume fraction in the centerline does not decrease below 0.1 ppm. Instead, the predicted flame heights according to 0.1 ppm soot volume fraction along centerline are longer than the measured flame heights.

For the six types of m-X flames, the flame heights comparison between the model and measured results is shown in Figure 4-27. Even though the simulation does not capture the smoking property of the m-X- Φ=∞-0.2N₂ flame, the predicted flame height is around 293mm, which is much higher than the predicted values for other flames, which is an indication of a nearly smoking flame for this condition. The trends caused by different equivalence ratios and dilution nitrogen flow rates are captured by the simulation. However, the model always predicted longer flames by at most 50% of the measured results.

![Figure 4-27 Comparison between flame heights from visible flames' appearance and predicted flame heights in model for m-X flames.](image-url)
3.4.2 Computational soot volume fraction distribution

Figure 4-28 presents the two-dimensional distributions of soot volume fraction in all flames. In order to show the distribution trends clearly, different scales are used for the contours. Qualitatively, the calculated soot volume fraction distributions are similar in all flames and consistent with the LII results shown in Figure 4-27 and Figure 4-28. At first glance, there is a very apparent drawback to the calculated distributions: the areas of soot regions are always larger in the simulation than in LII and even in luminous pictures, especially for the paraffin flames under partially premixed conditions. Both simulation and experiment concerns could explain the discrepancy: (1) the model was using acetylene for the soot nucleation and surface growth addition species, so the overestimated soot existing areas are due to the overlap between soot and acetylene; (2) in the LII measurements, the detection sensitivity was so low that part of the soot region might be missing.
Figure 4-28 Computational soot volume fraction distributions in all flames. (a) Φ=∞ conditions; (b) Φ=6 conditions; (c) Φ=∞ conditions.
The distributions of soot volume fraction are predicted much better in m-X flames, as indicated by Figure 4-29. The locations of the sooting regions for these flames in the simulations and experiments were reasonably consistent. For example, the measured trend that the soot regions occurred higher in 0.48L/min dilution nitrogen flames than in 0.2L/min dilution nitrogen flames was also captured by the simulation.

Quantitative analysis of soot volume fraction along centerline in flames is shown in Figure 4-30. Though the low soot volume fraction in Φ=2 flames could not be detected in LII and laser extinction measurement, the calculated values for Φ=2 flames are still shown in Figure 4-30 for indicating the equivalence ratio effect in simulations. In both computational and experimental results, the soot distributions show similar trends along centerline: the soot started to occur in the lower part of the flames, and then increased to the peak volume fractions downstream, followed by a decrease due to soot oxidation, and finally dropping to zero in all flames except the smoking M-X flame.
For the paraffin flames with C\textsubscript{7}, i-C\textsubscript{8}, and MCH, shown in Figure 4-30 (a), (b), and (c), the simulation results always indicate a higher amount of soot produced. In detail, the values of peak soot volume fractions along centerline are higher by up to 1.5 ppm, while the soot appearing region is larger, as mentioned in the discussion of the 2-D images. For these flames, the locations of soot concentration peaks are always predicted 10 mm downstream from the measured results for both equivalence ratio conditions. An interesting finding is that the soot volume fraction still remains high values (> 0.5 ppm) beyond 75 mm height above tube exit for the Φ=∞ and Φ=6 conditions.

The most significant discrepancy in quantitative soot volume fractions between the simulation and measured results lies in the m-X flames, as shown in Figure 4-30 (d) and (e) for 0.2 L/min and 0.48 L/min dilution nitrogen conditions respectively. Unfortunately, opposite to the experimental fact that the m-X flames produces the largest amount of soot, the simulation shows the lowest soot volume fractions in m-X flames compared to other paraffin flames. This finding could also be validated in the two-dimensional contours of soot volume fraction in Figure 4-28. Generally, the maximum soot volume fractions for m-X flames are higher in experiments than in simulation by a factor of 2-3. Especially for the smoking m-X-Φ=∞-0.2N\textsubscript{2} flame, the difference between the experiments and simulation was greatest.

For Φ=2 flames, soot volume fractions could not be detected in the experiments (< 0.5 ppm). However, the simulation predicted the maximum soot concentration in Φ=2 flames as approximately half the amount in Φ=6 flames. The predicted amounts of soot are in the range of 1-2 ppm and are substantially above the detection limit of 0.5 ppm.
Figure 4-30 Quantitative comparison between experimental and computational soot volume fraction distributions in all flames. (a) C7 flames; (b) i-C8 flames; (c) MCH flames; (d) m-X flames under 0.2 N2 conditions; (e) m-X flames under 0.48 N2 conditions.

3.4.3 Computational distributions of aromatics species

In the experiments, the LIF signals were collected according to two groups of different aromatic molecule sizes. It is necessary to explain how these signals could be used for comparison with the simulation results. The simulation model contains calculated mole fractions of a total of 206 species, among which are the aromatic species listed in Table 4-1. The corresponding values of the fluorescence cross sections for each species normalized to naphthalene, without consideration of quenching effect, were obtained from the literatures [159-162]. Assuming all the aromatic species were ideal gases, the mole fractions could be converted to mole concentrations (mole/m^3). By multiplying the
concentrations by the normalized LIF cross sections presented in the table, the corresponding calculated LIF signals were obtained from the simulation results.

Table 4-1 List of aromatic species in the model and their normalized fluorescence cross sections.

<table>
<thead>
<tr>
<th>No. of Rings</th>
<th>#</th>
<th>Species</th>
<th>Normalized Fluorescence Efficiency</th>
<th>No. of Rings</th>
<th>#</th>
<th>Species</th>
<th>Normalized Fluorescence Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>One-Ring Aromatics</td>
<td>63</td>
<td>Benzene</td>
<td>0.07</td>
<td>85</td>
<td>Naphthalene</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>65</td>
<td>Phenol</td>
<td>0.07</td>
<td>92</td>
<td>Methylnaphthalene</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>Benzaldehyde</td>
<td>0.07</td>
<td>95</td>
<td>Biphenyl</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>71</td>
<td>Toluene</td>
<td>0.07</td>
<td>97</td>
<td>Fluorene</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>72</td>
<td>Benzyl alcohol</td>
<td>0.07</td>
<td>98</td>
<td>Diphenylmethane</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>78</td>
<td>Phenyl acetylene</td>
<td>0.07</td>
<td>100</td>
<td>Bibenzyl</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>79</td>
<td>Styrene</td>
<td>0.07</td>
<td>99</td>
<td>Phenanthrene</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>Ethylbenzene</td>
<td>0.07</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>81</td>
<td>m-xylene</td>
<td>0.07</td>
<td>102</td>
<td>Pyrene</td>
<td>2.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>84</td>
<td>Indene</td>
<td>0.07</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

![Chemical structures for aromatic species]
3.4.3.1 Computational LIF signals from small aromatics

Based on the calculations, the two-dimensional distributions of small aromatics are shown in Figure 4-31, in which the results are grouped according to their equivalence ratios: (a) $\Phi=\infty$; (b) $\Phi=6$, and (c) $\Phi=2$.

Since m-xylene is a one-ring aromatic existing already in the fuel mixture, the maximum values of calculated LIF signals of small aromatics existed in the m-X-$\Phi=\infty$-0.2N$_2$ flame. A triangular cone observed at the tube exit in m-X flames indicates the distribution of m-xylene. The small aromatics’ LIF signals from all other flames were normalized to that maximum value. In order to display the distribution trends clearly, the scales for the contours were set differently based on various equivalence ratios. The basic trend of small aromatics’ distributions for paraffin fuels is similar to soot volume fraction distribution: the small aromatics start to appear at the edge of the flames initially and then move toward the center with increasing values and finally decay downstream.

For the fuel type’s effect, the paraffin flames show similar trends and values, while MCH flames are of slightly higher concentrations of small aromatics than the others. Due
to the existence of m-xylene, the m-X flames have substantially higher aromatic concentrations; while the paraffin flames are of lower aromatic concentrations. Considering the effect of the equivalence ratios, though the scale of contours reduces with more air added, the areas where small aromatics appear shrinks substantially as air is added to the flame. Especially for Φ=2 flames, the areas of small aromatics are too small to be noticeable for the paraffin flames.
Figure 4-31 Computational LIF signals from small aromatics in all flames. (a) Φ=∞ conditions; (b) Φ=6 conditions; (c) Φ=∞ conditions.
Detailed information about small aromatics’ distribution for the m-X flames is given in Figure 4-32. All the m-X flames show similar distribution trends: a triangular cone sits on the tube exit; however, quantitative difference exists. An interesting finding in Figure 4-32 is that there exists a “second” cone zone of relatively lower concentrations downstream in m-X-Φ=∞-0.48N2, m-X-Φ=6-0.2N2, and m-X-Φ=6-0.48N2 flames. This observation will be discussed further below.

Since there is no way to calibrate the LIF measurements in this experimental work, the best way to evaluate the simulation’s performance in predicting the aromatics’ distribution is to make a semi-quantitative comparison. In Figure 4-33, the semi-quantitative results from LIF measurements and computations for small aromatics along centerline of the flames are presented. In order to show trends more clearly, two different scales for the LIF data and the simulations: the left vertical axis is for normalized LIF
signals from small aromatics; while the right vertical axis is for the normalized computational LIF signals from small aromatics. As noted earlier, except for m-X flames, the experimental LIF results for Φ=2 flames were not obtained due to their weak signals.

For the paraffin flames shown in Figure 4-33 (a), (b), and (c), the basic trend of increasing to a peak and then decreasing to zero are shown in both experimental and simulation results. The predicted small aromatics usually start to occur later along the centerline than the experimental results indicated. The peaks are also located downstream in the simulation results, especially for Φ=∞ flames, while this trend is not true for Φ=6 flames. Quantitatively, the peak values in the simulation results are ~3 times larger than those collected from the experiments.
The comparison results of m-X flames are shown in Figure 4-33 (d) and (e) for 0.2 L/min and 0.48 L/min dilution nitrogen conditions respectively. Very similar trends can be found from both results: small aromatics’ LIF signals peak at the beginning of the flames and then decrease to zero rapidly downstream. The relative “plateau” regions present in LIF measurements also occur in the simulations, and a “second increase region” could even be observed in simulation especially for the 0.48 l/min dilution nitrogen conditions, which also explains the “second” triangle cone shown in Figure 4-32.

Another very interesting analysis is the quantitative comparisons of initial values. The LIF signal intensities at the tube exit should be proportional to the concentrations of m-xylene within the mixture, if differences in quenching effects are small. Furthermore,
the temperatures of the fuel jets are similar for different flame conditions. The normalized mole fractions of m-xylene for different flame conditions were calculated and are listed in Table 4-2. Also, the normalized LIF signals from small aromatics at the tube exit in the simulation and experiment are summarized in Table 4-2. Comparing the values in Table 4-2 validates that the quantitative ratios of the initial signals are consistent with the assumption above. The experimental results also show similar trends; however, the absolute values are slightly off but still acceptable given the uncertainty in the measurement.

<table>
<thead>
<tr>
<th>Flame</th>
<th>Normalized m-xylene mole fraction</th>
<th>Normalized LIF signals</th>
<th>Normalized computational signal</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-X-Φ=∞-0.2N₂</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>m-X-Φ=∞-0.48N₂</td>
<td>0.446</td>
<td>0.506</td>
<td>0.452</td>
</tr>
<tr>
<td>m-X-Φ=6-0.2N₂</td>
<td>0.418</td>
<td>0.434</td>
<td>0.421</td>
</tr>
<tr>
<td>m-X-Φ=6-0.48N₂</td>
<td>0.275</td>
<td>0.330</td>
<td>0.279</td>
</tr>
<tr>
<td>m-X-Φ=2-0.2N₂</td>
<td>0.193</td>
<td>0.164</td>
<td>0.195</td>
</tr>
<tr>
<td>m-X-Φ=2-0.48N₂</td>
<td>0.156</td>
<td>0.128</td>
<td>0.156</td>
</tr>
</tbody>
</table>

3.4.3.2 Computational LIF signals from large aromatics

Similar to the computational small aromatics distributions, the maximum calculated large aromatics LIF signal also occurs in the m-X-Φ=∞-0.2N₂ flame. This is as expected, since the m-X-Φ=∞-0.2N₂ flame also has the highest concentration of m-xylene and consequently was expected to produce greater amounts of large aromatics. As was done in the experimental results, the computational results for large aromatics from all other flames are normalized to the maximum value in the m-X-Φ=∞-0.2N₂ flame.
As shown in Figure 4-34, different scales for contours are used for various equivalence ratios to show the distribution trend clearly. At a given equivalence ratio, the calculated LIF signals from large aromatics are much weaker in the paraffin flames than in the m-X flames, especially for Φ=2 flames. The basic trend for all the flames is similar: the peaks moved from annular regions to the center and finally disappeared close to the tips of the flames. However, the areas are smaller and closer to the tube exit. In contrast, in the paraffin flames, the large aromatics started to occur relatively downstream at the edge of the flames.
Figure 4-34 Computational LIF signals from large aromatics in all flames. (a) $\Phi=\infty$ conditions; (b) $\Phi=6$ conditions; (c) $\Phi=\infty$ conditions.
The detailed distributions of computational large aromatics’ LIF signals for m-X flames are shown in Figure 4-35. Quantitative comparison indicates that the calculated LIF signals from large aromatics are highly dependent on the initial concentration of m-xylene in the mixture. For the flames under $\Phi=2$ conditions, the LIF signals from large aromatics were lower than the detection limit.

Figure 4-35 Computational LIF signals from large aromatics in m-X flames.

Figure 4-36 shows the quantitative comparison of large aromatics along centerline from LIF experiments and simulation results. Similar to the results for small aromatics, these results are grouped by the fuel types: (a) C$_7$ flames; (b) i-C$_8$ flames; (c) MCH flames; and (d) m-X flames under 0.2 L/min dilution nitrogen conditions; and (e) m-X flames under 0.48 L/min dilution nitrogen conditions. In contrast to the small aromatics, the scales for both experimental and computational results are the same for each given fuel type.
Figure 4.36 Comparison between experimental and computational LIF signals from large aromatics in all flames. (a) $C_7$ flames; (b) $i-C_8$ flames; (c) MCH flames; (d) m-X flames under 0.2 N$_2$ conditions; (e) m-X flames under 0.48 N$_2$ conditions.

The basic qualitative trends for large aromatics are similar to those for small aromatics and even to those for soot along centerline. However, for the paraffin flames, the computational peaks of large aromatics always occur about 5~10 mm farther downstream than is found in the experimental results. Compared with the model’s performance on small aromatics, the quantitative predictions of large aromatics are quite close to the experimental data for paraffin flames. The computational large aromatics’ LIF signals are nearly zero for $\Phi=2$ flames, which is quite consistent with the fact that the signals in $\Phi=2$ flames were below the experimental detection limit.

The results for m-X flames are shown in Figure 4.36 (d) and (e) for 0.2 L/min and 0.48 L/min dilution nitrogen conditions respectively. The model performs better for large
aromatics than for small aromatics both quantitatively and qualitatively. In addition, the higher flow rate of dilution nitrogen effect resulted in lower concentrations of large aromatics in the 0.48 l/min dilution nitrogen m-X flames. The maximum computational normalized LIF signals reduced by 50% as more dilution nitrogen added.

3.4.3.3 Relative comparison between small and large aromatics and soot

Corresponding to the experimental results shown in Figure 4-20, the comparison results of small and large aromatics and soot from the simulations are presented in Figure 4-37. Again, the m-X-Φ=6-0.2N₂ flame and MCH-Φ=∞ flame were selected for analysis.

By comparing the results in Figure 4-37 and Figure 4-20, it is found that the basic quantitative and qualitative trends are captured by the simulation for the m-X-Φ=6-0.2N₂ flame. However, for the paraffin MCH-Φ=∞ flame, a discrepancy lies in the prediction of relative locations of the aromatics and soot. In experiments, the soot starts to occur at the location where the large aromatics peak, while in simulation, the soot and large aromatics appear nearly simultaneously.
Figure 4-37 Typical computational locations of small and large aromatics and soot along centerline in flames. (a) m-X-Φ=6-0.2N₂ flame; (b) MCH- Φ=∞ flame.
3.4.4 Computational temperature distributions

The calculated distributions of temperature are shown in Figure 4-38. In addition to OH, CH, and soot, temperature distributions are frequently adopted by researchers to identify the flames’ shapes, especially in the less sooty flames, in which the highest temperature usually occurs around stoichiometric lines.

The flames are grouped according to their equivalence ratios ($\Phi=\infty$, $\Phi=6$ and $\Phi=\infty$), while the maximum temperature changes from 1820K to 2020K. As expected, the highest temperature zones (red area) are similar to the zones of OH distribution in Figure 4-25. Differences in temperature distribution could rarely be found between different flames under given equivalence ratios. However, as more premixing air was added, the high temperature zones were compressed to smaller regions and appeared closer to the tube exit. This trend is also consistent with the OH distribution analysis, since the stoichiometric line moved upstream and nearer to the tube exit due to more oxygen coming from the mixture.

Again, the temperature distributions in m-X flames are shown in Figure 4-39. All trends discussed above are also evident in the m-X flames. The increase of dilution nitrogen pushes the high temperature zones a little further away from the tube exit, while the temperature values are lower due to the nitrogen dilution effect.
Figure 4.38 Computational distribution of temperature in all flames. (a) $\Phi=\infty$ conditions; (b) $\Phi=6$ conditions; (c) $\Phi=\infty$ conditions.
3.4.4.1 Radial temperature distribution comparison

Since the model is unable to predict the flame heights correctly for paraffin flames, it is quite unfair to make any comparison of radial temperature distributions between the simulation and experiment, since it is difficult to select appropriate axial locations fairly. However, the flame heights of m-X flames were predicted reasonably consistently with experimental results. Hence, as shown in Figure 4-40, the radial temperature distributions at 5mm height above the tube exit in m-X flames are used to evaluate the simulation results.

The left part of Figure 4-40 shows the radial temperature distributions obtained by experiments in m-X flames, except for the $\Phi=2$ conditions, while the corresponding model results, including the $\Phi=2$ flames, are shown on the right half. The overall qualitative and quantitative trends show great consistency between experimental and simulation results with respect to the dilution nitrogen flow rates and equivalence ratios. In both results, the
introduction of premixing air increased the peak temperatures at the edge of the flames higher by ~50K, while more dilution nitrogen reduces those values by ~100K. Another finding is that the m-X-Φ-∞=0.2N₂ flame has the highest temperature in both results. However, the other flames show quite close values in the center in the simulation, while this trend was not observed in the experimental results. If the uncertainties of temperature measurement into consideration, this discrepancy between the simulation and measurement results is even more minor.

![Figure 4-40 Radial distribution of temperature comparison at 5mm height above the tube in m-X flames.](image)

### 3.4.4.2 Axial temperature distribution comparison

The temperature along centerline in the soot-free regions of flames is presented in Figure 4-41 and is also compared to the experimental results. For all flames in both experimental and computational results, a common “crossover” trend could be found: the partially premixed flames presented lower temperatures initially, due to dilution effects,
and increased to higher values downstream, caused by increased heat release from reactions due to the presence of oxygen in the fuel stream.

An obvious discrepancy between the model and experimental results lies in the quantitative comparison: at the beginning of the flames, the simulation always underestimates the values of temperatures, while it overestimates the temperatures downstream, especially after the “crossover” point.

Another interesting finding comes from the initial temperature used in the simulations. As mentioned previously, the simulation used a constant value (473K) for the temperature boundary condition at the tube exit. The reason for the selection of 473K was based on the measurements shown in Figure 3-4. However, the experimental results always display higher temperatures than the simulation and the previous measurements by ~100K. Keep in mind that the boundary temperature measurement in Figure 3-4 was measured under the condition that the flames were off. Based on the configuration of the temperature measurement device, the conduction effect from the flame front to the thermocouple bead via wires was reduced substantially. Consequently, it is believed that the higher temperature was caused by the radiation from the flame to the tube and the fuel mixture at the tube exit. The effect of the tube exit temperature, as a boundary condition, on soot volume fractions was studied by Smooke. It was found that the inlet temperature had a critical effect on the peak soot volume fractions on the centerline. However, the flames Smooke studied were much less sooty (<1ppm) than the flames in this paper. The sensitivity test of inlet temperature will be shown later in this chapter.
3.4.5 Computational rate of soot nucleation, growth, and oxidation

The individual reaction steps involved in the soot model and the rate of soot nucleation, growth, and oxidation are shown below [69]:

Nucleation [163]:

\[ C_2H_2 \rightarrow 2C_{soot} + H_2 \quad \text{with} \quad k_{N1} = 0.63 \times 10^4 e^{\frac{-21000}{T}} \left( \frac{1}{s} \right) \quad (4.1) \]

Surface growth [164]:

\[ C_{soot}H + H \rightarrow C_{soot}^* + H_2 \quad \text{with} \quad k_{S1} = 4.17 \times 10^7 e^{\frac{-6542}{T}} \left( \frac{m^3}{mol \cdot s} \right) \quad (4.2) \]

\[ C_{soot}^* + H_2 \rightarrow C_{soot}H + H \quad \text{with} \quad k_{S2} = 3.90 \times 10^6 e^{\frac{-5535}{T}} \left( \frac{m^3}{mol \cdot s} \right) \quad (4.3) \]
\[ C_{\text{soot}} + OH \rightarrow C_{\text{soot}}^* + H_2O \quad \text{with} \quad k_{S3} = 1.00 \times 10^4 \times T^{0.734} e^{\left( -\frac{719.6}{T} \right)} \left( \frac{m^3}{\text{mol} \cdot \text{s}} \right) \quad (4.4) \]

\[ C_{\text{soot}}^* + H_2O \rightarrow C_{\text{soot}}H + OH \quad \text{with} \quad k_{S4} = 3.68 \times 10^2 \times T^{1.139} e^{\left( \frac{8605}{T} \right)} \left( \frac{m^3}{\text{mol} \cdot \text{s}} \right) \quad (4.5) \]

\[ C_{\text{soot}}^* + H \rightarrow C_{\text{soot}}H \quad \text{with} \quad k_{S5} = 2.00 \times 10^7 \left( \frac{m^3}{\text{mol} \cdot \text{s}} \right) \quad (4.6) \]

\[ C_{\text{soot}}^* + C_2H_2 \rightarrow C_{\text{soot}}+2H + H \quad \text{with} \quad k_{S6} = 8.00 \times 10 \times T^{1.56} e^{\left( \frac{-1912}{T} \right)} \left( \frac{m^3}{\text{mol} \cdot \text{s}} \right) \quad (4.7) \]

Oxidation [45, 148]:

\[ C_{\text{soot}} + 0.5O_2 \rightarrow CO \quad \text{with} \quad k_{B1} = 7.15 \times 10^2 \times T^{0.5} e^{\left( \frac{-19800}{T} \right)} \left( \frac{m}{s} \right) \quad (4.8) \]

\[ C_{\text{soot}} + OH \rightarrow CO + H \quad \text{with} \quad k_{B2} = 106.0 \times T^{-0.5} \left( \frac{m}{s} \right) \quad (4.9) \]

\[ C_{\text{soot}} + O \rightarrow CO \quad \text{with} \quad k_{B3} = 55.4 \times T^{-0.5} \left( \frac{m}{s} \right) \quad (4.10) \]

\[ C_{\text{soot}} + CO_2 \rightarrow 2CO \quad \text{with} \quad k_{B4} = 6.35 \times 10^2 \times e^{\left( \frac{-19500}{T} \right)} \left( \frac{kg}{m^2 \cdot s} \right) \quad (4.11) \]

\[ C_{\text{soot}} + H_2O \rightarrow CO + H_2 \quad \text{with} \quad k_{B5} = 1.92 \times 10^2 \times e^{\left( \frac{-17600}{T} \right)} \left( \frac{kg}{m^2 \cdot s} \right) \quad (4.12) \]

\( k_j \) is the specific reaction rate of the \( j \)th reaction with units given in the bracket;

\( C_{\text{soot}}^* \) is an armchair site on the soot particle surface; and

\( C_{\text{soot}}^* \) is a corresponding radical;

The soot nucleation rate is:

\[ \dot{w}_{\text{nucleation}} = 2k_{N1} [C_2H_2] \quad (4.13) \]

The soot growth rate is:

\[ \dot{w}_{\text{growth}} = 2k_{S6} [C_2H_2] \left\{ \alpha \frac{X_{\text{soot}}}{N_A} A_{\text{soot}} \right\} \quad (4.14) \]

\[ \alpha = \frac{1}{2} \left\{ \tan \left( \frac{8168}{T} - 4.57 \right) + 1 \right\} \quad (4.15) \]

\[ X_{\text{soot}}^* = \frac{k_{S1}[H]+k_{S1}[OH]}{k_{S2}[H_2]+k_{S2}[H_2O]+k_{S3}[H]+k_{S6}[C_2H_2]} X_{\text{soot}} \quad (4.16) \]
The soot oxidation rate is:

\[
\dot{w}_{\text{oxidation}} = -k_B [O_2] A_{\text{soot}} - \{\varphi_{OH} K_{B2} X_{OH} + \varphi_O K_{B3} X_O + \varphi_{CO_2} K_{B4} X_{CO_2} + \varphi_{H_2O} K_{B5} X_{H_2O}\} p_{\text{atm}} A_{\text{soot}} \tag{4.17}
\]

The ‘−’ sign indicates that the soot was burnt by various species.

\[\begin{align*}
p_{\text{atm}} &= \text{the pressure in atm unit;} \\
A_{\text{soot}} &= \text{the soot surface area per unit volume;} \\
N_A &= \text{the Avogadro number;} \\
\chi_{\text{soot}} &= \text{the number density of armchair sites on the soot particle surface (a value of} \\
&\quad \text{2.32}\times10^{19} \text{ sites/m}^2 \text{ was set);} \\
\chi_{\text{soot}}^* &= \text{the number density of surface radicals;} \\
\alpha &= \text{a factor that attempts to capture a temperature-dependent “aging” process} \\
&\quad \text{that changes the number of surface sites available for reactions [165]; and} \\
\varphi_{OH}, \varphi_O, \varphi_{CO_2}, \varphi_{H_2O} &= \text{the collision efficiencies: 0.13, 0.5, 0.0015, and 0.0004} \\
&\quad \text{respectively.}
\end{align*}\]

This set of equations was used to calculate the distributions of rate of soot nucleation, growth, and oxidation in all flames; the results are presented in Figure 4-42, Figure 4-43, and Figure 4-44 respectively. Similar to previous discussion, the flames were grouped according to their equivalence ratios and were given various scales of contours to show the trends clearly.
Figure 4-42 Computational soot nucleation rate in all flames. (a) $\Phi=\infty$ conditions; (b) $\Phi=6$ conditions; (c) $\Phi=\infty$ conditions.
Figure 4-43 Computational soot growth rate in all flames. (a) \( \Phi=\infty \) conditions; (b) \( \Phi=6 \) conditions; (c) \( \Phi=\infty \) conditions.
Figure 4-44 Computational soot oxidation rate in all flames. (a) $\Phi=\infty$ conditions; (b) $\Phi=6$ conditions; (c) $\Phi=\infty$ condition
Two common trends could be found for all rates in all flames:

(1) The rates’ contours appear in the flames as triangular cones, and the sizes of these contours shrank and the contours moved upstream as more air was added;

(2) The quantitative difference for paraffin fuels under a given equivalence ratio is insignificant;

In Figure 4-42, since acetylene was the only nucleation species in the simulation, the soot nucleation rates appear in the same locations and appear close to the same values in m-X flames and paraffin flames. With more air premixing in the flames, the nucleation rate increases, as indicated by the scales. Actually, according to equations 4.1 and 4.13, the nucleation rate depends on the temperature and concentration of acetylene. Further analysis of the simulation results implies that the changing of nucleation rates is essentially the result of temperature variations.

In Figure 4-44, an inner oxidation curve could be found in partially premixed flames. Especially in Φ=2 flames, a whole arc appears upstream before the primary oxidation zone. This finding is consistent with the “double flame” structure shown in Figure 4-1 (c). Detailed analysis of the simulation results showed that nearly 99% of soot oxidation was completed by the radical OH, rather than by O, CO₂, and H₂O. With an increasing amount of premixing air, the absolute rate of soot oxidation becomes smaller.

3.4.6 Other findings in the simulation

According to the simulation performance discussed above, the most substantial discrepancy lies in the soot volume fraction distribution of m-X flames. Compared to the paraffin flames, the m-X flames show the heaviest amount of soot produced in experiments;
however, the simulation indicates the lowest concentrations of soot for m-X flames. Many factors were suspected to explain this inconsistency. First of all, the density and refractive indexes of soot in m-X flames were taken into consideration. Even though there might be some variations of soot density from different flames [166], the experimental methods of determining the soot density have relatively high uncertainties depending on the experimental methods. The selection of refractive index, which was used in the soot volume fraction calculations, could affect the quantitative soot volume fraction by as much as a factor of two. To this point, no results were located in the literature on the effects of fuel type on the refractive index of soot. Consequently, the two factors mentioned here could not explain the discrepancy between the model and the experiment for the m-X flames.

3.4.6.1 Boundary temperature effect

As described in sections 4.2.2 and 4.2.4.2, it was found that there is a discrepancy of boundary temperatures between the simulation and experiments. Also, the effects of initial temperature, investigated by Smooke, were found to be substantial for the less-sooty flames. Consequently, a new simulation with the boundary temperatures the same as those in the measured results was carried out for m-X flames by Dr. Katta. The soot volume fractions along centerline from the new results are shown in Figure 4-45. Unfortunately, the increased boundary temperatures only enhance the peak soot volume fractions by a very limited amount. Therefore, this temperature difference could not produce enough soot for the m-X flames.
3.4.6.2 Additional soot converted from potential sources

Since the calculated amount of soot produced in m-X flames is much lower than was measured in the experiment, a key question would be: what is the source of this soot? Hence, an analysis was carried out to determine the amount of soot that would be formed if all the carbons from different species were converted into soot. The species that were considered in this calculation are; acetylene, the small aromatics including m-xylene, the small aromatics excluding m-xylene, and the large aromatics. During the whole calculation procedure, the soot density was considered as constant (1.9 g/cm³).

Figure 4-46 indicates the additional soot volume fraction along centerline from all other potential sources in the m-X-Φ=∞-0.2N₂ flame. However, the additional soot volume...
fraction from acetylene alone is insufficient to fill the gap between the simulation and measured results. The results indicate that small aromatics, including \( \text{m-xylene} \), are a substantial source of carbon that could collectively produce enough soot to account to fill the gap between the simulations and the experiments for the \( \text{m-X flames} \).

![Figure 4-46](image)

**Figure 4-46** Equivalent soot volume fraction along centerline converted from the carbon in potential species.

### 3.4.6.3 Soot nucleation rate analysis

Besides acetylene, the models using other species for soot nucleation process are being carried out. In the simulation work, Dr. Katta also considered benzene as the nucleation species, and the rate of soot nucleation is shown in equations 4.18 and 4.19.

\[
\text{C}_6\text{H}_6 \rightarrow 6\text{C}_{\text{soot}} + 3\text{H}_2 \quad \text{with} \quad k_{\text{N2}} = 10^7 e^{\left(\frac{21000}{T}\right)} \left(\frac{1}{s}\right)
\] (4.18)
\[
\dot{w}_{\text{nucleation}} = 6kN_2 [C_6H_6] \quad (4.19)
\]

According to the calculation in the reference [165], the nucleation rate based on pyrene is calculated as follows:

\[
\dot{w}_{\text{nucleation}} = \frac{\nu_2}{\rho} \sqrt{\frac{4\pi k_B T}{C_{\text{soot}}N_{C,\text{pyrene}}}} \cdot d_{\text{pyrene}}^2 \cdot N_c^2 \cdot [\text{pyrene}]^2 \quad (4.20)
\]

\[
d_{\text{pyrene}} = d_A \sqrt{\frac{2N_{C,\text{pyrene}}}{3}}
\]

\[
\rho \quad = \quad \text{the density of gas mixture;}
\]

\[
C_{\text{soot}} \quad = \quad \text{the mass of a carbon atom;}
\]

\[
k_B \quad = \quad \text{the Boltzmann constant;}
\]

\[
N_{C,\text{pyrene}} \quad = \quad \text{the number of carbon atoms in pyrene;}
\]

\[
d_{\text{pyrene}} \quad = \quad \text{the diameter of a pyrene molecule; and}
\]

\[
d_A \quad = \quad \text{the size of a single aromatic ring;}
\]

From the calculations above, the soot nucleation rates based on acetylene, benzene, and pyrene could be derived in the simulation.

In the LIF measurement for large aromatics, assuming that pyrene is the major component in the group. Consequently, the LIF signals from large aromatics could be roughly considered as proportional to the concentrations of pyrene. Also, the temperature in soot-free regions was obtained in the experiment. Therefore, in equation 4.20, all variables except density of gas mixture were obtained from measurements. The computational gas mixture density information was used in estimating the pyrene nucleation rate.
Since the absolute concentrations of pyrene could not be calibrated from LIF measurements, the normalized soot nucleation rates were plotted for comparison, as shown in Figure 4-47. The data were from the centerline in the m-X-Φ=∞-0.2N₂ flame. Apparently, the soot nucleation based on acetylene occurs earlier than that based on benzene and later than that based on pyrene and large aromatics. Furthermore, the semi-experimental nucleation rate based on pyrene is in good agreement with the computational results. This finding indicates a potential direction for improving the soot model, at least in m-X flames: species other than acetylene might also contribute to soot nucleation and also to soot’s growth process.
Chapter 5 Conclusions and future work

5.1 Conclusions

The overall technical objective of this research was to understand the fuels’ molecular structure effects on pollutant species within co-flow laminar flames, both experimentally and computationally. The computational work was done by Dr. Katta of ISSI. In addition, the research explored the ability of the simulations to capture the experimental results and sought to identify ways in which the simulations could be improved.

The fuel matrix was designed to present various molecular structures. In order to validate and improve the chemical mechanisms in the model, four binary fuel mixtures comprised of the hydrocarbon compounds representative of the classes compounds that are expected in alternative aviation fuels. In each fuel mixture, n-dodecane was the base component. The second component was m-xylene, methylcyclohexane, iso-octane, or n-heptane that were selected to represent the molecular structures of aromatic, cyclo-paraffin, iso-paraffin, and n-paraffin. In addition, other fuels—including JP-8, SPK, pure iso-octane, and pure n-dodecane—were studied to provide a broader understanding of fuel structure effects. The binary mixture of m-xylene and n-dodecane was evaluated as a simple surrogate for JP-8.

A system was built to produce co-flow laminar jet flames burnt with these fuels. For each fuel blending, three equivalence ratios ($\Phi=\infty$, $\Phi=6$, and $\Phi=2$) were studied to evaluate the effects of jet fuel-air ratios on flames. Specifically polycyclic aromatic hydrocarbons and soot were studied via optical techniques. The temperature distributions in the soot-free regions in flames were obtained by thermocouple method.
Major observations and conclusions on the effects of fuel molecular structure and the performance of the simulations are presented below, based on the experimental and computational results.

### 5.1.1 Flame appearance

Experimental results indicate that m-X flames are longer than paraffin flames, while the latter flames are of similar appearance. For $\Phi=\infty$ condition, the m-X flame was smoking; for $\Phi=6$ and $\Phi=2$ conditions, the m-X flames were longer than paraffin flames by ~$20\%$ (or 10 mm) and ~$10\%$ (or 3 mm) respectively. Except the smoking m-X- $\Phi=\infty$-0.2N$\textsubscript{2}$ flame, the flame lengths reduced by ~10mm and ~26mm from $\Phi=\infty$ to $\Phi=6$ and to $\Phi=2$ conditions respectively. Furthermore, m-X flames have almost the same appearance as the JP-8 flames.

In the simulation results, the flames’ calculated shapes based on both the maximum OH contours and the soot existing regions are larger than the experimental outcomes, especially for partially premixed flames. In addition, the simulation did not capture the smoking phenomenon experimentally found in the m-X-$\Phi=\infty$-0.2N$\textsubscript{2}$ flame. Also, the simulation failed to predict the significant difference between m-X and paraffin flames. Lastly, the model was able to predict the effects of equivalence ratios on flames’ shapes in consistent trends with experiments.
5.1.2 Soot volume fraction distribution

Both experimental and computational distributions of soot volume fraction show trends that are consistent with previous research conclusions. Quantitative measurements imply that the m-X flames produced the highest amount of soot, while the paraffin flames showed very similar soot concentrations. The peak values of soot volume fraction along centerline were higher in m-X flames than in the paraffin flames by a factor of 2-4. Besides, the m-X and JP-8 flames showed great consistency for soot distributions.

Generally, the simulation predicted the soot volume fraction distributions consistently with experimental results. However, the model did not capture the smoking in the m-X-Φ=∞-0.2N₂ flame. Opposite of the measured results, the model predicted the lowest amount of soot would be produced in m-X flames. Soot volume fractions of the paraffin flames were of similar and were consistent between the model and the experimental results.

Qualitatively, the model always presents larger areas of soot regions, especially for partially premixed flames. Quantitatively, except for the m-X flames, the computational results overestimate the peak values of soot volume fraction along centerline by ~50%.

Experimentally, the peak values of soot volume fractions along centerline decrease by ~30% from Φ=∞ to Φ=6 conditions; while this percentage became ~20% in the simulation results. It was suspected that the soot concentration in Φ=2 flames was below the detection limit (~0.5 ppm) in experiments; however, the simulation predicted the soot volume fraction in Φ=2 flames could be at most ~1.5 ppm and ~1ppm for paraffin fuels and m-X fuel respectively.
5.1.3 Aromatics distribution

Two groups of aromatic species were measured according to their molecular sizes: “small aromatics,” which contain 1 and 2 aromatic rings; or “large aromatics,” which contain 3 and 4 aromatic rings. Concentrations of aromatics from the simulations were weighted with LIF cross-section to allow a semi-quantitative comparisons between the simulations and experiments.

(1) Small aromatics:

Experimentally, the m-X flames had the maximum LIF signals at the beginning of the flames due to the LIF from the m-xylene within the fuel mixture. The paraffin flames produced the peak small aromatics LIF signals lower by one order of magnitude, normally at lower regions of flames. The paraffin fuels were performing similarly both quantitatively and qualitatively. For all flames, the peak values of small aromatics LIF signals reduced by 50% from Φ=∞ conditions to Φ=6 conditions. The qualitative trends were consistent in m-X and JP-8 flames; however, JP-8 was showing higher signal intensities than m-X by a factor of at most two.

Qualitatively, the model was able to predict the distribution trends of small aromatics consistently with experimental results. For m-X flames, the simulation results indicated reasonably well in small aromatics existing regions; however, the quantitative discrepancy lied in the beginning of m-X-Φ=2 flames. For paraffin flames, the small aromatics existing areas moved ~10mm downstream in simulations than in measurement for non-premixed conditions. For the partially premixed flames burnt with paraffin fuels, the locations where the small aromatics started to occur moved ~10mm downstream in simulation; while the peaks
locations were quite close in simulation and experiments. Even though the computational and measuring results are only semi-quantitative and must be viewed with caution, the peak values of small aromatics LIF signals were overestimated in simulation by a factor of around three.

(2) Large aromatics:

In experiments, the values of LIF signals were always ten times higher from small aromatics than from large aromatics. The m-X flames also had the highest amount of large aromatics LIF signals compared to the paraffin flames, whose signal intensities were again lower by one order of magnitude. The normal distribution trends for all flames were similar: the signals climbed to their peaks at middle height in flames, and then decreased to zero downstream. However, the large aromatics existing regions are much broader for m-X flames than in paraffin flames, which means the signals started to occur earlier and disappeared later in m-X flames. However, the measured peak values along centerline in Φ=6 flames are about 25% than the values in Φ=∞ flames. In addition, m-X and JP-8 flames showed similar qualitative trends of large aromatics distributions, even though there existed some quantitative differences.

Similar distribution trends of large aromatics could be found in simulation. Again, the simulation estimated the regions of large aromatics occurring relatively downstream than in measurements. The model’s performance of quantitative estimation was much better for large aromatics than for small aromatics. The quantitative changings of large aromatics LIF signals caused by fuel types and equivalence ratios were almost captured by the simulation results.
5.1.4 Temperature distribution

Temperature measurements via thermocouple were made only in soot-free regions in the flames, due to the special configuration of the thermocouple probe that limited the ability to accurately locate the thermocouple bead during rapid insertion. The experimental and computational results indicated that there was no differences in temperature distribution caused by various fuel types within the uncertainty of the measurement. In addition, m-X and JP-8 flames showed almost the same temperature distribution, taking measurement uncertainty into consideration. The trends of temperature distributions were captured by the simulation; however, the simulation always predicted lower temperature at the beginning of flames and predicted higher temperature downstream in flames. The former discrepancy was explained by the fact that the radiation from the soot in the flames was heating the mixture coming out the tube exit. It is suspected that the overestimated heat release from the reactions resulted in the latter discrepancy.

In summary, both soot and aromatic pollutants are produced highest amount in the fuel mixtures containing aromatic component; while the paraffin fuels are performing very similarly. The current model is able to predict quite well for these pollutants within co-flow laminar flames; however, the model failed to estimate the difference caused by the existence of aromatic component in fuel mixture.
5.2 Future work

5.2.1 Experimental work

In order to further validate and calibrate the model, it would be better if some key intermediate species could be measured, such as acetylene, benzene, naphthalene, etc. The flames could be investigated with a triple quadrupole mass spectrometer to obtain such results.

Since the whole project’s aim is to understand the effects of the fuels’ molecular structures on emissions from gas turbine engine combustors, the fuel mixtures will also be tested in a GTE model combustor. These future experimental results will also be used to improve the model.

5.2.2 Simulation work

Obviously, the most serious discrepancy of the simulation work lies in the soot produced in m-X flames. The model used in this dissertation selected acetylene as the nucleation base, with additional species used for the soot surface growth. A simulation using the new chemical mechanism SERDP 2014 and a new soot model (nucleation with benzene or/and pyrene) is being conducted.
## Appendix A Detailed information of JP-8 and SPK fuel

### Table A-1 Compositions and properties of SPK fuel.

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<th>Density (g/cc)</th>
<th>Molecular Weight (g/cc)</th>
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</tr>
</thead>
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<table>
<thead>
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<th>#H</th>
<th>Class</th>
<th>Mole Fraction</th>
</tr>
</thead>
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<td>24</td>
<td>iso-C11</td>
<td>0.316349096</td>
</tr>
<tr>
<td>10</td>
<td>22</td>
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<td>0.313976856</td>
</tr>
<tr>
<td>9</td>
<td>20</td>
<td>iso-C09</td>
<td>0.156081561</td>
</tr>
<tr>
<td>12</td>
<td>26</td>
<td>iso-C12</td>
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</tr>
<tr>
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<td>28</td>
<td>iso-C13</td>
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<td>9</td>
<td>18</td>
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<td>0.017074111</td>
</tr>
<tr>
<td>8</td>
<td>18</td>
<td>iso-C08</td>
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</tr>
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<td>24</td>
<td>n-C11</td>
<td>0.009061287</td>
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<td>0.008477103</td>
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<td>9</td>
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<td>n-C09</td>
<td>0.003582753</td>
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Table A-2 Composition and properties of JP-8.

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<th>Density (g/cc)</th>
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<td>Class</td>
<td>Mole fraction</td>
</tr>
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<td>cycloaromatic-C13+</td>
<td>1.4%</td>
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<tr>
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<td>6.2%</td>
<td>C2-benzene</td>
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<td>5.4%</td>
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<td>4.6%</td>
<td>monocyclo-C08</td>
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<td>C8+ benzenes</td>
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<td>n-C12</td>
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<td>diaromatic-C11</td>
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<tr>
<td>C6-benzene</td>
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<td>C1-benzene</td>
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<td>n-C14</td>
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<tr>
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<td>1.4%</td>
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</table>
Appendix B Fortran code of Fourier inversion

This is the main piece of code for inverting the laser extinction measurement into soot extinction coefficients as described in Chapter 2 and 3. More details about the principle of this calculation could be found in the cited papers.

Program Inversion

```fortran
INTEGER,PARAMETER ::NX = 48,NY = 48
DIMENSION PHI(0:NX),PROJ(0:NX),CONV(0:NX),PROJ1(0:NX)
DIMENSION Z(0:NX,0:NY)
INTEGER KR,K,KABS
XPOS = 6
YPOS = 6

PI=ACOS(-1.)
N = 100
M = NX-1
A = 2./M
PIN = PI/N
C2 = -1./(2.*PI*A*N)
DELTA = 0.25
PHI = 0.
PHI(0) = 2./(PI*A*N)
DO K=1,M-1
    PHI(K)=C2/((K-1)*(K-1)-.25)
ENDDO

Z = 0.
CONV = 0.
PROJ = 0.
open(unit=1,file='inpbin.txt')
open(unit=2,file='fort.1')
do i = 0,M+1
    read(1,*) PROJ(i)
    if(i<(M/2)) then
        PROJ(i) = PROJ(i)/2.
    endif
ENDDO
```


endif
write(2,*) PROJ(i)
enddo
close(1)
close(2)

DO 20 J=1,N
if(J.eq.2) then
do ii = 0,M+1
   PROJ(ii) = PROJ(M+1 - ii)
endo
dendif

THETAJ = (J-1)*PIN
COSTHTAJ = COS(THETAJ)/XPOS
SINTHTAJ = SIN(THETAJ)/XPOS
COSDELOA = COSTHTAJ*DELTA/A

DO 30 KR = 0,M
   CONV(KR) = 0
DO 40 K = 0,M
   KABS = IABS(KR-K) + 1
   CONV(KR) = CONV(KR)+PROJ(K)*PHI(KABS)
40 CONTINUE
30 CONTINUE

DO 51 IY = 0,NY
   Y1 = -YPOS + 2*YPOS*IY/NY
   R = (-XPOS*COSTHTAJ+SINTHTAJ*Y1+1)/A - COSDELOA
DO 50 I = 0,NX
   R = R + COSDELOA
   L = R
   IF(L.LE.0.OR.L.GE.M)GO TO 50
   Z(I,IY) = Z(I,IY)+(L+1-R)*CONV(L)+(R-L)*CONV(L+1)
50 CONTINUE
51 CONTINUE
20 CONTINUE
!DO 60 J = 1,NY
!  DO 61 I = 1,NX
!  Z(I,J) = AMAX1(0.9,Z(I,J))
!  Z(I,J) = AMIN1(1.1,Z(I,J))
!  61 CONTINUE
!60 CONTINUE

open(unit=3,file='fort.3')
!do j = 1,NY
  write(3,'(49F8.3)') ((Z(i,j)/XPOS,i=0,NX), j=0,NY)
!enddo

end Program Inversion
Appendix C Experimental results for $C_{12}$, pure-$i-C_8$ and SPK flames

C.1 Flame visible appearance and flame heights

Figure C-1 Visible appearances of flames burnt with $C_{12}$, Pure-$i-C_8$, and SPK.
Table C-1 Flame heights comparison for $C_{12}$, Pure-i-$C_8$, and SPK flames.

<table>
<thead>
<tr>
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<th>$\Phi=\infty$</th>
<th>$\Phi=6$</th>
<th>$\Phi=2$</th>
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<tbody>
<tr>
<td>$C_{12}$</td>
<td>55.4</td>
<td>45.1</td>
<td>28.7</td>
</tr>
<tr>
<td>Pure-i-$C_8$</td>
<td>62.7</td>
<td>48.5</td>
<td>29.3</td>
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<tr>
<td>SPK</td>
<td>61.3</td>
<td>47</td>
<td>29.2</td>
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</tbody>
</table>

C.2 Soot volume fraction distribution

The Pure-i-$C_8$ fuel missed the LII measurements, so only the laser extinction measurement of Pure-i-$C_8$ flames are shown below.

Figure C-2 Distributions of soot volume fraction in $C_{12}$ and SPK flames via LII.
Figure C-3 Soot volume fraction along centerline of $C_{12}$ and SPK flames. (a) $\Phi=\infty$ flames; (b) $\Phi=6$ flames.
Figure C-4 Radial distributions of soot volume fraction for Pure-i-C₈ flames. (a) $\Phi=\infty$ flames; (b) $\Phi=6$ flames.
Figure C-5 Line of sight extinction measurement along centerline for Pure-i-C₈ flames.
C.3 Aromatics LIF signals distribution

Figure C-6 Normalized LIF signals from small aromatics in experiments for C_{12} and SPK flames. (a) C_{12} flames; (b) SPK flames.
Figure C-7 Normalized LIF signals from large aromatics in experiments for $C_{12}$ and SPK flames. (a) $C_{12}$ flames; (b) SPK flames.
C.4 Temperature in soot-free regions distribution

Figure C-8 Radial distribution of temperature at 5mm height above tube exit in C_{12}, Pure-i-C_8, and SPK flames. Left: Φ=∞ flames; Right: Φ=6 flames.
Figure C-9 Temperature distribution along centerline in soot-free regions in flames burnt with C_{12}, Pure-i-C_8, and SPK. (a) Φ = ∞ flames; (b) Φ = 6 flames.
Appendix D Simulation results for C\textsubscript{12} and Pure-i-C\textsubscript{8}

Note: The model does not have the information for Pure-i-C\textsubscript{8}-\Phi=2 flame.

D.1 Flame shapes based on OH

Figure D-1 Computational distributions of OH mole fraction in flames. (a) C\textsubscript{12} flames; (b) Pure-i-C\textsubscript{8} flames.
D.2 Soot volume distributions in flames

Figure D-2 Computational distributions of soot volume fraction in flames. (a) C_{12} flames; (b) Pure-i-C_{8} flames.
D.3 Calculated LIF signals from aromatics distribution in flames

Figure D-3 Computational distributions of small aromatics LIF signals in flames. (a) C_{12} flames; (b) Pure-i-C_{8} flames.
Figure D-4 Computational small aromatics LIF signals along centerline in (a) \( \text{C}_{12} \) flames and (b) Pure-\( \text{i-C}_8 \) flames.
Figure D-5 Computational distributions of large aromatics LIF signals in flames. (a) C₁₂ flames; (b) Pure-i-C₈ flames.
Figure D-6 Computational large aromatics LIF signals along centerline in (a) C$_{12}$ flames and (b) Pure-i-C$_{8}$ flames.
D.4 Temperature distribution in flames

Figure D-7 Computational distributions of temperature in flames. (a) C_{12} flames; (b) Pure-i-C_{6} flames.
Figure D-8 Computational temperature distributions along centerline in flames. (a) $C_{12}$ flames; (b) Pure-i-C$_8$ flames.
D.5 Rates of soot nucleation, surface growth, and oxidation

Figure D-9 Computational distributions of soot nucleation rates in flames. (a) C\textsubscript{12} flames; (b) Pure-i-C\textsubscript{8} flames.
Figure D-10 Computational distributions of soot surface growth rates in flames. (a) C\textsubscript{12} flames; (b) Pure-i-C\textsubscript{8} flames.
Figure D-11 Computational distributions of soot oxidation rates in flames. (a) $C_{12}$ flames; (b) Pure-$i-C_8$ flames.
Appendix E Filters and PMT specifications

Filter Data
Appendix F Radiation correction for thermocouple
Temperature measurement

Assuming the thermocouple bead sitting in the flame was not experiencing heat transfer from flame to the bead via the thermocouple wire in terms of conduction.

So, the energy balance for the thermocouple bead is:

\[
A_{TC} h (T_{g} - T_{TC}) = \sigma \varepsilon (T_{TC}^{4} - T_{b}^{4}) A_{TC} \tag{F.1}
\]

\(A_{TC} = \) surface area of the thermocouple bead;

\(h = \) heat transfer coefficient in terms of convection;

\(T = \) Temperature,

index \(g\) is gas, index \(TC\) is thermocouple bead, index \(b\) is background;

\(\sigma = \) Stephan – Boltzman constant;

Assuming \(T_{b}^{4} \ll T_{TC}^{4}\), then equation F.1 becomes:

\[
T_{g} - T_{TC} = \Delta T = \frac{\sigma \varepsilon}{h} T_{TC}^{4} \tag{F.2}
\]

According to the definition of Nusselt number:

\[
N_{\mu} = \frac{hd}{k} \tag{F.3}
\]

d = the diameter of thermocouple bead;

\(k = \) the thermal conductivity of gas mixture;

So, equation F.2 becomes:

\[
\Delta T = \frac{\sigma \varepsilon d}{k N_{\mu}} T_{TC}^{4} \tag{F.4}
\]

In Equation F.4, \(T_{TC}\) is the measuring temperature from thermocouple.

In the measurement, the diameter of thermocouple bead was \(\sim 2.5 \times 125 \mu m\).
So, the parameters including $\varepsilon, k, and N_\mu$ need to be identified.

(1) Emissivity of the thermocouple bead $\varepsilon$

For R type thermocouple, the appropriate estimation of $\varepsilon$ is:

$$\varepsilon = 0.18 + 0.05 \times \left( \frac{T - 1273}{500} \right) \quad 1273K \leq T \leq 1773K$$

$$\varepsilon = 0.23 \quad T > 1773K$$

(2) Conductivity of gas $k$

Since the majority of the gas mixture is nitrogen, so it is reasonable to use the property of nitrogen to represent the property of the mixture.

$$k = \exp\{a + b\ln(T/300)\}$$

$a = 1.856; b = 0.752 \quad for \; 300K \leq T \leq 3000K$

(3) Nusselt number $N_\mu$

For spherical bead:

$$N_\mu = 2.0 + 0.236P_r^{0.33}R_e^{0.606}$$

$P_r = Prandtl number, assuming constant 0.7 in this calculation;$

$R_e = Reynolds nuber$

$$R_e = \frac{\rho v d}{\mu}$$

$\rho = density \; of \; gas \; mixture;$

Again, use the property of nitrogen, which is the majority of gas mixture to represent the density of gas mixture.

$$\rho = \frac{MW_{N_2}P}{RT}$$

$MW_{N_2} = the \; molecular \; weight \; of \; nitrogen;$

$P = the \; pressure, \; which \; is \; 1 \; atm;$

$R = gas \; constant \; of \; nitrogen;$

$T = almost \; the \; same \; as \; measured \; temperature$
\[ \mu = \text{viscosity of gas mixture}; \]

*For nitrogen:*

\[ \mu = \frac{aT^{1.5}}{b + T} \]

\[ a = 1.697 \times 10^{-3} \quad b = 339.4 \]

\[ v = \text{velocity of gas mixture, assuming 60cm/s in this calculation}. \]

Finally, the radiation corrected temperature could be obtained:

\[ T_g = T_{tc} + \Delta T \]
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