EFFECTS OF FUEL MOLECULAR STRUCTURE ON EMISSIONS
IN A JET FLAME AND A MODEL GAS TURBINE COMBUSTOR

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ABSTRACT

The present study aims to advance the current understanding of the effect of fuel molecular structure on emissions. This study is a part of a larger initiative, which involves a collaborative effort between several experimental and computational groups. A series of experiments and companion simulations progress in complexity, which helps to develop a fundamental understanding of emissions under wide range of experimental conditions. The study focused on understanding how the chemical structure of the fuel affects emissions in jet flames under non-premixed and rich-premixed conditions, and testing the effect of fuel volatility on soot emissions in a model gas turbine combustor.

A test matrix comprised of four binary fuel mixtures was prepared by mixing n-dodecane with m-xylene, n-heptane, iso-octane, and methylcyclohexane. These four hydrocarbons represent the four major hydrocarbon classes found in alternative fuels: aromatic, normal paraffin, branched paraffin, and cyclo-paraffin. The spatially resolved soot volume fraction measurements were obtained in these flames using laser induced incandescence (LII) and laser extinction (LE). Additionally, measurements of aromatic species measurements, in two different size ranges, were obtained using planar laser induced fluorescence (LIF). Furthermore, temperature measurements were obtained using R-type thermocouples in the non-sooting regions of the flame. The fuels were studied under both non-premixed and rich-premixed (jet equivalence ratio of 24 and 6) conditions. CHEMKIN simulations, using a published fuel chemical mechanism, have been used to interpret the aromatic-LIF results and understand differences in the pathways to soot precursors for different fuel molecular structures.

The results for the effects of fuel molecular structure on emissions indicate that aromatic fuel substantially affects the peak levels of aromatic species and soot. The trends in peak small aromatics, large aromatics, and soot volume fraction are consistent amongst the four molecular structures: m-xylene produces the highest, followed by methylcyclohexane and iso-octane, and then n-heptane. The results from premixed flames (jet equivalence ratio of 24 and 6) indicate that the effect of fuel structure on maximum soot volume fraction is independent of the jet equivalence ratio. Additionally, the peak soot volume fraction
location shifts from the flame annular region to the centerline with premixing. Fuel structure appears to affect the jet equivalence ratio at which the transition from an annular to uniform soot field occurs. The data suggest that the key factor in determining the jet equivalence ratio at which the transition occurs is the peak amount of soot in the non-premixed flame. The greater the amount of soot in the annular region, the more air must be premixed before the annular peak is reduced to levels similar to the centerline. The findings from this study led to two research questions. First, what physical and chemical processes are responsible for the shift in the peak soot volume fraction location from the flame annular region to the centerline? Second, how do different aromatic fuel molecular structures impact soot formation and the distribution of the soot volume fraction in the jet flames?

To answer the first question, iso-octane flames were studied both experimentally and numerically at a range of jet equivalence ratios. Numerical simulations were performed by Dr. Xuan’s group at Penn State. The simulation shows that the location of peak PAH dimer concentration shifts from the annular region in the non-premixed flame to the centerline in the premixed flame, resulting in a shift in the regions where soot nucleation and PAH condensation rates peak. The PAH dimer concentration decreases with premixing, resulting in a decrease of soot nucleation rate. The reduction in soot nucleation rate, in turn, reduces soot number density, and therefore, soot surface area available for soot growth processes due to surface reactions and PAH condensation.

To investigate the second question, four aromatic fuels, \( n \)-propylbenzene/\( n \)-dodecane, toluene/\( n \)-dodecane, \( m \)-xylene/\( n \)-dodecane, and 1,3,5-trimethylbenzene/\( n \)-dodecane were studied in the jet flame. Comparison of the four aromatic fuels indicates that at a particular jet equivalence ratio, the location of first detection of large-aromatics LIF signal, and hence, LII signal, is at a similar height above the tube exit. Quantitatively, LII results show that the \( n \)-propylbenzene/\( n \)-dodecane, toluene/\( n \)-dodecane, and \( m \)-xylene/\( n \)-dodecane flames, within measurement uncertainty, produce similar levels of peak soot, while 1,3,5-trimethylbenzene/\( n \)-dodecane produces a higher level of peak soot. Furthermore, CHEMKIN simulations were performed to investigate the differences in the fuel pyrolysis
pathways for the aromatic fuels leading to the differences in PAH formation and therefore, soot.

Finally, a model gas turbine combustor has been successfully operated. Three fuels were studied: $n$-heptane/$n$-dodecane, $n$-hexadecane/$n$-dodecane, and JP-8. The soot volume fraction at the combustor exit was measured using laser extinction. The results indicate that the fuel volatility did not affect the soot emissions in the model combustor operating at global equivalence ratios of 1.0 to 1.8. The absence of the impact of fuel volatility on soot emission could be due to the unique design of the injector and combustor, and hence, it is recommended to test the fuel matrix in other types of combustors.
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ABBREVIATIONS

\( \bar{K}_{\text{ext}} \) mean (total) cross section for extinction
\( \dot{Q}_{\text{cat}} \) heat transfer due to surface induced catalytic reactions
\( \dot{Q}_{\text{conc}} \) convection between the gas and the thermocouple
\( \dot{Q}_{\text{cond}} \) conduction along the thermocouple wires
\( \dot{Q}_{\text{rad}} \) radiation between the thermocouple and the surrounding gas
\( A_{TC} \) surface area of thermocouple bead
\( A_{abs} \) mass specific absorption cross-section
\( A_s \) surface area of the particle
\( C_{abs} \) the particle absorption cross section
\( D_{30} \) diameter of average particles
\( D_s \) equivalent diameter of the particle
\( E_{b,\lambda} \) blackbody spectral irradiance
\( G_r(\lambda) \) wavelength response function for the detector and optics
\( f_v \) Soot volume fraction
\( H_v \) enthalpy of vaporization
\( I_o \) intensity of incident light
\( K_{\text{ext}} \) extinction coefficient
\( MW_{N_2} \) molecular weight of nitrogen
\( M_s \) soot mass concentration as a function of time
\( M_v \) molecular weight of the vapor
\( N_{AV} \) Avogadro’s number
\( N_V \) molecular diffusion flux
\( Q_{abs} \) absorption efficiency
\( Q_{ext} \) extinction efficiency of a single particle
\( T_\infty \) gas temperature
\( T_b \) wall/background temperature
\( T_g \) gas temperature
\( T_s \) particle temperature
\( T_{tc} \) thermocouple bead temperature
\( T_w \) temperature of the radiant surroundings
\( V_{mv} \) probe volume
\( c_p \) heat capacity at constant pressure
\( c_s \) specific heat of the soot particle
\( f_v \) particle volume fraction
\( m_s \) mass of a particle
\( \lambda_{det} \) signal detection wavelength
\( \rho_s \) mass density of the particle
2-D two-dimensional
\( C_7 \) \( n \)-heptane/\( n \)-dodecane
\( C_{12} \) \( n \)-dodecane
\( C_{16} \) \( n \)-hexadecane/\( n \)-dodecane
CI confidence interval
CO carbon monoxide
\( D \) diameter of particle
DOD  Department of Defense  
FAA  Federal Aviation Administration  
FT  Fisher-Tropsch fuel  
FWHM  full width half maxima  
h  heat transfer coefficient  
HAB  height above burner(from tube exit)  
HACA  H-abstraction-C\textsubscript{2}H\textsubscript{2}-addition  
HAP  hazardous air pollutants  
HRJ  Hydoprocessed renewable jet  
HRTEM  High-resolution transmission electron microscopy  
Inf  diffusion/non-premixed flame  
i-C\textsubscript{8}  iso-octane/n-dodecane  
K  thermal conductivity of gas mixture  
L  path length the light beam traverses through  
LE  laser extinction  
LIF  laser induced fluorescence  
LII  laser induced incandescence  
m  complex refractive index of particles  
MCH  methylcyclohexane/n-dodecane  
mX  m-xylene/n-dodecane  
NDF  neutral density filter  
N\textsubscript{2}  nitrogen  
NO\textsubscript{x}  oxides of nitrogen
O₂  oxygen
P  number of active sites
PAH  polycyclic aromatic hydrocarbon
PB  n-propylbenzene/n-dodecane
Phi  equivalence ratio
r  radial location
scfm  standard cubic feet per minute
slpm  standard liter per minute
TQMS  Triple Quadrupole Mass Spectrum
TMB  1,3,5-trimethylbenzene/n-dodecane
TOL  toluene/n-dodecane
TSI  Threshold sooting index
UHC  unburnt hydrocarbons
UNICORN  Unsteady Ignition and Combustion using Reactions
UV  ultra-violet
YSI  Yield sooting tendency
σ  Stephan- Boltzmann constant
ϕ_{jet}  jet equivalence ratio
ϕ_{global}  Global equivalence ratio
Ω  solid angle
N  number density of particles
Nu  Nusselt number
P(D)  particle size distribution function
<table>
<thead>
<tr>
<th>Symbol</th>
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<td>Pr</td>
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<tr>
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<td>Reynolds number</td>
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<td>g(Ds)</td>
<td>normalized volume weighted</td>
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<td></td>
<td>distribution function</td>
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<tr>
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<td>thermocouple emissivity</td>
</tr>
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<td>wavelength of light</td>
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<tr>
<td>μ</td>
<td>kinematic viscosity</td>
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<tr>
<td>ρ</td>
<td>density</td>
</tr>
<tr>
<td>τ</td>
<td>time of LII signal collection</td>
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PREFACE

The research work conducted herein was carried out under the guidance of my advisors Dr. Jacqueline O’Connor and Dr. Thomas A. Litzinger in the Department of Mechanical Engineering, The Pennsylvania State University, University Park. The research presented in this thesis was a part of a larger project ‘The Science of Emissions from Alternative Fuels (WP-2145)’ funded by the Strategic Environmental Research and Development Program (SERDP). Therefore, some of the discussions in the Introduction (Chapter 1), experimental overview (Chapter 3), and results (Chapters 4-5, 8) presented in this thesis are available online in the final project report, which is posted by the funding agency, SERDP. Additionally, soot and temperature measurements results presented in Chapters 4 and 5 for non-premixed and $\phi_{jet}=6$ flames were obtained originally by Dr. Yefu Wang. These results are presented here as a means to compare the spatially-resolved aromatic species measurements, obtained by the author, with the soot volume fraction results. The data analysis and conclusions are original work of the author. The work presented in Chapter 6 was carried out in collaboration with Dr. Yuan Xuan at the Pennsylvania State University. The numerical work was performed by Abhishek Jain. Besides the experimental work, the author is responsible for undertaking the data analysis and data reduction of the numerical results, provided by Dr. Xuan, to interpret the experimental results. The literature review (Chapter 2), experimental overview (Chapter 3), analysis, results (Chapters 4-8), and conclusions (Chapter 9) that are presented in this thesis have been either published or are under review in the following publications:


• Makwana, A., Linevsky, M., Iyer, S., Santoro, R., Litzinger, T., & O’Connor, J. “Effect of aromatic fuels and premixing on aromatic species and soot distributions in laminar, co-flow flames at atmospheric pressure.” *Combustion and Flame*. Accepted (Chapter 7)

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On this day, I feel proud that I got the opportunity to pursue my Ph.D. as a member of Center for Combustion, Power and Propulsion (CCPP) at Penn State. Throughout my years at CCPP, my journey has been fruitful due to the continuous support and collaboration with several current members as well as alumni of CCPP. First and foremost, I am thankful to my advisors, Dr. Jacqueline O’Connor and Dr. Thomas A. Litzinger, for their tremendous support, guidance, and encouragement throughout my graduate program, which made this project successful. The optimistic, calmness, and pragmatic nature of my advisors made my journey at Penn State a truly memorable one. I am grateful to Dr. O’Connor for her great mentorship in all aspects of graduate life including going out of the way to help with professional development, and to get best out of oneself. I hope I can engrave in my own career, her strong leadership and ethical qualities. Dr. Litzinger has been my role model ever since we first met; the productive and insightful discussions with him have helped me develop a critical way to face any challenge. In addition, I will miss his sense of humor, something that I really enjoyed during our discussions.

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Chapter 1 Introduction

In 2016, energy used by the Department of Defense (DOD) accounted for approximately 57% of the total federal energy consumption; the DOD consumed approximately 86 million barrels of fuel [1], and 54% of the total fuel was purchased outside of the United States. Military gas turbine engines, which are the major source of emissions on military bases, consume approximately 70% of the fuel purchased by the DOD [2]. The DOD is pursuing numerous initiatives to reduce its fuel needs and shift their focus to more diverse fuel sources. The DOD recognizes that the use of alternative fuels will help to make the fuel supply more flexible and resilient against disruptions through the use of multiple, reliable fuel stocks. Additionally, new fuel sources can help reduce the dependence on traditional fuels. Furthermore, stricter environmental requirements, worldwide air traffic growth, and unsteady fuel prices all has led to an increased interest in alternative jet fuels [3].

The aviation industry currently mandates that potential alternative fuels should be completely interchangeable with petroleum derived fuels without the need to modify aircraft engines or other aircraft and fuel-handling components [4]. A number of studies have focused on understanding the fundamental combustion behavior of alternative jet fuels. These extensive efforts have led to the approval of Fisher-Tropsch Synthetic Paraffinic Kerosene (FT-SPK) fuel blend in 2009 (Annex 1 ASTM D7566), Hydroprocessed renewable jet (HRJ) in 2011 (Annex 2 of ASTM D7566), Synthetic Isoparaffin (SIP) in 2014 (ASTM D7566/D1655), Fisher-Tropsch Synthetic Kerosene with Aromatics in 2015 (ASTM D7566/D1655), and Alcohol to Jet Synthetic Paraffinic Kerosene (ATJ-SPK) in 2016 (ASTM D7566/D1655) [1]. A fuel is acceptable if the physical properties of the fuel falls within the acceptable ranges
(ASTM D4054) and satisfy other characteristics of the current petroleum-derived jet fuels. For this reason, alternative fuels are used as ‘drop-in’ fuels with the traditional approved fuels. The quantity of the alternative fuels that can be added to traditional fuels, like JP-8 or Jet-A, depends on the chemical and physical properties of the alternative fuel. Colket et al. [5] define ‘drop in’ aviation fuels as “composed solely of hydrocarbons (HCs), but produced from alternative sources such as bio-derived feedstocks.” Alternative jet fuels derived from microorganisms, pyrolysis oil, and alcohols [6] have unusual molecular distributions relative to the current approved fuels. The gas phase kinetics and hence, the combustion behavior, are affected by the fuel composition [7]. This necessitates the need to understand the chemical and physical effects of fuel molecular structure on the combustion behavior.

The differences in the properties of the ‘drop-in’ alternative fuels and traditional fuels affect the emission characteristics of the engine [8]. Annex 16 of the International Civil Aviation Organization (ICAO) [9] outlines emission standards for aircraft engines. This standard applies to all turbine engine aircraft (turbojet and turbofan) and outlines the emission compliance requirements for both smoke and gaseous pollutant emissions. The smoke emission and gaseous pollutants (HC, CO or NOx) are measured in terms of smoke number and mass emission (grams), respectively. The engine emissions need to be tested for a complete landing and take-off (LTO) cycle; the definition of the LTO cycle depends on whether the aircraft operates at subsonic or supersonic speeds. For subsonic speeds, LTO includes take-off (0.7 min, 100% thrust), climb (2.2 min, 85% thrust), approach (4.0 min, 30% thrust), and taxi/ground idle (26 min, 7% thrust). For supersonic speeds, LTO cycle includes take-off (1.2 min, 100% thrust), climb (2.0 min, 65% thrust), descent (1.2 min, 15% thrust), approach (2.3 min, 34% thrust), and taxi/ground idle (26 min, 5.8% thrust). The regulatory levels for gaseous
emissions, as defined in Annex 16, is defined differently depending on the rated thrust and date of manufacture of the individual engine.

The type of emissions varies with the engine power [10]. At low engine power, unburned hydrocarbons (UHC) and carbon monoxide (CO) are emitted; however, with an increase in engine power, emission indices of UHC and CO reduce. At high engine power, oxides of nitrogen (NOx) and soot are the major pollutants. Bulzan et al. [10] found that the use of synthetic paraffinic-like alternative fuels, both neat and in blends with petroleum-derived fuels, resulted in significant reduction in soot emissions, including soot number density and particle mass. These authors reported little or no change in NOx emissions between traditional and alternative-sourced fuels. Additionally, at low engine powers, the use of alternative fuels impacts the composition of the UHC emissions [11], including partially-oxygenated hydrocarbons and polycyclic aromatic hydrocarbons (PAH). The aromatic species are of interest not only because they are believed to be the precursors to soot formation, but also because they are among the hazardous air pollutants emitted by gas turbine engines [12, 13]. The use of alternative fuels can hence impact the air quality differently as compared to conventional fuels. The differences in the emission characteristics between a newly developed alternative fuel and conventional fuel highlight the need to focus research efforts on understanding how the fundamental properties of the fuel can affect emissions; the knowledge gained from such programs will also help to streamline new fuel approval processes.
1.1 Research Program

1.1.1 Overall research program

The work presented in this thesis is a part of the collaborative Department of Defense-Industry-University research program to obtain data and develop fundamental models required for accurate simulation of emissions from gas turbine engines burning alternative fuels [11]. The collaborative program was motivated by two major considerations. First, gas turbine engines, which are the major source of emissions on military bases, consume approximately 70% of the fuel purchased by DOD [2]. Second, at the time the program was begun, very little information was available on the changes in emissions that could occur when alternative fuels are integrated into the DOD jet fuel supply. Subsequent to the start of this program, the Federal Alternative Jet Fuels Research and Development Strategy was written. This strategy includes a recommendation for collecting fundamental data on the effects of alternative fuels on emissions [14].

The overall program, outlined in Figure 1-1, involves a collaborative effort between experiment and computational groups. A series of experiments and companion simulations progress in complexity to develop a fundamental understanding of emissions from gas turbine engines burning alternative fuels under a wide range of conditions.
Figure 1-1 Research plan to study emissions from alternative jet fuels [15].

1.1.2 Research program questions: Penn State

The study at Penn State involves understanding the effects of fuel molecular structure on emissions in laminar jet flames under non-premixed and rich-premixed conditions, and testing the effect of fuel volatility on emissions in a model gas turbine combustor. The key research questions explored in this thesis are:

1. What are the effects of fuel composition changes on PAH and soot in jet flames?
2. What are the effects of premixing the fuel jet on the relative tendency of the fuels to produce PAH and soot in the jet flames?
3. How does the structure of a single-ring aromatic fuel impact the soot processes in jet flames under non-premixed and rich-premixed conditions?
4. What are the effects of premixing on the soot sub-processes for a high molecular weight fuel?
5. What is the effect of the fuel volatility on soot emission in both a jet flame and a model gas turbine combustor?

The thesis is outlined as follows. Chapter 2 provides a summary of the previous studies involving the effect of fuel molecular structure on emissions. In Chapter 3, the experimental setup, fuel matrix, flame conditions, and experimental techniques are described. Chapter 4 discusses the effect of fuel chemical composition on polycyclic aromatic hydrocarbons and soot formation in non-premixed, laminar jet flames. The fuels include four binary fuel mixtures containing \( n \)-dodecane and a compound representing one of the fuel major hydrocarbon classes found in “drop-in” alternative aviation fuels produced from non-petroleum sources – aromatic, normal paraffin, branched paraffin, and cyclo-paraffin. While Chapter 4 focuses on flames with non-premixed fuel jets, Chapter 5 presents results for flames with partially-premixed fuel jets at jet equivalence ratios of \( \phi_{\text{jet}} = 24 \) and 6. Chapter 6 expands on Chapters 4 and 5, with a focus on understanding the effects of premixing on the soot distribution in laminar, co-flow flames with \( \text{iso-octane} \) fuel at a range of jet equivalence ratios, using both experimental and numerical methods. In Chapter 7, the effects of one-ring aromatic fuel structure on the aromatic species and the soot volume fraction in laminar, co-flow flames at atmospheric pressure are discussed under both non-premixed and rich-premixed flame conditions. CHEMKIN simulations are used to understand the differences in the pathways of fuel decomposition and formation of soot precursors for four one-ring aromatic fuels. The effects of fuel volatility on soot emissions in a model gas turbine combustor are discussed in Chapter 8. In Chapter 9, major outcomes of the current work and opportunities for future work are discussed.
Chapter 2 Literature review

Soot formation has traditionally been studied because soot emission contributes to global warming and raises health concerns [16]. Additionally, understanding the effects of soot radiation on heat transfer in combustion devices has been an area of active research [17-19]. The soot formation process has been historically studied in many flame configurations, which include diffusion flames [20, 21], premixed flames [22, 23], opposed jet flames [24, 25], turbulent flames [26], fuel spray flames [26], and diesel engines [27]. Irrespective of the flame type, these studies demonstrate that the basic soot formation processes are universally similar. A number of review papers outline important soot formation processes [28-34]. The following section describes each soot formation process in detail based on Ref. [31].

2.1 Soot formation process

Soot formation can be divided into four major processes: soot precursor formation, soot inception, and two types of particle surface reactions, soot growth and soot oxidation. These processes are shown in Figure 2-1.
2.1.1 Soot particle precursors

A number of principal paths have been proposed for the processes that lead to soot particle inception. These are based on inception from polyacetylenes, ionic species, or polycyclic aromatic hydrocarbons (PAHs). Current evidence suggests, based on computational and experimental data [36, 37], that PAHs are precursors to the nascent soot particles.

In fuels containing no aromatic components, the parent fuel has to first decompose, and then the products produced from breakdown of fuel react to form one or two ring aromatics, including benzene, styrene, phenylacetylene, and naphthalene [34]. The pathways to the formation of the first aromatic ring depend on the initial fuel structure, as that structure determines the initial pool of radicals that are formed from fuel breakdown [16].

Figure 2-1 Soot formation processes [34, 35].
single/two ring aromatics grow to form larger polycyclic aromatic hydrocarbons (PAH). In paraffinic fuels, it is therefore important to understand the pathway to the formation of the first aromatic ring. In a fuel containing an aromatic component, the aromatic fuel itself can form radicals containing an aromatic ring, which can react through several pathways to form larger polycyclic aromatics hydrocarbons [16]. Hence, by bypassing the initial fuel decomposition and aromatic ring formation steps, aromatic fuels can result in earlier soot inception.

In paraffinic fuels, formation of the first ring is believed to be the rate determining step in the path to the formation of large aromatics. The two main pathways to the first ring aromatics are

\[
\begin{align*}
  n - C_4H_3 + C_2H_2 & \rightarrow C_6H_5 & 2-1 \\
  n - C_4H_5 + C_2H_2 & \rightarrow C_6H_6 + H & 2-2
\end{align*}
\]

Reaction 2-1 was suggested by Frenklach [38] based on detailed kinetic simulation of a pyrolysis process in a shock tube. Reaction 2-2 is important at low temperature [39, 40]. Miller and Melius [41] proposed that the \(n\)- forms of \(C_4H_3\) and \(C_4H_5\) are less stable than their corresponding \(iso\)- forms. They proposed that the reactions 2-3 and 2-4 would form the one ring aromatic.

\[
\begin{align*}
  C_3H_3 + C_3H_3 & \rightarrow C_6H_6 & 2-3 \\
  C_3H_3 + C_3H_3 & \rightarrow C_6H_5 + H & 2-4
\end{align*}
\]

Other odd carbon atom pathways suggested in literature [42-44] are

\[
C_5H_5 + CH_3 \rightarrow \text{benzene} + H + H & 2-5
\]
The diffusion Monte Carlo study by Kroidis et al. [45] showed that \( n \)-forms have higher stability. This finding re-established the importance of the even carbon pathway to the first ring formation, as in reactions 2-1 and 2-2. Another pathway to the initial ring formation is the reaction between the stable propargyl radical and the most abundant species, acetylene, to form a cyclopentadienyl radical

\[
C_5H_5 + C_5H_5 \rightarrow \text{naphthalene} + H + H
\]

The cyclopentadienyl radical reacts to form benzene [42, 44]. Numerical studies [31] have reported that reaction 2-7 is 10\( ^2 \)-10\( ^4 \) times faster compared to reactions 2-3 and 2-4 due to higher concentration of acetylene compared to propargyl radical in a combustion environment. Although all the discussed pathways could play a role to the first ring formation, reaction 2-7 is probably the dominant one.

The ‘\( \text{H-abstraction-C}_2\text{H}_2\)-addition’ (HACA) mechanism, proposed by Frenklach and Wang [46], is the widely accepted pathway to the formation of PAHs from the one-ring aromatic. It has two principle steps.

\[
A_i + H \rightarrow A_i^- + H_2
\]  

\[
A_i + C_2H_2 \rightarrow \text{products}
\]

\( A_i \) is an aromatic molecule and \( A_i^- \) is its radical. The first step activates a molecule to form a radical for the growth by acetylene in the second step. The first step of activation can be initiated by other reactions as well, depending on the conditions in the experiment. The data
from shock tube and flame experiments [38, 40, 47] suggest that the H abstraction by gaseous hydrogen is the dominant pathway. The growth of aromatic species can also occur by radicals other than acetylene, which involves methyl, propargyl, and cyclopentadienyl [48]. Numerical simulations have concluded that though the initial step of aromatic formation can occur through different pathways depending on the fuel type and combustion environment, the acetylene-based growth step is an important step to the aromatic growth.

2.1.2 Particle inception

The inception of solid soot particles from gas-phase species is the least understood part of the soot formation process. In the initial soot model by Frenklach et al. [38], soot was defined to develop when PAH species grew above a certain size. It was assumed to be a completely chemical phenomenon. However, this model under-predicted the soot particles size. The initial model was then modified to include the physical phenomenon of collision of PAH molecules to form PAH dimers, trimers, and so on. The two processes, PAH growth due to chemical pathways and PAH dimer formation, occur simultaneously. The formation of PAH dimers serves as a bridge to the transition from the gas phase to the inception of the solid soot particle.

2.1.3 Soot growth

The soot growth can occur by both physical and chemical processes. The physical processes include particle coagulation and particle agglomeration. During particle coagulation, the soot particles collide and coalesce to form new spherical particles, impacting the evolution of the soot particle density. Particle agglomeration causes the soot particles to stick to each other and form chain-like structures. This physical process determines the evolution of soot number
density in a combustion environment and the chain-like structure of the soot. However, the total soot mass is conserved in this process.

The chemical processes include surface reactions, which contribute to increasing the soot mass. The growth of soot particles in non-premixed and premixed flames is believed to occur predominantly due to the presence of acetylene [49-51]. The growth of soot due to other radicals like aromatics is a debated topic in the community, as it runs counter to the HACA mechanism. The surface of the soot particle is assumed to be similar to the edge of a PAH molecule. H abstraction activates a site for attack by a radical, which can either result in growth or oxidation. The soot surface growth rate declines with the extent of soot growth due to surface ageing [29, 50, 51]. Soot ageing can result from decrease in H atom concentration or decrease in the number of active sites on the soot surface [46, 52, 53]. The former results in the decrease of the kinetic driving force for the HACA mechanism, while the latter results in the decrease in the soot surface activity. The soot surface growth does not change the soot number density. The amount of soot exiting the combustor is a competition between the growth of the soot particles and oxidation of the soot particles, discussed next.

2.1.4 Soot oxidation

Soot oxidation results from the attack of oxidizing species on the active surface sites on the soot surface. O₂ molecules and OH radicals are considered the dominant species that cause the oxidation of the soot particles. The soot oxidation determines the total mass of soot emitted from any combustion device.

The oxidation of an aromatic radical by O₂ can also hinder further aromatics growth. Additionally, the effect of the oxidizer occurs at the beginning of the aromatics growth. The
environment suitable for soot inception needs to be rich in H radicals and lean in O$_2$ molecules. The removal of carbon mass prior to the first ring formation is also important. The effect of the oxidizer on the small molecules depends on the concentration of the oxidizer. When a small amount of oxidizer is added, the high temperature pyrolytic reactions enhance the production of the radical pool, leading to an increase in the soot formation. However, increased amount of oxidizer can result in oxidation of radicals that form the first ring [40, 54], resulting in a decrease in the amount of carbon available for aromatic ring formation.

2.2 Soot formation in laminar co-flow flames

Laminar diffusion and premixed flames play an important role in understanding the fundamental processes occurring in a practical combustion system. They provide an environment that has all processes of soot formation and oxidation: soot particle formation, growth, and burnout. Numerical simulation of these experiments is tractable, and hence, aid in the development validation of detailed gas phase chemistry and soot models. In addition, they permit easy access to diagnostics methods to obtain accurate species, temperature, and soot measurements. An extensive amount of research has been done in laminar diffusion and premixed flames to understand the effect of pressure [55-58], molecular structure [59, 60], diluents [61, 62], and additives [63-65] on the soot volume fraction. The present thesis investigates the effect of fuel molecular structure on emissions for high molecular weight fuels; a brief review of previous studies, involving high molecular weight fuels, with a focus on effects of molecular structure on emissions, is discussed in this section.
2.2.1 Effect of fuel molecular structure on soot: Non-premixed flames

Calcote and Manos [66] studied the effect of molecular structure in C₂-C₁₆ fuels on soot formation in both premixed and non-premixed flames. They developed the threshold soot index (TSI), ranking fuels from 0 (least sooting) to 100 (highest sooting), to provide a comparison of sooting tendency of different fuels. In non-premixed flames, they found TSI increased with the increase in the number of the carbon atoms. The aromatics fuel had higher TSI as compared to the paraffin fuels for non-premixed flames.

Olson et al. [60] measured TSI, soot concentration, and corresponding emission temperatures at half the total smoke point flame heights for 42 pure hydrocarbons in a laminar non-premixed flame using a wick-fed burner at atmospheric pressure. They also compiled results from previous studies and reported data for 103 pure hydrocarbons. They found alkanes had a lower sooting tendency as compared to the aromatics fuels. Furthermore, maximum soot volume fraction at flame half-heights for aromatic fuels were twice as large as compared to the alkanes. These studies began to quantify how fuel molecular structure affects sooting propensity of a fuel. McEnally and Pfefferle [67] developed yield sooting indices (YSI) for 6 cycloaliphatics and 62 aromatics in a coflow methane/air non-premixed flame. The YSI work has been extended for oxygenated hydrocarbons [68], nonvolatile aromatic hydrocarbons [69], and unsaturated esters [70]. In these studies, they found YSI correlated well with TSI and they found YSI strongly dependent on the fuel molecular structure.

Similar to the investigation undertaken in the present study, Lemaire et al. [71] used two binary mixtures, Surrogate 1 with 70% n-decane/30% α-methylnaphthalene by volume and Surrogate 2 with 80% n-decane/20% α-methylnaphthalene by volume, to match a commercial low-sulfur diesel fuel, which contained 23% n-paraffin, 25% branched paraffin, 7% cycloparaffin, 17%
of aromatics, 8% of esters, and 20% of unknown composition by volume. Surrogate 2 was designed to match the TSI value of the commercial fuel. The fuels were atomized using a high-efficiency nebulizer and burned in a turbulent flame. Spatially resolved data on soot and soot precursors were obtained using LII and LIF, respectively. The results indicate that the Surrogate 2 produces very similar soot and soot precursors to the commercial diesel whereas Surrogate 1, which has more aromatics in the mixture, produces higher levels of soot.

In work by Witkowski et al. [72], diesel fuel, gasoline, jet fuel, various synthetic fuels, and surrogate mixtures were studied in the laminar co-flow diffusion flame. Both LII and extinction measurements were taken to obtain the soot volume fraction distribution in the flames. In addition, thermophoretic sampling of soot was accomplished using a pneumatically actuated sampling probe. It was found that increasing the concentration of toluene in a mixture with n-heptane would cause more rapid soot formation rates; however, the soot morphology was not affected substantially by the different fractions of toluene. A mixture of 70%vol n-tetradecane and 30%vol toluene produced very similar soot volume fractions to that produced by diesel containing 31.1%vol of aromatic components. However, the primary particle size and aggregate size measurements of the mixtures were 17 nm and 47 nm, respectively, as compared to 19 nm and 56 nm for the diesel fuel; the authors concluded that the mixture had a lower soot surface growth rate than diesel.

Recently, Zhang et al. [73] investigated the effect of n-propylbenzene addition to n-dodecane on soot volume fraction and primary particle number density in a methane laminar co-flow diffusion flame. The n-dodecane mole fraction was 3% of the total fuel flow rate. n-propylbenzene was then added to the fuel by replacing n-dodecane, keeping the inlet total carbon flow rate constant. They reported that soot volume fraction increased with the increase
in the mole fraction of \( n \)-propylbenzene. Daca et al. [74] studied soot formation in a methane
coop-flow diffusion flame doped with toluene and \( n \)-heptane at 1-6 and 1-8 atmospheric pressure,
respectively. The toluene/methane flame had higher maximum soot volume fraction and soot
yield as compared to the \( n \)-heptane/methane flame. Furthermore, the toluene/methane flame
had a weaker dependence of maximum soot and soot yield on pressure as compared to the \( n \)-
heptane/methane or methane flame.

2.2.2 Effect of fuel molecular structure on soot: Partially-premixed flames

The work of Calcote and Manos [66] is one of the earliest systematic efforts to determine the
effect of molecular structure on soot. They compiled results from other studies in both
premixed [75-79] and non-premixed flames [63, 80-84] for fuels from \( C_2 \) to \( C_{16} \). In order to
compare sooting tendency of different fuels, they developed the threshold soot index (TSI). In
this method, the fuels were ranked from a value of 0 (least sooting) to 100 (highest sooting).
In premixed flames and non-premixed flames, they found that with the increase in the number
of the carbon atoms, TSI value increased. Additionally, in both non-premixed and premixed
flames, the aromatic fuels had higher TSI as compared to the paraffin fuels. Furthermore, iso-
alkane fuels had slightly higher TSI than \( n \)-alkane fuels.

Olson and Pickens [59] measured the TSI for 55 pure hydrocarbons from \( C_3-C_{16} \) in a laminar
premixed flame at atmospheric pressure. They found TSI increased with the increase in the
number of carbon atoms for a given chemical class. The increase in TSI with carbon number
was more rapid for molecules having less than six carbon atoms as compared to the molecules
having more than six carbon atoms. Additionally, sooting tendency was dependent on the
molecular structure, and the aromatic fuels had a higher TSI as compared to the alkanes.
Since the early work of Calcote and Manos and Olson and Pickens, many studies have focused on understanding the pathways to soot precursors and soot in premixed flames. The early work on soot mechanisms focused on gaseous fuels, which includes flames of methane, ethylene, propane, and methane/ethane/propane fuels doped with higher hydrocarbons for e.g., [22, 85-92]. These studies have aided in understanding the effect of premixing on soot through physical and chemical effects. In these studies, the soot volume fraction decreased in most of the flames with premixing. However, with ethylene and acetylene fuel, the soot volume fraction initially increased with slight premixing, and then decreased at higher level of premixing [87, 93]. The study of partially premixed ethylene flames for e.g., [87, 88] reported the peak soot volume fraction increases until equivalence ratio of 24 and with further addition of air, the peak soot volume fraction decreases. The reason for the increase in soot with premixing has been attributed to the differences that occur in fuel breakdown due to oxidative pyrolysis, which provide favorable pathways to benzene formation [22]. Chernov et al. [94] numerically investigated the partial premixing effects on soot in ethylene flames. The numerical model found good qualitative and quantitative match to soot trends with premixing in ethylene flames studied by Arana et al. [87]. The authors’ found that on centerline, soot growth is due to both PAH and acetylene related processes; the higher inception rates led to the initial increase in soot yield. In annular region, soot growth is primarily due to HACA growth; higher acetylene yield resulted in the initial increase in soot yield for equivalence ratio of 24.

In addition, soot has been studied in premixed flames of large n-alkane fuels [95-97]. Inal and Senkan [95] studied an n-heptane premixed flat flame at two different equivalence ratios, 1.91 and 2.1. They found that the flame with higher equivalence ratio produced higher concentrations of aromatics and soot. Abid et al. [96] studied the evolution of soot in a
premixed flat flame using $n$-dodecane as the fuel at an equivalence ratio of 2 for two different maximum flame temperature of 1807 K and 1875 K. They found the soot size distribution was bi-modal, and the nucleation mode was stronger as compared to the ethylene flame. de Andrade Oliveira et al. [97] measured the PAH and soot in vaporized $n$-heptane and $n$-decane flames over an equivalence ratio range of 3.7 to 8.5. They found a linear correlation between peak PAH and peak soot in these two fuels.

$iso$-octane flames have been studied previously by Paul and Datta [98]. This study investigated the structural change of soot precursors as a function of height above the burner (HAB) in a co-flow premixed flame. However, the soot volume fractions are not reported in this work. The study by Bakali et al. [99] on $iso$-octane and $n$-heptane premixed flat flames found differences in the C$_4$-C$_7$ intermediate decomposition products formed from these two fuels. These differences in the intermediate decomposition products from parent fuel underlines the importance of the chemical effect of fuel molecular structure on pathways to soot formation.

The studies involving cycloalkane premixed flame include that of Alfe et al. [100], which investigated the soot nanostructure from a cyclohexane flame, and Li et al. and Hansen et al. [101, 102], which investigated the different pathways to benzene formation in cycloalkane fuels. However, these cycloalkane fuel studies do not report soot volume fraction measurements.

The aromatic fuel, $m$-xylene, has been studied previously in diffusion flames [56]; however, the effect of premixing on soot precursors and soot has not been investigated. The most studied aromatic fuel under premixed condition is benzene [39, 86, 103, 104]. The most related study involving aromatic premixed flame is that of McEnally et al. [86]. They investigated effect of premixing in benzene-doped methane flames from a non-premixed condition until equivalence
They found premixing resulted in an increase in the concentration of cyclopentadienyl, which can form naphthalene through the reaction of two cyclopentadienyl radicals. However, naphthalene concentration and soot reduced with increasing levels of premixing.

Huang et al. [105] investigated the effects of partial premixing on the soot nanostructure, using benzene and ethylene fuels, in partially premixed Bunsen flames. The HRTEM image analysis showed higher curvature of soot lamella for the partial premixed flames as compared to the non-premixed flames, demonstrating C₅ incorporation in the lamella due to the presence of air. The authors’ established that premixing the fuel jet would affect the soot nanostructure due to the impact of premixing on the soot formation pathways. Additionally, Vander Wal et al. [106] investigated the soot nanostructure using HRTEM for two fuels: a coal-based Fischer-Tropsch and standard JP-8. The soot samples were collected on the TEM grid from the exhaust of an Auxiliary power unit (APU) at three different power levels. The Fischer-Tropsch is primarily composed of paraffinic components while JP-8 contains approximately 18% aromatic components. At each power level, the HRTEM analysis demonstrated differences in the soot nanostructure obtained from Fischer–Tropsch and JP-8 fuel; the Fischer-Tropsch soot was more fullerenic than JP-8 fuel. The study demonstrated that the composition of the fuel can impact the soot formation chemistry and hence, the soot nanostructure.

2.2.3 Effect of aromatic fuel molecular structure on soot

Conventional jet fuels are typically composed of four main classes of molecules: \textit{n}-paraffins, \textit{iso}-paraffins, cycloparaffins, and aromatics [107]. Aromatic molecules form a significant fraction of the total volume of hydrocarbons present in diesel and gasoline fuels as well [108, 109]. These aromatic molecules produce substantially higher soot as compared to the aliphatic
hydrocarbons because of their role in the formation of soot precursors, polycyclic aromatic hydrocarbons (PAH) of molecular weight 500-1000 amu [34].

A number of studies have focused on the oxidation [110-113], laminar flame speed [114, 115], and shock tube pyrolysis [116, 117] of aromatic fuels. However, experimental studies reporting spatial distribution of aromatics and soot for aromatic fuels under non-premixed and premixed conditions are limited. Calcote and Manos [66] and Olson et al. [60] investigated the effect of fuel molecular structure on soot formation. In these studies, threshold soot index (TSI) is used to compare the sooting propensity of the fuels. McEnally and Pfefferle developed yield sooting indices (YSI), and used these to compare the sooting tendency of aromatic fuels [67, 69]. These studies on TSI and YSI quantify how aromatic fuel molecular structure affects fuel sooting propensity on a global basis.

Zhang et al. [118] studied the effect of addition of n-propylbenzene and n-dodecane on soot volume fraction ($f_v$), primary particle diameter, and number density in a methane laminar coflow non-premixed flame. Three different fuel mixtures of n-propylbenzene and n-dodecane were studied by keeping inlet carbon flow rate constant. The mole fraction of the n-propylbenzene and n-dodecane was 3% of the total fuel flow rate. Zhang et al. [118] found that the effect of aromatic chemistry was found to be stronger along the centerline, as the aromatic component increased both the soot inception and surface growth processes. In the annular region of the flame, the aromatic component influenced only the soot inception process by providing a higher population of soot incipient particles. Moss and Aksit [119] reported the $f_v$ measurement using laser extinction, temperature using thermocouples, and mixture fraction measurements using mass spectroscopy for a binary mixture of 77% by volume n-decane and 23% by volume 1,3,5-trimethylbenzene in a non-premixed flame. They also developed a
flamelet-based two-equation model to predict soot. The study reported that the soot model with a surface growth mechanism involving benzene and one without benzene as the contributing species yielded similar soot volume fractions.

Conturso *et al.* [120] studied the sooting tendency of *n*-propylbenzene, *iso*-propylbenzene, and 1,3,5-trimethylbenzene in a counter-flow ethylene non-premixed flame. The fuel stream of ethylene was doped with 10%, 20%, and 30% of total carbon with the aromatic fuels. They compared the results with toluene and xylene fuels from their companion study [121]. They found that *iso*-propylbenzene had a higher tendency of particulate formation as compared to the *n*-propylbenzene; this observation was contradictory to earlier studies [69, 122] of sooting tendency of aromatic molecules. The authors’ concluded that the differences in their study could be a result of flame configuration, counterflow versus co-flow. Secondly, the level of the second fuel level in their study was 20% of total carbon flow rate, which could change the flame structure; the previous work [69, 122] used small amounts, 2-500 ppm, of dopants. Furthermore, the study reported that increasing the number of methyl groups on the aromatic ring didn’t have an effect on the sooting tendency of the fuels. They found toluene, the three xylenes, and 1,3,5-trimethylbenzene had similar sooting tendencies. Pena *et al.* [123] investigated the effect of methyl group on aromatic fuels, as in benzene, toluene, and *m*-xylene, on the physical and chemical characteristics of soot generated using the ASTM standard smoke point apparatus. They found that increasing the number of methyl groups on aromatics resulted in an increase in TSI. Furthermore, they measured soot oxidation kinetics using a thermogravimetric analyzer. They found that at low conversion levels (below 30%), benzene and *m*-xylene had the highest and the lowest reactivity towards oxygen, respectively. At high
conversion levels, benzene and toluene had the highest and the lowest reactivity towards oxygen, respectively.

In addition to non-premixed flames, partially-premixed flames are of practical importance in gas turbine engines, where fuel and air first mix in the primary zone of the combustor. Harris and Weiner [124] studied soot particle growth in ethylene and ethylene/toluene flames in a premixed flat flame configuration. They found that for a particular C/O ratio, the soot inception was higher in toluene/ethylene flames as compared to ethylene flames. However, the rate of surface growth per unit area was higher in the ethylene flame as compared to the toluene/ethylene flame due to higher concentration of acetylene in the ethylene flame. D’Anna et al. [125] characterized the chemistry of n-heptane (C/O=0.7 and 0.8) and 90% vol n-heptane/10% vol n-propylbenzene (C/O=0.8) in a McKenna burner. The addition of n-propylbenzene to n-heptane resulted in the increase in benzene and PAH concentration, which resulted in earlier occurrence of and increased levels of soot inception in an n-propylbenzene/n-heptane flame as compared to an n-heptane flame. However, the final soot loading was found to be similar in both the n-propylbenzene/n-heptane and n-heptane flames. Modelling by these same authors found that in the n-heptane flame, the larger contribution of soot mass growth, due to slightly higher temperature and earlier, larger presence of acetylene, counterbalanced the higher soot inception in the n-propylbenzene/n-heptane flame.

These previous studies show that the effect of an aromatic fuel on soot loading depends on the flame conditions, which drive the soot inception and growth processes. Furthermore, the premixed flame studies [86, 87, 91, 93] indicate that premixing can change the distribution of the intermediate products formed from fuel decomposition. This change in intermediate products can result in either an increase or decrease of soot emission, depending on the fuel
type and level of premixing. These points highlight the need to systematically investigate the
effect of premixing on soot precursors and soot under similar flame conditions to that of non-
premixed flames.

2.2.4 Effect of fuel volatility on soot emission

Besides the influence of the fuel chemical properties on emissions discussed so far, physical
properties of the fuel are important in real combustion devices where spray formation, breakup,
and vaporization play a critical role on combustion physics. Pertinent physical properties
include viscosity, density, freeze point, molecular weight, and surface tension [126].

Alternative jet fuels often have different physical properties as compared to conventional jet
fuels [5], which makes it challenging to integrate new fuels in the current fuel supply chain
without systematic fuel testing in different devices. This testing is complicated by the fact that
the different injectors or combustors can be affected differently based on their particular
configuration. The National Jet Fuels Combustion Program [5] was designed to understand
how fuel properties would impact combustion processes, with a final goal to streamline the
fuel certification process. The current work focuses on how fuel volatility impacts soot
formation, and therefore, an overview of these studies is presented here.

Naegeli and Moses [127] investigated the effects of fuel molecular structure on soot formation
in a high-pressure combustor. Six fuels were designed that had same hydrogen content but
different chemical structures. They measured flame radiation as a means to indicate the sooting
tendency of the six fuels. They found that the final boiling point of the fuel did not affect the
soot formation and fuels with higher aromatic content produced higher level of soot. Reeves
and Lefebvre [128] examined the effects of several fuel properties on pollutant emission in
tubo-annular and annular engine combustion systems. The fuels investigated included JP4,
JP8, five blends of the JP4, five blends of the JP8, and a No. 2 diesel fuel. They found that exhaust smoke emissions were dependent on the type of injector, combustion pressure, and primary zone air-fuel ratio.

Additionally, the n-hexadecane fuel, studied here, is representative of the molecular weight of components of jet fuel [7] and diesel fuel [108]. For example, Eddings et al. [129] studied a six component surrogate (Hex-11 and Hex-12) as a possible surrogate to match the volatility (the boiling point distribution) and sooting tendency of JP-8. The Hex-11 and Hex-12 had 5 mol % and 12 mol % of n-hexadecane as one of the surrogate components, respectively. The sooting limit and polycyclic aromatic hydrocarbons (PAH) formation of n-hexadecane have been studied in a micro-flow reactor at equivalence ratios of 1.5–4.5, and 4, respectively [130]. Pastor et al. [131] studied mixtures of n-decane and n-hexadecane fuels in a diesel engine. They found an increase in the n-hexadecane concentration resulted in an increase in the amount of soot formed in the flame. Douce et al. [132] studied soot formation from n-hexadecane by the shock tube method.

Studies of the effects of boiling point on emissions require that studies be conducted in systems that include fuel sprays. In order to determine whether changes in boiling point resulting from the use of alternative fuels may affect soot production, studies were conducted in a model combustor. The hypothesis of the study was that fuels with varying volatility will have an effect on the fuel droplet vaporization processes and hence, on fuel-air mixing and emissions. A fuel with a higher boiling point, i.e., a heavier hydrocarbon fuel, is expected to produce larger initial droplet sizes than a lighter hydrocarbon [133, 134]; if the droplet vaporization time is longer than the convection time of the droplet from the injector exit to the flame front, the droplets will burn in a diffusion flame at a stoichiometric condition. As a result of this potentially
incomplete vaporization, a heavier hydrocarbon fuel will likely have higher soot emissions as compared to a fuel with a lower boiling point.

2.2.5 Numerical modelling: Soot model

Future advances in the design of combustion-based aero-propulsion engines will rely, in part, on computational modeling predictions of fuel combustion kinetics. An accurate model for predicting emissions must include both gas-phase chemical kinetic models and a soot model. The gas-phase chemistry determines how the species evolve across the combustion region, which directly couples with the soot model to determine the region of soot nucleation and soot surface reaction rates for both growth and oxidation.

Soot models typically fall into three categories: method of moments [52], discrete sectional method [135], and stochastic approach [136]. In the current work performed by Dr. Xuan’s group, the soot model employed is the method of moments and is taken from Ref. [137], which is a simplified version of that presented in Ref. [138]. Soot particles are considered as fractal aggregates and geometrically described based on the total volume, \( V \), and total surface area, \( S \). The population of the soot particles is statistically described using a bi-variate soot Number Density Function (NDF), \( n(V; S) \), and is approximated by two delta functions, following previous work [20]. The evolution of soot is determined by transporting key soot moments

\[
M_{x,y} = \int \int n(V,S)V^xS^y dVdS \tag{2-10}
\]

of the soot NDF using the following transport equation

\[
\frac{\partial M_{x,y}}{\partial t} + \nabla \cdot (\mathbf{u}^* M_{x,y}) = \dot{\omega}_{x,y} \tag{2-11}
\]
Where

\[ \mathbf{u}' = \mathbf{u} - 0.556(\nu/T)\nabla T \]

is the velocity vector accounting for thermophoresis effects [139], \( \nu \) is fluid kinematic viscosity, and \( \omega_{x,y} \) accounts for the various contributions from soot nucleation, condensation, surface growth, and oxidation [138].
Chapter 3 Experimental Overview

This chapter describes the burner and the burner system used in this study. This is followed by a description of the methodology for fuel selection and the flame conditions selected for each fuel, the theory and experimental set-up of the micro-thermocouple for temperature measurement, laser extinction, laser induced incandescence, and laser induced fluorescence. The final section describes the laser extinction results obtained for the ethylene diffusion flame to compare with the previous published results [20].

3.1 Experimental apparatus

3.1.1 Burner

A co-annular laminar flame burner is used to study soot formation in a well-characterized, steady, laminar flame. This burner is similar to the co-annular laminar flame burner used by Santoro et al. [20]. The burner consists of two concentric brass tubes as shown in Figure 3-1. The inner fuel tube diameter is 0.436 inch, and the wall thickness is 0.032 inch. This tube protrudes 0.157 inch above the exit plane of the co-flow air. The outer air tube has a 4 inch inner diameter. The annular co-flow region contains a series of screens, 3/32 inch glass beads, and honeycomb to provide a uniform exit velocity profile.

Two major modifications from the original burner design by Santoro et al. [20] were made to prevent fuel vapor condensation in the fuel tubing. First, the burner was modified to allow the use of heating tape and insulation around the inner fuel tube. The installation of the insulation required cutting the annular-flow honeycomb, approximately 0.1 inch thickness, around the fuel tube. Second, a 0.125 inch outer diameter tube is used inside the 0.436 inch inner fuel tube in order to increase the fuel-air mixture velocity. The smaller tubing helps to reduce the
residence time of the mixture in the tubing and reduce the possibility of fuel pyrolysis before the exit of the tube. The top of the 0.125 inch tubing is connected to 1.5 inch length, 0.308 inch inner diameter tube. To condition the flow, this tubing is filled with 3/32 inch diameter glass beads topped by two screens. A 1-inch length gap exists between the screen and tube exit.

Figure 3-1 Burner design [140].

3.1.2 Burner and vaporization system

The fuel and air delivery system for the burner is shown in Fig. 3-2. A previously built jet flame burner system [140] was re-designed during the course of this work to improve the reliability and durability of the vaporizer system. The new design enabled rapid switching between the base flame and the binary mixture, which made it possible to troubleshoot the
burner and maintain operational consistency from day-to-day. The new system is comprised of two-vaporizers, where the \textit{n}-dodecane is supplied using a Isco 500D syringe pump (rated flow rate accuracy \( \pm 0.5\% \)) and the second fuel component is supplied by a Chemyx Nexus 6000D (rated flow rate accuracy \( \pm 0.04\% \)) syringe pump. Two separate vaporizers are used, both of which consist of a brass Swagelok tee filled with fiberglass [141].

The energy for fuel vaporization is provided by heating tapes that are wrapped around the tubing system and Swagelok assembly. The heating tapes are wrapped from 30 cm below the mixing chamber to the end of the burner inner tube. K-type thermocouples are placed on the inside of the tubing system to monitor the temperature at critical locations, as shown in Fig. 3-2. The temperature in the inside of the tubing system is maintained at \( 250\° \pm 10\° \) C in order to completely vaporize the fuel while minimizing fuel pyrolysis in the vaporizers and fuel delivery lines. The fuel temperature at the exit of the burner, without the flame, is measured to be less than \( 200\° \) C, as shown in Appendix A. The residence time of the fuel mixture in the vaporizer and heated tubing is approximately 2 sec. Re-condensed fuel captured at the exit of the fuel tube was analyzed with gas chromatography, shown in Appendix B, for each fuel mixture to ensure that no fuel pyrolysis has occurred in the tubing system. The flames are allowed to burn for a minimum of 45 minutes prior to taking any measurements to reach thermal equilibrium with the chimney and the burner itself. During this run time, the vaporizer system also achieves thermal equilibrium. Flame height is monitored as an indicator of achievement of thermal equilibrium and as an indicator of the presence of cold spots in the vaporizer, which would lower fuel flow rate, and therefore, the flame height.
A brass chimney (400 mm long) with four symmetrically located slots sits surrounding the burner. The slots provide access for the laser beam/sheet and the thermocouple probe as well as for capturing visible light images of the flame. This chimney helps to prevent air currents from disturbing the flame. Screens are placed on the top of the chimney to create a slight positive pressure inside the chimney, which prevents air from entering the four slots. The burner assembly can be moved in both the horizontal and vertical direction using a pair of stepper motor (Velmex PK266) and Velmex bi-directional slide. The step resolution is 6.5 μm and 5 μm in horizontal and vertical directions, respectively.

3.1.3 Air delivery system

The flow rate of premixed air and nitrogen is controlled by mass flow controllers (Brooks Instruments 5850 series). The mass flow controllers are calibrated using a bubble meter. The nitrogen is 99.9% pure industry grade.

The co-flow air is set at a constant flow rate of 4 scfm. The co-flow air is supplied from an air compressor and is filtered. The upstream pressure is set to 80 psi and flow rate is controlled.
using a metering valve. The flow rate is monitored using a Teledyne Hasting LAFM-5 laminar flow element and a mass flow meter. The flow meter is calibrated using a turbine flowmeter.

### 3.2 Fuel test matrix

In the present study, three fuel test matrices are selected in order to study the effects of molecular structure and fuel volatility on emissions. The first fuel test matrix is comprised of binary mixtures of a normal paraffin with another normal paraffin, an *iso*-paraffin, a cycloparaffin, and an aromatic specie. These four fuel structures, normal paraffins, *iso*-paraffins, cycloparaffins, and aromatics, collectively represent the four molecular classes found in a real aviation fuel. Traditional jet fuels like JP-8 and Jet-A, and alternative jet fuels like Fisher-Tropsch and hydroprocessed renewable jet (HRJ) fuels, significantly vary in their chemical composition, physical properties, and distillation curves \([7, 142, 143]\). However, the basic chemical structures present amongst all fuels is the same. This fuel selection strategy provides a basis for understanding the effects of specific type of chemical compound on emissions.

One aim of the study is to successfully predict emissions from realistic fuels and combustor configurations. This necessitates selecting hydrocarbons for which chemical mechanisms, thermo-physical properties, and transport properties are well-developed and characterized. An *n*-paraffin is selected as the base fuel, and other chemical classes are blended to create binary fuel mixtures. *n*-Dodecane is selected as the fuel in which four other fuels (*n*-heptane, *iso*-octane, methylcyclohexane, and *m*-xylene) representing each of the chemical classes are blended. The important properties of these binary mixtures are presented in Table 3-1(a).

The reason to select *m*-xylene as the aromatic specie is the availability of a validated chemical mechanism for this molecule \([56]\). The composition of *m*-xylene/*n*-dodecane mixture is set at
25% m-xylene by volume to match the maximum volume fraction of aromatics permitted in JP-8 under ASTM D1319 specification [144]. This volume fraction of m-xylene corresponds to a carbon mole fraction within the binary mixture of 0.292. For the other three binary fuel mixtures, the volume fraction of the compound added to the n-dodecane is set such that the carbon fraction from the added compound is the same as the carbon fraction from m-xylene in the m-xylene/n-dodecane fuel.

The second fuel test matrix is used to study the effect of fuel volatility on emissions. The fuel matrix, shown in Table 3-1 (b), is comprised of two binary mixtures: n-heptane/n-dodecane, and n-hexadecane/n-dodecane, a high boiling point fuel. n-Hexadecane has a boiling point of 287˚C as compared to 216˚C for n-dodecane and 98˚C for n-heptane. The two binary mixtures are chosen such that the carbon fraction of n-dodecane and the added hydrocarbon is constant.

To investigate the effect of aromatic fuel molecular structure on soot precursors and soot, four single-ring aromatic fuels, n-propylbenzene, toluene, m-xylene, and 1,3,5-trimethylbenzene, are also studied. The fuel test matrix is comprised of four binary fuel mixtures of n-dodecane with n-propylbenzene, toluene, m-xylene, and 1,3,5-trimethylbenzene. The n-dodecane fuel used in this study is meant to represent the n-alkane class in a real fuel [7]. The n-alkanes represent a significant volume fraction of conventional fuels, and hence, the decomposition of the n-dodecane builds a radical pool similar to that in real fuels. The use of binary mixtures also helps to retain similar thermal conditions in the fuel decomposition region, and therefore, isolates the chemical effect of the aromatic fuel. The aromatic fuels were chosen to understand the role of the number of methyl groups and the lengthening of the aliphatic chain on the aromatic ring in aromatic and soot formation. The fuel mixtures and some of their properties are outlined in Table 3-1 (c).
### Table 3-1 Fuel Test Matrix

(a) The binary fuels listed in Table 3-1 (a)-(c) are studied in a laminar, co-flow, axisymmetric burner. The flames investigated are non-premixed (equivalence ratio of “infinity”) and rich premixed (equivalence ratio of 24 and 6) in order to have fuel rich conditions similar to those

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Liquid Fuel flow rate (ml/min)</th>
<th>Liquid volume fraction</th>
<th>Carbon fraction</th>
<th>Mole fraction</th>
<th>H/C ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m$-xylene mixture (m-X)</td>
<td>0.200</td>
<td>25.0%</td>
<td>0.292</td>
<td>38.2%</td>
<td>1.90</td>
</tr>
<tr>
<td>$n$-heptane mixture (C$_7$)</td>
<td>0.218</td>
<td>31.3%</td>
<td>0.292</td>
<td>41.4%</td>
<td>2.20</td>
</tr>
<tr>
<td>iso-octane mixture (i-C$_8$)</td>
<td>0.217</td>
<td>30.6%</td>
<td>0.292</td>
<td>37.8%</td>
<td>2.19</td>
</tr>
<tr>
<td>methylcyclohexane mixture (MCH)</td>
<td>0.209</td>
<td>28.4%</td>
<td>0.292</td>
<td>41.4%</td>
<td>2.12</td>
</tr>
<tr>
<td>Pure $n$-dodecane (C$_{12}$)</td>
<td>0.211</td>
<td>100%</td>
<td>0.292</td>
<td>100%</td>
<td>2.17</td>
</tr>
</tbody>
</table>

(b) The binary fuels listed in Table 3-1 (a)-(c) are studied in a laminar, co-flow, axisymmetric burner. The flames investigated are non-premixed (equivalence ratio of “infinity”) and rich premixed (equivalence ratio of 24 and 6) in order to have fuel rich conditions similar to those

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Liquid Fuel flow rate (ml/min)</th>
<th>Liquid volume fraction</th>
<th>Carbon fraction</th>
<th>Mole fraction</th>
<th>H/C ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$-hexadecane mixture (C$_{16}$)</td>
<td>0.2097</td>
<td>28.4%</td>
<td>0.292</td>
<td>23.5%</td>
<td>2.15</td>
</tr>
<tr>
<td>$n$-heptane mixture (C$_7$)</td>
<td>0.2180</td>
<td>31.3%</td>
<td>0.292</td>
<td>41.4%</td>
<td>2.20</td>
</tr>
</tbody>
</table>

(c) The binary fuels listed in Table 3-1 (a)-(c) are studied in a laminar, co-flow, axisymmetric burner. The flames investigated are non-premixed (equivalence ratio of “infinity”) and rich premixed (equivalence ratio of 24 and 6) in order to have fuel rich conditions similar to those

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Liquid Fuel flow rate (ml/min)</th>
<th>Liquid volume fraction</th>
<th>Carbon fraction</th>
<th>Mole fraction</th>
<th>H/C ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$-propylbenzene mixture (PB)</td>
<td>0.2004</td>
<td>25.1%</td>
<td>0.292</td>
<td>35.4%</td>
<td>1.92</td>
</tr>
<tr>
<td>toluene mixture (TOL)</td>
<td>0.1995</td>
<td>24.8%</td>
<td>0.292</td>
<td>41.3%</td>
<td>1.87</td>
</tr>
<tr>
<td>$m$-xylene mixture (mX)</td>
<td>0.2000</td>
<td>25.0%</td>
<td>0.292</td>
<td>38.2%</td>
<td>1.90</td>
</tr>
<tr>
<td>1,3,5-trimethylbenzene mixture (TMB)</td>
<td>0.2003</td>
<td>25.1%</td>
<td>0.292</td>
<td>35.4%</td>
<td>1.92</td>
</tr>
</tbody>
</table>
in the primary zone of an aircraft engine combustor. Diffusion flames play an important role in practical combustion systems, where fuel and oxidizer mixing is the rate-limiting process during combustion. Diffusion flames also displace significant soot production, growth and burnout processes, ostensibly similar to those in real engines. A nitrogen flow rate of 0.2 slpm is used to carry the vaporized fuel. The total carbon flow rate is held constant for all flames at 0.0111 mole/min. The carbon flow rate is fixed to match carbon flow from the base flame, a 75% \textit{n}-dodecane and 25% \textit{m}-xylene mixture. The experimental conditions are provided in Table 3-2.

In the aromatic fuel study, the fuel jet dilution level is increased from standard burner operation at 0.2 slpm to 0.48 slpm N\textsubscript{2} flow rate. The 0.48 slpm N\textsubscript{2} dilution level was selected to be consistent with the previous work involving the \textit{m}-xylene/\textit{n}-dodecane fuel [145, 146], in which 0.48 slpm N\textsubscript{2} flow rate resulted in a non-smoking flame for the \textit{m}-xylene/\textit{n}-dodecane fuel.

The fuel volatility study for fuels listed in Table 3-1 (c) is investigated in a model gas turbine combustor. This experiment replicates the complexity of bulk mixing, turbulent mixing and spray as present in real combustor operating on liquid fuels. This combustor has been used in previous studies on combustion instability, soot, and emissions [147-150]. In the current study, effect of fuel volatility on soot emission for equivalence ratio in range 0.8-1.8 is studied. The experimental setup and results are discussed in Chapter 8.
### Table 3-2 Flame conditions

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Equivalence ratio (Φ)</th>
<th>Fuel flow rate (ml/min)</th>
<th>Nitrogen flow rate (L/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-xylene mixture (m-X)</td>
<td>0.2000</td>
<td>0.20 and 0.48</td>
<td></td>
</tr>
<tr>
<td>n-propylbenzene mixture (PB)</td>
<td>0.2004</td>
<td></td>
<td></td>
</tr>
<tr>
<td>toluene mixture (TOL)</td>
<td>0.1995</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,3,5-trimethylbenzene mixture (TMB)</td>
<td>0.2003</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-heptane mixture (C&lt;sub&gt;7&lt;/sub&gt;)</td>
<td>Inf, 24 and 6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>iso-octane mixture (i-C&lt;sub&gt;8&lt;/sub&gt;)</td>
<td>0.218</td>
<td></td>
<td></td>
</tr>
<tr>
<td>methylcyclohexane mixture (MCH)</td>
<td>0.209</td>
<td>0.20</td>
<td></td>
</tr>
<tr>
<td>n-hexadecane mixture (C&lt;sub&gt;16&lt;/sub&gt;)</td>
<td>0.2097</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pure n-dodecane (C&lt;sub&gt;12&lt;/sub&gt;)</td>
<td>0.211</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 3.4 Temperature measurement

Temperature measurements are obtained using a 125 micron Pt/Pt-13% Rh fine-wire, uncoated R-type thermocouple, based on the design of Ref. [140]. The thermocouple configuration is shown in Figure 3-3. The thermocouple apparatus consists of a single ceramic tube (OmegaTite 200) that is fixed on a horizontal translation stage. The thermocouple wires pass through two holes inside the ceramic tube. One side of the thermocouple wires are affixed to the connector, and at the other end, the wires are bent at 90 degrees to point vertically down approximately 3 mm. This configuration was used to minimize conduction effects caused by radial temperature gradients on the thermocouple reading. Temperature measurements were obtained every 1 mm in both the radial direction and axially along centerline from the burner exit by moving the burner in a horizontal or vertical direction. In regions containing soot, soot particles deposited on the thermocouple junction. When this occurred, the junction is cleaned by moving it to a
non-sooting region of the flame. The data for temperature measurement are collected by a National Instruments data acquisition system at a sampling rate of 10 samples/sec for 3 sec. The uncertainty in temperature measurement and spatial location is estimated to be ± 100 K and ± 0.5 mm.

![Thermocouple configuration](image)

**Figure 3-3 Thermocouple configuration.**

3.4.1 Radiation correction

A radiation correction is applied to the thermocouple temperature measurements to account for the heat transfer occurring at the thermocouple bead. A schematic of a laboratory type thermocouple is shown in Figure 3-3. The discussion here is based on the work by Shaddix [151]. An energy balance at the thermocouple bead is given by Equation 3-1

\[
\dot{Q}_{\text{cat}} + \dot{Q}_{\text{conc}} + \dot{Q}_{\text{rad}} + \dot{Q}_{\text{cond}} = \rho c_p V \frac{dT_{tc}}{dt}
\]

Where each term from left to right represents heat transfer due to surface induced catalytic reactions, convection between the gas and the thermocouple, radiation between the thermocouple and the surrounding gas, and conduction along the thermocouple wires. The right hand side represents the transient heating or cooling of the thermocouple.
The accuracy of the temperature measurement increases if the convection is the dominant mode of heat transfer to and from the thermocouple bead. Catalytic and conduction heat transfer are difficult to quantify in a combustion environment. Therefore, attempts are made to minimize these modes of heat transfer. The conduction heat transfer results from both heat transfer to the thermocouple wires and the effect of the temperature gradient in the gas phase on the measured thermocouple temperature. A good approach to minimize the effect of conduction due to the temperature gradient is to align the thermocouple wires along an isotherm. The energy loss to the thermocouple wires can be reduced by using sufficiently long and thin thermocouple wires. The catalytic effects are heating effects due to radical recombination on the thermocouple surface. It is difficult to quantify, but it can be eliminated using non-catalytic coating like silica, BeO/Y2O3, and alumina based ceramic.

In steady state measurements, assuming conductive and catalytic heat transfers are negligible, the energy balance in Equation 3-1 reduces to Equation 3-2

\[
A_{TC} h (T_g - T_{TC}) = \sigma \varepsilon (T_{TC}^4 - T_b^4) A_{TC}
\]

where \(A_{TC}\) is surface area of thermocouple bead.; \(h\) is the heat transfer coefficient between gas and thermocouple wire; \(T_g\) is gas temperature; \(T_{TC}\) is measured thermocouple bead temperature; \(T_b\) is wall/background temperature; \(\sigma\) is Stephan- Boltzman constant; and \(\varepsilon\) is thermocouple emissivity. The radiation term is estimated by considering thermocouple as gray-emitting surface enclosed in large, isothermal diffuse-gray surface. For relatively cold surrounding, \(T_b^4 \ll T_{TC}^4\). Equation 3-2 reduces to:

\[
T_g - T_{TC} = \Delta T = \frac{\sigma \varepsilon d}{k Nu} T_{TC}^4
\]
where Nusselt number, $Nu = \frac{hd}{k}$; $k$ is the thermal conductivity of gas mixture; $d$ is the thermocouple bead diameter. The bead is approximated as spherical and the Nusselt number is estimated by a correlation from Eckert and Drank [152].

$$Nu = 2.0 + 0.236Pr^{0.33}Re^{0.606}$$  \hspace{1cm} 3-4

where $Pr$ is Prandtl number of the gas mixture, assumed to be 0.7; $Re$ is Reynolds number given by Equation 3-5

$$Re = \frac{\rho vd}{\mu}$$  \hspace{1cm} 3-5

where $\rho$ is the density of the gas mixture; $v$ is the velocity of the gas mixture at thermocouple bead; $\mu$ is the kinematic viscosity of the gas mixture.

The diameter of the thermocouple bead is approximately 2.5 larger than the wire diameter. The velocities typically range from 30-250 cm/sec inside the flame [21] and a value of 60 cm/sec is considered for the radiation correction. It is difficult to estimate the composition of the gas mixture throughout a diffusion flame. Hence, the conductivity, viscosity, and density of the gas is approximated to be that of nitrogen.

$$k = \exp\{a + b \ln(T/300)\}; a = 1.856; b = 0.752 \text{ for } 300K \leq T \leq 3000K$$  \hspace{1cm} 3-6

$$\mu = \frac{aT^{1.5}}{b + T}; a = 1.697 \times 10^{-3}; b = 339.4$$  \hspace{1cm} 3-7

$$\rho = \frac{MW_{N_2}P}{RT}$$  \hspace{1cm} 3-8

where $MW_{N_2}$ is the molecular weight of nitrogen; $P$ is pressure; $R$ gas constant for nitrogen; and $T$ is measured temperature.
The emissivity for Pt/Pt-13% Rh is taken from Bradley and Entwistle [153].

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

\[ \varepsilon = 0.23 \quad T > 1773K \]

Substituting Equations 3-4 to 3-9 in Equation 3-3, \( \Delta T \) can be calculated. The radiation corrected temperature is given by \( T_g = T_{TC} + \Delta T \).

3.5 Laser Extinction

Light extinction is one of the most widely used optical techniques for soot diagnostics. The detailed description of this method is provided in Ref. [154-156].

When a beam of light passes through a particle cloud, the intensity of light decreases through the particle cloud due to the presence of particles in the light path. This extinction is the result of both light absorption and light scattering by the particles, as shown in Figure 3-4 [157].

![Image](Figure 3-4 Extinction by a collection of particle [157].)

The intensity of attenuated light after passing through the particles is related to the intensity of the incident light by Lambert-Beer’s law, given in Equation 3-10

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

3-10
where, $I_o$ is the intensity of incident light ($W/m^2$); $K_{ext}$ is the extinction coefficient for a cloud of particles (1/m), $L$ is the path length the light beam traverses through (m).

The extinction coefficient that represents the sum of total scattering and absorption is given by Equation 3-11

$$K_{ext} = N\bar{K}_{ext}$$ 3-11

where, $N$, the number density of particles ($m^{-3}$)

$ar{K}_{ext}$ the mean (total) cross section for extinction, which is given by Equation 3-12

$$\bar{K}_{ext} = \frac{\pi}{4} \int_0^\infty Q_{ext} \left[ \frac{\pi D}{\lambda}, \hat{m}(\lambda) \right] P(D)D^2dD$$ 3-12

where, $Q_{ext}$ is the extinction efficiency of a single particle; $D$ is the diameter of particle ($\mu m$); $P(D)$ is the particle size distribution function.

The extinction efficiency depends on the particle density, size, and properties of the individual particle, particularly its refractive index. This efficiency can be approximated by using Mie Theory, which assumes that the size of the particle is much greater than the wavelength of light incident on the particles. This simplification leads to a tractable solution for the light absorption and scattering of an arbitrary radius and complex refractive index (the real part in the refractive index indicates the phase velocity, while the imaginary part represents the extinction coefficient) [155, 157]. This form is given by Equation 3-13

$$Q_{ext} = Q_{abs} + Q_{sca}$$

$$= -4x\text{Im} \left( \frac{m^2 - 1}{m^2 + 2} \right) + \frac{8}{3} x^4 \text{Re} \left( \frac{m^2 - 1}{m^2 + 2} \right) + \ldots$$ 3-13
where $m$ is complex refractive index of particles.

When all particle sizes are small compared with the wavelength of light $[x = \pi D/\lambda \ll 1]$, Rayleigh theory can be applied to approximate the extinction efficiency. Hence, the scattering term, which is proportional to $x^4$, can be neglected in comparison to the absorption term, which is proportional to $x$. The extinction efficiency is given by Equation 3-14

$$Q_{\text{ext}} = 4x E(\bar{m}) \quad 3-14$$

where, $E(\bar{m}) = -\text{Im}\left(\frac{m^2-1}{m^2+2}\right)$

Inserting Equations 3-14 and 3-12 in Equation 3-11, the expression for the extinction coefficient can be found, as in Equation 3-15

$$K_{\text{ext}} = \pi^2 \frac{1}{\lambda} E(\bar{m}) N \int_0^\infty P(D)D^3 dD \quad 3-15$$

The particle volume fraction, $f_v$, is then defined by Equation 3-16 [158]

$$f_v = \frac{\pi}{6} N \int_0^\infty P(D)D^3 dD \quad 3-16$$

By combining Equations 3-15 and 3-16,

$$f_v = \frac{\lambda K_{\text{ext}}}{6\pi E(\bar{m})} \quad 3-17$$

The particle volume fraction can be calculated if the extinction coefficient and $E(\bar{m})$ is known, where $E(\bar{m})$ is a function of the refractive index of the particles. The extinction coefficient is calculated experimentally by using Equation 3-103-10. By knowing the incident light, $I$, and
transmitted light, $I_o$, and the path length, the extinction coefficient and further the path integrated particle volume fraction, $f_v$, can be calculated. The local extinction coefficient can be obtained from path integrated extinction coefficient using suitable topographic inversion technique [159, 160].

3.5.1 Light extinction: Application to measuring soot volume fraction.

The Equation 3-17 derived using Rayleigh theory is applicable for spherical particles with $x<<1$. Typically, soot particles have a size distribution of 10 to 70 nm in diesel engines [157], while experiments in ethylene diffusion flame have shown primary particle size reaching 60 nm [20]. The 60 nm particle size results in $x=0.36$ for argon-ion lasers operated at 514.5 nm. Moreover, the soot particles are present as chain agglomerates, though the primary particles are approximately spherical. Hence, it would be most appropriate to apply the Rayleigh approximation to individual soot particles and smallest agglomerates. However, this approximation is widely used in the soot community to derive soot volume fraction in jet flames [20, 56, 157]. In flame regions having highly branched soot agglomerates, simultaneous measurement of scattering cross-section would yield the accurate extinction due to absorption by soot [161].

3.5.2 LE setup

The laser extinction measurements are obtained using a Coherent Innova 70 (2W) argon-ion laser at a 514.5 nm wavelength, shown in Figure 3-5. The laser output is 0.5 W and the beam is chopped at 1000 Hz using a mechanical chopper. A beam splitter (30%:70%) is used to deflect and monitor the incident laser beam ($I_o$) by a PIN-10D silicon photodiode. A neutral density filter (NDF) is used before this photodiode to reduce the beam intensity so that the
A set of convex and concave lens are used to expand the laser beam before the photodiode measuring, $I_o$. The laser beam is focused on the flame using a 350 mm focal length lens. The transmitted power, $I$, is measured using a similar photodiode fitted on an integrating sphere. The integrating sphere is used to reduce the beam steering effects generated as the laser beam passes through the flame. The output signals from both photodiodes are converted to voltages using a trans-impedance amplifier and then fed into a lock-in amplifier to reduce the noise from the surrounding environment. The data are collected by a National Instruments data acquisition system (NI-PCI-6110) at a sampling rate of 10 samples/sec for 4 sec.

The line-of-sight measurements are obtained every 0.25 mm in the radial direction and 1 mm intervals along the centerline. The extinction profiles are deconvoluted using a Fourier inversion technique [162].

The choice of the refractive index of soot is key to calculating soot volume fraction. The refractive index depends on the wavelength of the light source. The most widely quoted value of refractive index of soot is $m = 1.57-0.56i$, attributed to the work of Dalzell et al. [163].
However, Smyth *et al.* [161] showed that this value was not presented in work done Dalzell *et al.* [163]. The study done by Smyth *et al.* [161] showed that the soot volume fraction obtained using \( m = 1.57 - 0.56i \) instead of the actual mean refractive index, \( m = 1.56 - 0.46i \), from work of Dalzell *et al.* [163], would yield soot volume fraction that are lower by 17%. The choice of refractive index can affect the soot volume fraction by as much as a factor of two. In the present study, \( m = 1.57 - 0.56i \) is used to derive the soot volume fraction in order to maintain consistency with the previous published work [56, 147].

### 3.6 Laser Induced Incandescence

Laser Induced Incandescence (LII) is produced when the soot particles are irradiated with a laser. The laser heats the soot particles to the vaporization temperature and consequently, the radiation from the soot particles can be used as a measure of the soot volume fraction.

The soot volume fraction derived using LE over a finite path length requires either the soot volume fraction to be uniform or use of tomographic technique to yield local values. However, LII has the ability to provide spatially and temporally resolved two-dimensional soot profiles. This method can also provide soot volume fraction measurements in spatially non-uniform particle fields. LII, when combined with laser scattering experiment, can also provide mean aggregate sizes.

#### 3.6.1 LII theory

The transient energy balance on a single soot particle or aggregate is used to develop a model to calculate the quantity of soot volume fraction based on the LII signal [164]. The energy balance can be represented as
\[
\frac{d(c_s T_s)}{dt} - \frac{H_v d m_s}{M_v} dt = q C_{abs} - h A_s (T_s - T_\infty) - \int_0^\infty 4 C_{abs} E_{b,\lambda}(T_s) d\lambda + \int_0^\infty 4 C_{abs} E_{b,\lambda}(T_w) d\lambda
\]

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) energy loss from the particles 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, represented in terms of convection; (3) energy loss due to radiative emission; (4) energy gain due to radiative absorption. Radiative absorption can be neglected in an atmosphere that lacks a heated environment. The heat transfer coefficient in the collisional cooling rate term needs to include both the continuum and the free molecular regime considering some particle sizes can be small or of the same order of the mean free path of the surrounding gas.

The rate of change of mass of spherical particles as a result of the laser-induced vaporization is given by Equations 3-19 and 3-20. These equations are valid for a stationary particle surface in which vapor diffusion is the only transport process

\[
\frac{d m_s}{dt} = -\frac{N_v \pi D_s^2 M_v}{N_{AV}}
\]

where \(D_s\) is the mean free path.
\[
\frac{dm_s}{dt} = \frac{\pi}{2} \rho_s D_s^2 \frac{dD_s}{dt} + \frac{\pi \rho_s}{6 T_s} D_s^3 \frac{dT_s}{dt}
\]

3-20

where \(\rho_s\) is the mass density of the particle; \(D_s\) is the equivalent diameter of the particle; \(N_v\) is the molecular diffusion flux; and \(N_{AV}\) is the Avogadro’s number.

Equations 3-19 and 3-10, when substituted in equation 3-18 with constant or average \(c_s\), gives equation 3-21

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

3-21

where \(A_{abs}\) is the mass specific absorption cross-section and \(Q_{abs}\) is the absorption efficiency. Equations 3-21 and 3-19, when solved simultaneously, give time-dependent temperature distribution and particle size. The last term in equation 3-21 is the source of the detected LII signal. The LII signal from a particular location within a laser beam or sheet is given by equation 3-22

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

3-22

where \(V_{mv}\) is the probe volume; \(\Omega\) is the solid angle; \(\tau\) is the time of LII signal collection; \(M_s\) is soot mass concentration as a function of time; \(W(t)\) 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, \(D_{30} = \int D^3 f(D_s) dD_s\); and \(G_r(\lambda)\) is the relative wavelength response function for the detector and optics.

An important criteria to successfully apply LII is that the equivalent sphere diameters or the primary size particles satisfy the Rayleigh criteria. The emitted incandescence is proportional...
to $D_s^p$, [165] where $p = 3 + 0.154\lambda_{det}^{-1}$. $\lambda_{det}$ is the signal detection wavelength. This shows that the LII signal is proportional to the particle volume fraction. Furthermore, the value of $p$ approaches 3 as the detection wavelength increases. However, as the detection wavelength increases, the interference from flame luminosity also increases.

A wide range of parameters can affect the LII technique. These include laser beam profile, laser energy intensity, excitation and detection wavelength, imaging gate width, imaging gate delay after the laser pulse, and probe volume determined by the optics and measurement device. The next section explains how these parameters affect LII.

3.6.2 Parameters affecting LII measurement

3.6.2.1 Laser excitation energy, laser intensity profile, and excitation wavelength

When a soot particle is irradiated with laser light, the incandescence from the particle depends on the incident energy. If the laser energy is weaker than or on the order of the cooling terms in equation 3-18, the particle will be slightly heated but it would lose heat quickly. In this case, there is no measurable LII signal. When the energy deposited to the soot is more than the cooling terms in equation 3-18, the particles are heated to temperatures higher than the surrounding temperature. If the soot particles are heated to temperatures lower than the 4000 K, the equilibrium soot vaporization temperature [166], the LII signal is linearly dependent upon the incident fluence. When the soot particles are heated to the vaporization temperature or above, the additional energy results in soot vaporization. At these temperatures, the LII signal is only weakly dependent on laser beam intensity. This range of laser intensity is called the “plateau region” for the LII signals. The variation of LII signals with laser fluence for three different laser energy profile is shown in Figure 3-6.
The normalized LII signal as a function of laser intensity for three different beam profiles is shown in Figure 3-6. The laser pulse with a uniform cross-sectional energy profile is labelled as *uniform*. The LII signal changes significantly with laser intensity until approximately 3E7 W/cm². After this point, vaporization begins and the signal starts to decrease. As the soot particles vaporize and reduce in size, the LII signal produced by smaller particles is lower. A laser pulse with cross-sectional energy profile as Gaussian in two-dimensions is labelled as *focused*. The curve follows similar profile as that of uniform profile until 3E7 W/cm², after which the signal continues to increase at a slower rate. This is because the area of the beam cross section meeting the LII energy threshold increases. This compensates for the LII signal losses due to vaporization of soot particles in the center of the beam. A focused laser sheet, which is Gaussian in one axis and nearly uniform along other axis, is labeled as *2-D sheet*. The LII signal curve lies in between the curves for *uniform* and *focused* beam.

Figure 3-6 Variation of LII signal with laser fluence for different laser energy profile [167].
Any excitation wavelength can be used for LII for which the soot absorbs strongly enough so that the soot particles can be heated to the vaporization temperature. The use of 1064 nm is preferable as it meets the Rayleigh criteria and also avoids the signal interference from PAH fluorescence.

### 3.6.2.2 Spectral detection region, detection width and timing.

The detection wavelength is selected to avoid major noise and particle size dependence. There are major four sources of interference in LII signal. Three of them are laser induced: PAH fluorescence, C$_2$ fluorescence, and Mie scattering. The fourth is non-laser-induced flame luminosity.

The flame luminosity is essentially blackbody radiation from soot particles at a flame temperature of approximately 1800-2200 K and from chemiluminescence. The background flame luminosity increases with increasing collection wavelength in accordance with Planck’s blackbody equation. The LII signals can be corrected for background luminosity by subtracting the background image. However, for turbulent flames, it is not possible to subtract the flame luminosity due to unsteadiness. In this case, shorter collection wavelength can help to reduce the noise. This would increase the particle size dependence of the LII signals.

Mie scattering occurs due to the elastic scattering of the incident laser light. It occurs at the same wavelength as the incident source and same time as the laser pulse. This interference can be avoided by delaying the LII signal collection by several nanoseconds after the laser pulse or by using a proper bandpass filter that eliminates the incident laser wavelength. C$_2$ fluorescence can produce interference in the wavelength region ~420 nm and ~620 nm [168]. The use of narrowband filters in the wavelength range ~450 nm can eliminate C$_2$ fluorescence.
interference [167]. This approach would also eliminate the PAH fluorescence for excitation laser wavelengths of 532 nm or 1064 nm. This is because PAH fluorescence is red-shifted with respect to the excitation wavelength. This method would not eliminate PAH for a UV laser source. The lifetime for PAH or C₂ fluorescence is shorter compared to the soot incandescence. Hence, a slight delay of the LII signal collection following the laser pulse can also help eliminate the interference. However, the LII signals vary with time and decay exponentially after the laser pulse due to cooling. Additionally, the smaller particles cool faster than the larger particles due to higher surface area to volume ratio. Hence, the LII detection window should be timed shortly after the laser pulse. The delay in signal detection would disproportionally weigh the signal towards the larger particles as compared to the smaller particles. This strategy can help avoid PAH and C₂ fluorescence and minimize particle size differences in the LII signal.

3.6.3 LII calibration

The LII signals can be calibrated to yield quantitative results. The most commonly used approach is calibration with light extinction measurements of the soot volume fraction. In regions having low soot concentration, LII can be calibrated using cavity ringdown measurement of soot concentration [169, 170]. Some studies have used gravimetric measurement of soot mass to calibrate the LII signal intensity [171].

3.6.4 LII setup

Two-dimensional soot volume fractions are obtained using laser induced incandescence (LII) [164]. The setup for LII is shown in Figure 3-7. An Nd:YAG laser (Spectra Physics GCR 270-10, 10Hz, 7 ns, 532 nm) is used as a light source to irradiate the soot particles. The Gaussian 9
mm laser beam is expanded into a 55 mm vertical laser sheet using a plano-convex cylindrical and focused using a convex lens. Based on the work by Quay [167], the laser beam is focused outside the flame location; in the current study, the focus point is located at the periphery of the tube exit, where the laser sheet leaves the flame. A combination of a 532 nm half-wave plate and a 532 nm Glan-Thompson prism are used to vary the laser fluence. A laser fluence of 0.3 J/cm² is used for the LII experiment; at this fluence, 22.5 mm of the laser sheet is in the ‘plateau’ region of LII technique [164]. Hence, the complete two-dimensional soot profile is compiled by combining three or four separate images of the flame at different downstream locations.

**Figure 3-7 Setup for LII measurements**

The incandescence from soot is collected at 90 degrees to the laser sheet, as shown in Figure 3-7 by a Princeton Instruments ICCD camera with a sensor size of 512x512 pixels using an f/2.8 105 mm UV lens. The camera response to intensity is tested by use of neutral density filters and the response is found to be linear for both LII and LIF experiment. A narrow band
interference filter centered at 430 nm with 10 nm FWHM is used in front of the UV lens [172].

The optical setup resulted in a resolution of 0.1 mm/pixel. A 20 ns gate delay from the start of the laser pulse is used to avoid interference from Elastic/Mie scattering from soot particles. The LII signal collection over a gate width of 100 ns. The delay time and collection time were selected in order to minimize the effects of particle size on the LII signal while achieving satisfactory signal-to-noise. The intensifier gain on camera is 140 on a scale from 0-255.

LII signals for each flame condition are summed across multiple images collected from consecutive laser pulses to improve the signal-to-noise ratio and remove the effects of slight unsteadiness and fluctuations present in the flame. The number of images collected is varied from 50 to 100 depending on the signal-to-noise level; the laser pulse is monitored for shot-to-shot energy variation. These shot-to-shot energy variations are found to be five percent of the time-averaged signal. A background image of the flame with no laser sheet is captured under the same conditions (gate width, gate delay, gain of intensifier, accumulations) for which LII is collected. The accumulated background image is subtracted from accumulated LII image to correct LII signals for flame luminosity and the dark counts inherent in amplified signal collection system. The result is corrected for pixel-to-pixel responsivity of the detector, which is obtained using a uniform light source. At the high laser intensity required to reach the saturation region of LII, the laser sheet had variations in intensity that resulted in variations of ± 40% in the LII signal. These variations showed up as “banding” in the LII images. A correction method similar to the one used in Ref. [167] is applied to reduce the variation in LII signal due to variations in laser intensity. The correction reduced the percentage variation in the soot volume fraction due to non-uniformity in the laser intensity to within the measurement uncertainty of ±15%.
The LII signals are calibrated from soot volume fraction measurements obtained using laser extinction. For purposes of comparing soot volume fractions among the flames, the estimated uncertainty due to statistical variation of LII calibration data and the uncertainty associated with laser extinction is ± 15%. The work by Santoro et al. [20] shows that gas phase absorption at 514.5 nm can affect the extinction measurement by 10%. In the current study, the LII calibration factors in regions of the calibration flame with and without detectable LIF [146] all fall within the uncertainty of ± 15%. The agreement in LE and LII at three heights indicates the effect of PAH absorption in LE is non-resolvable within the measurement uncertainty. The uncertainty in the absolute soot volume fraction in a given flame will be greater than ±15% primarily due to the uncertainty in the index of refraction of soot [161]. The comprehensive summary of past studies presented by Smyth and Shaddix [161] shows that at 514.5 nm, the choice of refractive index of soot can result in approximately a factor of two uncertainty in the absolute soot volume fraction in LE. In addition, the work by Kholghy et al. [173] experimentally found, in a co-flow laminar flame of 69% n-decane, 20% propylbenzene and 11% propylcyclohexane by molar composition, that in flame regions of T < 1500 K, liquid-like particles are visible using transmission electron microscopy. However, these liquid-like particles are transparent to visible light. The work by Shaddix and Smyth [174] reports that in a flickering ethylene flame with peak soot volume fraction of 18-20 ppm, the maximum signal extinction correction of LII signal is 32%. Based on the work by Shaddix and Smyth [174], the maximum LII signal extinction in smoking flames in our study is expected to be 30%.

3.7 Laser Induced Fluorescence

In the present study, laser induced fluorescence (LIF) is used to obtain qualitative measurement of aromatic hydrocarbons in the jet flames. Polycyclic aromatic hydrocarbons (PAH) are
believed to be the precursors of soot [31, 46, 175]. The current computational soot models approximate that first soot particles are formed from PAH e.g. pyrene dimerization is used as the nucleation reaction in several soot models [176, 177]. Therefore, the aromatics LIF measurements obtained from jet flames can be used to validate and improve soot models.

Aromatic molecules exhibit broadband fluorescence over a wide range of excitation wavelengths [178, 179]. The spectral distribution of the fluorescence signal is dependent on the excitation wavelength. The study by Zizak et al. [180] found that different classes of aromatics molecules fluoresce at different wavelength depending on the size of the aromatics molecule. The fluorescence wavelength shifts to longer wavelength as the molecule size increases, as shown in Figure 3-8. This is because the difference of energy levels between the excited state and ground state decreases with increasing size of the PAHs. This property is used in the present study to identify two different classes of aromatics, single/two ring aromatics and molecules having three-five rings, by collecting the LIF signal over two different wavelength ranges. A combination of WG320 and UG11 filters transmit fluorescence in the range from 320 nm to 380 nm, which corresponds to the small aromatics (1 and 2 rings). A 500FS20-50 filter transmit fluorescence in the range from 488 nm to 514 nm, which corresponds to the large aromatics (three - five rings). The spectral response of the filters is provided in Appendix C. Additionally, the near-UV wavelength excitation of small PAHs would excite the molecule to the lower rovibrational levels of the first excited state, S₁ [181]. However, shorter UV excitation wavelength and higher temperatures in the flame can excite the PAH molecules to higher excited states or higher rovibrational levels in S₁. The LIF-signal is hence generated when these excited molecules undergo radiative transitions to the ground
Large PAHs have a larger number of excited electronic states and a high number of quantum states per energy increment.

Figure 3-8 Relationship between the size of PAH and their spectral properties [180].

The optical arrangement for the LIF experiment is same as the LII setup as shown in Figure 3-7. The second harmonic generator is replaced with a fourth harmonic generator to produce 266 nm wavelength laser light. The energy of laser pulse is set at 585 µJ to minimize LII interference while maintaining acceptable LIF signal levels. The camera is gated-on 20 ns before the laser pulse for 170 ns total duration. The number of images collected is varied from 50 to 200 depending on the signal-to-noise level. The aromatics-LIF images are corrected to account for the non-uniform laser sheet energy, background, and spatial responsivity of the collection optics. A background image is obtained under the same experimental parameters as the LIF experiment without a laser, and this image is subtracted from the LIF image. The intensity variation across the laser sheet is obtained using a vapor acetone box using the same experimental settings that are used for LIF in the flames. At 585 µJ pulse energy, the laser
sheet tested satisfactorily for linear response/regime when using a vapor acetone box and aromatic-LIF.

The LIF signal captured by the camera can be related to the number density of the species if the fluorescing species, local temperature, fluorescence yield, collection efficiency of camera, and camera response function are known [182]. In the present study, the LIF of small and large aromatics is collected from a number of different species, and fluorescence yield and quenching effects for all the aromatics are not well characterized. As a result, only semi-quantitative comparisons can be presented in this paper. Additionally, the transmission curves of the bandpass filters and quantum efficiencies of aromatics vary significantly for the small and large aromatics. As a result, it is not possible to directly compare the image intensities between the small and large aromatic images as an indication of relative aromatic concentration.

3.8 Burner Validation

The ethylene diffusion flame studied by Santoro et al. [20] is used on the modified burner as a validation case to ensure the results match those of the original burner design. The ethylene flow rate for these tests is 0.231 slpm and co-flow air flowrate 2.26 scfm. The soot volume fraction in new burner is within ±1 ppm at the peaks in the profiles for most heights above the burner except at 60 mm height above the burner (HAB). This is considered a good match to the original burner design considering 15% uncertainty in the laser extinction technique at intermediate flame heights [183]. The soot volume fraction profiles are wider in the new design; this is believed to be an effect of the experimental enclosure in the new design, which includes a chimney and the stabilization plates on top of the chimney.
Figure 3-9 Soot volume fraction comparison with the previous published results: (a) radial comparison at 10 mm, 20 mm and 40 mm HAB (b) radial comparison at 50 mm, 60 mm and 70 mm HAB.
Chapter 4 Effect of fuel composition on soot and aromatic species distributions: non-premixed fuel

This chapter focuses on the effect of fuel chemical composition on PAH and soot formation in non-premixed, laminar jet flames. The fuels include four binary fuel mixtures containing \( n \)-dodecane and a compound representing one of the fuel major hydrocarbon classes found in “drop-in” alternative aviation fuels produced from non-petroleum sources – aromatic, normal paraffin, branched paraffin, and cyclo-paraffin.

The chapter begins with the comparison of the visible flame images and temperature profiles for the four binary fuel mixtures and base, \( n \)-dodecane flame. Following this, aromatic species and soot volume fraction results are discussed. Additional analysis shows the trends in the spatial development of small aromatics, large aromatics, and soot volume fraction. The soot volume fraction and temperature measurement results presented in this chapter were obtained by Dr. Wang [140]. The soot volume fraction results are presented here as a mean to compare the aromatic species and soot volume fraction result measurements.
4.1 Visible flame images

Figure 4-1 shows visible light images of the flames from the five fuels. In order to allow comparison of the flames, the images were all captured with a digital camera using the same settings, ISO=80, f-stop = 3.6 and exposure time = 1/13 seconds. In the images, the orange and white regions are luminosity from the soot. Although not clearly evident due to the exposure used, lines of blue luminosity were present in the non-sooting regions. The blue light results from emissions from species such as CH* within the flame sheet. The \textit{m}-xylene fuel is displayed at the left side of the image set; it is positioned to the left so that its position is consistent with that in the image sets for LIF and LII, which require different scales for results from the \textit{m}-xylene fuel than for the paraffin fuels. For the paraffin fuels, all of the soot produced within the flame is oxidized and the flame tip is “closed”. For the \textit{m}-xylene fuel, soot is not completely oxidized and luminosity from soot is evident over the entire height of the image. The tips of the paraffin flames fluctuated with a maximum fluctuation of ±2 mm. These fluctuation cause gradients in luminosity near the flame tip in the images. Long exposure time images of the flames show that the visible blue flame is separated from the top of the fuel tube by approximately 1mm.

The flame heights, which are defined as the length of the flame from the tube exit to the visible flame tip are shown in Fig. 4-1. The height for the \textit{m}-xylene flame cannot be identified because the tip of the flame is not closed. The height of the \textit{n}-heptane flame is smaller than for the other three paraffinic flames, which would be consistent with slightly lower soot levels, as discussed in Section 4.4. However, given the fluctuations in flame heights and the uncertainty in determining flame height, the heights of the paraffinic flames are equivalent.
4.2 Temperature measurements

Radial temperature profiles were measured at 5 mm and 15 mm above the fuel tube exit, and axial profiles were measured along the centerline to a height 20 mm. The measurements were taken with a resolution of 1 mm. In order to minimize the distortion of the flames by the thermocouple probe during the radial temperature measurements, only half (-10 mm to 0 mm) of the flame was measured. The temperatures were corrected for radiation effects using the method described in [21] and briefly discussed in Appendix D; the maximum correction was 100 K. The uncertainty in positioning the thermocouple is ± 0.5 mm.

Figure 4-2 shows the radial temperature profiles for all five fuels. Qualitatively, all flames show similar trends: the temperature peaks at the edge of the flames, 5 to 6 mm in radial position, decreases to the ambient air temperature near 10 mm and to the centerline temperature of approximately 800 K. The maximum temperature is approximately 1650 K for the \( n \)-heptane fuel and 1600 K for the other fuels. For the paraffin fuels, at 15 mm HAB, the peak
temperature increases to 1750-1800 K due to lower heat loss to the burner. The temperature was not measured in m-xylene/n-dodecane flame at 15 mm HAB due to heavy soot deposition on the thermocouple.

Figure 4-2 Radial Temperature Profiles at 5mm above the exit of the fuel tube

Figure 4-3 shows the axial temperature distribution for each of the five fuels until 20 mm HAB. The axial temperature distribution along the centerline is the same for all fuels within experimental uncertainty. For all the flames, the temperature increases from 650 K near the tube exit to 1200 K at 20 mm. Further downstream, the differences in the soot volume fraction among the five fuels can change the local temperatures due to soot radiation. The effect of radiation is most significant for the m-xylene fuel because it produces much higher levels of soot than the paraffin fuels. The work by Smooke et al. [184] in co-flow ethylene diffusion flames shows that the peak centerline temperature decreased by approximately 220 K when peak soot volume fraction in the flame increased from 1 ppm to 18 ppm. The trends in axial and radial temperature measurements are similar to the results found in co-flow flames for e.g., [185, 186].
4.3 Small and large aromatic species.

For fuels that do not contain aromatic compounds, formation of the first ring aromatic is considered to be the rate-determining step to soot formation [16, 32]. The first ring formation will be affected by the initial fuel structure and temperature. The temperature measurements for all the flames, discussed in Section 4.2, shows that the temperature distribution up to 20 mm above the fuel tube exit is quite similar for all the fuels in this study. Hence, the differences in LIF signals from aromatics that are visible amongst the four paraffin fuels can be attributed primarily to the chemical effect of the second component in the fuel. For fuels that contain single-ring aromatic compounds, such as $m$-xylene, formation of double-ring aromatics will be rate determining for soot formation [67]. The presence of $m$-xylene in the fuel would be expected to lead to higher levels of naphthalene and higher PAH species compared to pure $n$-dodecane and the paraffin fuel mixtures. Figure 4-4 shows the LIF data for the five test fuels for small aromatic species. As discussed in the chapter 3, calibration was not possible so
camera counts are plotted. Two different color scales are used for the \textit{m}-xylene and paraffin fuels. The scale for the \textit{m}-xylene fuel has a maximum of \(1.7 \times 10^4\) whereas the scale for the paraffin fuels has a maximum of \(3 \times 10^4\). The outer boundary of the LIF images is not clear in the pseudo color plots. In order to provide a clearer indication of the outer boundary of the LIF signal, a contour has been added to each plot that corresponds to 20\% of the maximum small aromatics signal level of the base \textit{n}-dodecane flame. The absolute count level for the contour corresponds to 3\%, comparable to the percentage noise of the camera detector for 95\% confidence interval, of maximum signal in the \textit{m}-xylene flame.

The \textit{m}-xylene fluoresces when excited with 266 nm light and produces a “triangular” region of strong fluorescence located between 0 and 5 mm above the exit of the fuel tube. Fluorescence from the \textit{m}-xylene decreases due to reaction and diffusion, and possibly also from quenching by oxygen molecules that diffuse toward the centerline. The LIF signal reaches a local minimum before increasing again as aromatic species are formed from reaction intermediates. Given the wavelength range used in detecting small aromatics, the newly formed aromatic species that cause the increase in the LIF signal are expected to have one or two-rings. With the formation of aromatic species, the signal levels rise back up to levels similar to those from the \textit{m}-xylene. However, the total number density of small aromatics at the tube exit and newly formed aromatic species different because of differences in the temperature and fluorescent yield of \textit{m}-xylene and newly formed aromatic species. At higher heights, the signal level decreases, eventually dropping to the detection limit on the centerline at approximately 35 mm. The decreasing LIF signal from the small aromatics is due to reaction to form larger PAH, which fluoresce at wavelengths outside of the detection window. Quenching by molecular oxygen that is diffusing toward the centerline may also play a role in
Figure 4-4 Planar LIF images for small aromatic species. Note that a different scale is used for the m-xylene fuel. (a) m-xylene/n-dodecane (scale on left side); (b) n-dodecane (scale on right side); (c) n-heptane/n-dodecane (scale on right side); (d) iso-octane/n-dodecane (scale on right side); (e) methylcyclohexane/n-dodecane (scale on right side).

Figure 4-5 Planar LIF images for large aromatic species. Note that a different scale is used for the m-xylene fuel. (a) m-xylene/n-dodecane (scale on left side); (b) n-dodecane (scale on right side); (c) n-heptane/n-dodecane (scale on right side); (d) iso-octane/n-dodecane (scale on right side); (e) methylcyclohexane/n-dodecane (scale on right side).
the decreasing LIF signal from the fuel. The 2-D spatial distribution of small aromatics, shown in Fig. 4-4, is similar for the four paraffin fuels: the small aromatics LIF signal is first detected in the annular region at 3-5 mm HAB and on centerline at 5-7 mm HAB. For the paraffin fuels, the relative level of peak signal for small aromatics are C12: 1.00, i-C8: 1.30, MCH: 1.35 and C7: 0.95. The procedure to obtain the relative level of aromatics is discussed in Appendix E.

The planar images of LIF from large aromatic species are presented in Fig. 4-5. As was the case for small aromatic species, two different color scales are used for the m-xylene and paraffin fuels. The scale for the m-xylene fuel data has a maximum of 7.5x10^4 whereas the scale for the paraffin fuels has a maximum of 2.2x10^4. The plots include a contour corresponding to 20% of the maximum small aromatics signal level of the n-dodecane fuel mixture in order to illustrate the spatial extent of the fluorescence from large aromatic species, defined in this study as three-five rings.

For the m-xylene fuel, the LIF from large aromatics species is first detected at heights that lie just above the location of the triangular region of fluorescence from m-xylene; the lowest height at which the LIF from large aromatics is detected is ~3 mm. The most intense region of LIF from large aromatics lies in an annular region located between approximately 10 and 20 mm above the fuel tube exit. At a particular HAB, the local flame temperature should also be considered when comparing the aromatic-LIF signal on annular region and centerline. Previous studies, for example, [187, 188] of effects of temperature on LIF from aromatic hydrocarbons have shown that increasing the temperature leads to a decrease in the LIF signal intensity. The effect of temperature on the LIF signal could not be estimated in our flames due to a lack of knowledge of composition of the aromatic species, local temperature, and temperature sensitivity of LIF from the aromatic species in these flames. For the paraffin fuels, the spatial
extent of the LIF from large aromatic species is noticeably smaller than that for the \( m \)-xylene fuel. The first detection of LIF from large aromatics occurs at higher heights than for the \( m \)-xylene fuel: \(~6\text{ mm}\) for the paraffin fuels. As was the case for LIF from small aromatic species, among the paraffin fuels, the LIF from large aromatic species is highest for the \( iso \)-octane and MCH fuels and lowest for the \( n \)-heptane fuel. For the paraffin fuels, the relative level of peak large aromatics are \( \text{C12: 1.00, i-C8: 1.31, MCH: 1.36 and C7: 0.85} \); the procedure for determining the peak is the same as that used for the small aromatic species.

In this study, “small” aromatic LIF measurements provide information about not just one-ring, but also two-ring aromatics. The formation of two-ring aromatics from one-ring aromatics can be due to HACA mechanism, which has been shown to work similarly for a range of fuels \([31]\), and reaction of propargyl radical with benzyl radical \([16, 189]\). Additionally, two cyclopentadienyl radicals can also form naphthalene \([190]\). Parallel simulation efforts conducted in the overall research program show that the flames considered in this study have similar concentrations and distributions of acetylene, indicating that the formation of two-ring aromatics from one-ring aromatics due to HACA mechanism would be similar for the paraffin fuels \([11]\).

Previous work provides insights into the chemical pathways to form the first ring for each of the paraffin fuels. In the \( n \)-heptane/\( n \)-dodecane blend, the \( n \)-heptane would react to form olefins in the range of ethene to 1-hexene, while \( n \)-dodecane can form alkyls in the range of ethene to 1-dodecene. Further reaction of these alkenes lead to formation of unsaturated species, such as the propargyl radical, that react to form the first aromatic ring \([16]\). A detailed chemical mechanism developed as part of the overall research program \([11]\) was used to compare the pyrolysis of the pure \( n \)-dodecane and the \( n \)-heptane/\( n \)-dodecane fuel blend. Those simulations
showed that \( n \)-dodecane decomposes more quickly than \( n \)-heptane leading to higher concentrations of reaction products, including the species that form the first aromatic ring.

In the \( iso \)-octane/\( n \)-dodecane flame, the alkyl radicals formed from \( iso \)-octane decomposition react to form \( iso \)-butene and propene as major first step decomposition products [191]. The propene and \( iso \)-butene can form propadiene through pathways described in [47, 192, 193]. The propadiene is closely related to the propargyl radical [192], which can lead to benzene formation through self-addition reaction [16, 194]. These paths to propadiene most likely result in more benzene in the \( iso \)-octane/\( n \)-dodecane flame, and hence, more small aromatics as compared to the \( n \)-alkane fuels.

For methycyclohexane/\( n \)-dodecane, the literature suggests several paths to form the first ring. At higher temperatures, the methycyclohexane fuel would primarily decompose through unimolecular dissociation to form 1-heptene, 2-heptene and a small fraction of other heptenes [195]. The 1-heptene and 2-heptene can further decompose through allylic C-C fission (high temperature) or/and 6-center elimination (lower temperature) depending on the flame condition [16]. At high flame temperatures, 1-heptene would form allyl and \( n \)-butyl, while 2-heptene would form 1-methyl-allyl and \( n \)-propyl by allylic C-C fission. The allyl and 1-methyl-allyl would subsequently dissociate to form propadiene and butadiene, respectively. The propadiene would produce propargyl radical and butadiene would form \( C_4H_5 \) and \( C_4H_3 \). These three radicals are known to be involved in reactions to form benzene [16].

For the \( m \)-xylene/\( n \)-dodecane, a single ring aromatic species is present in the fuel, so the first aromatic ring does not need to form from small reaction products. Thus, formation of multi-ring aromatic species will occur much more quickly than for the paraffin fuels. The \( m \)-xylene can undergo reactions with products from the reaction of \( n \)-dodecane to form a second aromatic
ring. Consequently, this fuel would be expected to have larger number of two-ring aromatic species than the paraffin fuels, which is consistent with the substantially higher LIF signal from small aromatic species for the \( m \)-xylene fuel as compared to the paraffin fuels. Growth of the third and fourth aromatic rings will occur via hydrogen abstraction and acetylene addition. The greater number of two-ring species in the \( m \)-xylene fuel will lead to larger concentrations of three and four-ring species, and therefore, stronger LIF for large aromatic species for the \( m \)-xylene fuel compared to the paraffin fuels.

4.4 Soot

While the LIF measurements show the qualitative differences in soot formation processes driven by changes in fuel molecular structure, the LII measurements provide quantitative information about soot volume fraction in the flames and the impact that fuel molecular structure has on soot. The two-dimensional distribution of soot volume fraction for the five fuels are shown in Fig. 4-6. As discussed in the chapter 3, variation in laser intensity across the sheet resulted in “banding” of the LII images; the variation associated with the banding is within the measurement uncertainty of \( \pm 15\% \). Because \( m \)-xylene fuel resulted in much higher soot volume fractions than the paraffin fuels different ranges were used for the plots. For the \( m \)-xylene, the maximum is 18 ppm and for the paraffin fuels it is 8 ppm. An iso-contour of 1 ppm is shown for each fuel in order to illustrate the spatial extent of the soot volume fraction.

The soot fields for the paraffin fuels have a similar overall shape. Soot is first detected in annular regions at a height of approximately 15 mm. As height increases the annular region of soot growths in width toward the centerline of the flame until soot is detected on the centerline at approximately 30 mm above the fuel tube exit. Finally, the soot regions become narrower as the soot is oxidized. The first appearance of soot in annular region and then on centerline at
Figure 4-6 LII images of soot showing soot volume fraction distribution for (a) m-xylene/n-dodecane (scale on left side); (b) n-dodecane (scale on right side); (c) n-heptane/n-dodecane (scale on right side); (d) iso-octane/n-dodecane (scale on right side); (e) methylcyclohexane/n-dodecane (scale on right side).

Further downstream location is consistent with the results in co-flow flames [20, 118]. For the m-xylene fuel, soot is first detected at approximately 5 mm above the fuel tube exit, substantially closer to the burner exit than for the paraffin fuels. The maximum soot levels remain in a narrow annular region for the m-xylene fuel unlike the paraffin fuels for which the maximum soot is distributed in a larger region about the centerline.

The relative trends in the amount of soot in the flames matches the relative trends observed in the magnitudes of the small and large aromatic species. The m-xylene fuel produces the most soot, more than twice the amount of any of the paraffin fuels. Within the paraffin fuels, iso-octane and MCH produce similar amounts of soot, and n-heptane the least. The relative trends in soot are consistent with known trends from past studies of the effect of fuel structure on soot in diffusion flames and with the TSI value for each of the compounds. The TSI values are: 2.0,
5.4, 6.0, 8.0, 42.0 for \( n \)-heptane, \( n \)-dodecane, methylcyclohexane, \( iso \)-octane, and \( m \)-xylene, respectively [60].

4.5 Trends in small and large aromatic species and soot

Composite images of the aromatics species and soot are presented in Fig. 4-7 for \( m \)-xylene, \( iso \)-octane and pure \( n \)-dodecane to illustrate the relationships among the small and large aromatics and soot and also differences among the fuels. Different scales are used for the \( m \)-xylene and paraffin fuels to reveal the differences in spatial distributions. A nominal streamline is shown for the \( m \)-xylene fuel as a visual reference for the location of peak LIF signals and soot.

For the \( m \)-xylene fuel, LIF from small aromatic species is detected at the exit of the fuel tube due to fluorescence from the \( m \)-xylene. The LIF signals decreases as the \( m \)-xylene diffuses and reacts. A local minimum is reached and then the LIF from small aromatics increases because of the formation of one and two-ring species from the reaction products. Further along the streamline, the LIF from small aromatics begins to decrease as the LIF signal from large aromatics increases. The signal from large aromatics then decreases. LII from soot is also present along the streamline where the signal from large aromatic species is decreasing. Thus, it is likely that condensation reactions are consuming the large aromatic species and contributing to the total mass of soot. Additionally, the large aromatic species can also be consumed by forming new incipient soot particles.

Comparison of the composite plots for the \( m \)-xylene fuel to those for the \( iso \)-octane fuel and the \( n \)-dodecane shows a basic similarity in the spatial relationships of regions of peak small aromatics, large aromatics and soot. This spatial or temporal transition of aromatics to soot in
Figure 4-7  Small and large aromatic species and soot for the \( m \)-xylene and \textit{iso}-octane fuels along with \textit{n}-dodecane flame. The white line is a nominal streamline. The \( m \)-xylene and paraffin fuels are on different scales, as shown in Table 4-1.

Table 4-1 Contours for the small aromatics, large aromatics, and soot for \( m \)-X and paraffin fuels shown in Figure 4-7.

<table>
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<th>Small max on scale [counts]</th>
<th>Small contour [counts]</th>
<th>Large max on scale [counts]</th>
<th>Large contour [counts]</th>
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</table>

c-co-flow flames is consistent with the results of previous studies [56, 196]. However the plots also illustrate the effects of the aromatics in the fuel and also the effect of the \textit{iso}-paraffin versus pure normal paraffin. Comparison of the \( m \)-xylene plots to those for the paraffin fuels shows that the presence of aromatics substantially increases the spatial extent of the regions over which aromatic species are detected. The addition of the \( m \)-xylene to the \textit{n}-dodecane
results in a smoking flame in which oxidation does not completely consume all of the soot produced. The use of the same base fuel in all of the flames and the same initial conditions yields flames that are quite similar in terms of temperature fields except in the sooting region. The work of Smooke et al. [184] suggests that the higher soot levels could reduce the peak centerline temperatures for the $m$-xylene fuel by approximately 150 K compared to the paraffin fuels. Comparing the plots for the iso-octane fuel to the pure $n$-dodecane fuel shows how similar the spatial distributions of aromatic species and soot are for these two fuels. The plots also show that the branched paraffin leads to increases in peak signal levels from the aromatic species and in the maximum soot volume fraction.
Chapter 5 Effect of fuel composition on soot and aromatic species distributions: premixed fuel

This chapter presents results from investigations of the effects of fuel composition on aromatic species and soot in laminar co-flow flames with partially-premixed fuel jets. While Chapter 4 focuses on flames with non-premixed fuel jets, this chapter presents results for flames with partially-premixed fuel jets at jet equivalence ratios of $\phi_{\text{jet}} = 24$ and 6. Dr. Wang [140] obtained the soot volume fraction and temperature measurement results at the $\phi_{\text{jet}} = 6$ condition. The results for the $\phi_{\text{jet}} = 24$ cases and the two-dimensional aromatic species distribution at the $\phi_{\text{jet}} = 6$ were obtained by the present author.
5.1 Visible flame images

Figure 5-1 shows the visible flame image for all the fuels at jet equivalence ratios of 24 and 6. The visible flame images for non-premixed flames are also included in this figure from Wang et al. [145]. The images are taken using a Canon A640 camera with same camera operating parameters (ISO = 80, f-stop = 3.6 and exposure time = 1/13 seconds). From left to right in each image, the fuels are \textit{m}-xylene/\textit{n}-dodecane (m-X), pure \textit{n}-dodecane (C12), \textit{n}-heptane/\textit{n}-dodecane (C7), \textit{i}-octane/\textit{n}-dodecane (i-C8), and methylcyclohexane/\textit{n}-dodecane (MCH). At each $\phi_{\text{jet}}$, flames images taken at long exposure time show that the visible blue flame is separated from the top of the fuel tube by approximately 1mm. Figure 5-1 (b) shows that the \textit{m}-xylene/\textit{n}-dodecane flame is smoking at $\phi_{\text{jet}} = 24$. The smoking nature of the flame indicates that the soot produced is not completely oxidized and leaves from the flame tip. In contrast, under the same experimental conditions, the flames with paraffin fuels do not emit soot from the flame tip. In this work, the visible flame height (Table 5-1) is defined as the distance from the tube exit to the tip of the flame. The tip of the flame, as shown for C12 - $\phi_{\text{jet}} = 24$ flame in Fig. 5-1 (b), is defined by the farthest sooting point from the tube exit obtained using the visible flame images. The tip of the non-smoking flames had fluctuations of $\pm 2$ mm over the course of an experiment.

At $\phi_{\text{jet}} = 6$ condition, shown in Fig. 5-1 (c), the \textit{m}-xylene/\textit{n}-dodecane flame has a closed tip and does not emit soot. Additionally, at $\phi_{\text{jet}} = 6$ the \textit{m}-xylene/\textit{n}-dodecane flame length is longer than that of all the paraffin fuels by 9 mm. The longer flame is likely the result of higher soot production in the mixture with \textit{m}-xylene, as the soot requires more time, or flame length, to oxidize completely. The flame heights are decreased with addition of air from $\phi_{\text{jet}} = 24$ to 6, which is consistent with previous work [22]. The paraffin fuels flame height reduces by
Figure 5-1 Visible flame images obtained at (a) $\phi_{jet}=\text{Inf}$ (b) $\phi_{jet}=24$ (c) $\phi_{jet}=6$. 
Table 5.1 Flame heights [mm] obtained using visible flame images from Figure 5.1.

<table>
<thead>
<tr>
<th>$\phi_{\text{jet}}$</th>
<th>m-X</th>
<th>C$_{12}$</th>
<th>C$_{7}$</th>
<th>i-C$_{8}$</th>
<th>MCH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inf</td>
<td>Smoking</td>
<td>57.1</td>
<td>55.1</td>
<td>58.5</td>
<td>56.2</td>
</tr>
<tr>
<td>$\phi_{\text{jet}}$ = 24</td>
<td>Smoking</td>
<td>56.0</td>
<td>53.0</td>
<td>56.8</td>
<td>55.5</td>
</tr>
<tr>
<td>$\phi_{\text{jet}}$ = 6</td>
<td>53.2</td>
<td>45.3</td>
<td>45.3</td>
<td>45.3</td>
<td>44.8</td>
</tr>
</tbody>
</table>

approximately 20% at the $\phi_{\text{jet}}$ = 6 condition as compared to the corresponding $\phi_{\text{jet}}$ = 24 flames. Furthermore, at all three $\phi_{\text{jet}}$, soot luminosity is observed at lower HAB in the m-xylene flame compared to the four paraffin fuels. The presence of soot luminosity at lower HAB in the m-xylene flame is expected since the one-ring aromatic species formed from m-xylene would result in earlier formation of larger PAHs, leading to soot inception at lower HAB in m-xylene flame compared to the paraffin fuels (see additional discussion in sections 5.3 and 5.4).

5.2 Temperature measurements

Figure 5.2 and 5.3 shows the radial (at 5 mm HAB) and axial temperature profiles for all five fuels for $\phi_{\text{jet}}$=24 and 6 flames, respectively. Within experimental uncertainty in temperature measurements of $\pm$ 100 K, the flames show the same trends in both the radial and axial directions for both jet equivalence ratios. The trends in radial and axial directions are identical to those observed in non-premixed flames, discussed in Wang et al. [145]. The temperature near the burner exit is well above the 470 K that is maintained in the vaporizer and fuel delivery system due to heat feedback from the flame to the burner. Simulations and measurements by Smooke et al. [184] indicate that the effect of soot radiation on gas temperatures could be as large as 200 K for the smoking m-xylene/n-dodecane flames.
Figure 5-2 (a) Radial temperature profiles at 5mm HAB; (b) axial temperature profiles for $\phi_{\text{jet}} = 24$.

Figure 5-3 (a) Radial temperature profiles at 5mm HAB; (b) axial temperature profiles for $\phi_{\text{jet}} = 6$.

5.3 Small and large aromatic species

The understanding in the literature is that in paraffin fuels, the formation of the first ring aromatic is the rate-determining step to soot formation [16, 32]. The first ring formation process is dependent on the initial fuel structure and temperature. As was observed in non-premixed flames [145], the temperature fields up to 20 mm HAB are similar in the five fuels
at each $\phi_{\text{jet}}$, which indicates that the differences in aromatics amongst the four paraffin fuels are primarily due to the chemical effect of the “second” fuel component. In contrast, the soot formation in a fuel with an aromatic component (one ring) is determined by the rate of double-ring aromatic formation [67].

The LIF signal depends on several factors, including aromatic species concentration, particular aromatic species that are excited, temperature and collisional quenching [197]. In this study, as will be discussed later, the peak in LIF signal from paraffin fuels occurs approximately at the same location at given $\phi_{\text{jet}}$, so flame conditions in the location of peak LIF should be similar for the paraffin fuels. In contrast, in $m$-xylene fuel, the peak in LIF signal occurs at lower HAB compared to the paraffin fuels, as will be discussed later in the paper, indicating differences in the local flame conditions compared to the paraffin fuels. Therefore, direct comparisons of the LIF from the paraffin and $m$-xylene fuels are not made in this paper because differences in the local conditions, especially temperature, will cause differences in LIF signal levels. In the rest of the Chapter, semi-quantitative comparison for the peak LIF signals in paraffin fuels are presented and the direct comparison of quantitative information between paraffin and $m$-xylene fuels are not done. Furthermore, in premixed flames, the LIF signals near the tube exit would be quenched due to the presence of oxygen in the fuel stream. Further support for interpreting the LIF results as representative of gas phase aromatics comes from work by McEnally et al. [22], who used PAH-LIF and compared these to GCMS measurements of gas-phase aromatics. The results of this study showed that the trends in PAH-LIF measurements with premixing matched the GCMS results closely.

Figure 5-4 shows the comparison of the 2-D LIF signals obtained for small aromatics at $\phi_{\text{jet}} = 24$. In all 2-D LIF figures comparing the five fuels, part (a) is small aromatics for $m$-xylene/$n$-
dodecane fuel, which uses the scale on the left side of the figure. Parts (b), (c), (d), and (e) show the 2-D profiles of the small aromatics for \textit{n}-dodecane, \textit{n}-heptane/\textit{n}-dodecane, \textit{iso}-octane/\textit{n}-dodecane, and \textit{m}-xylene/\textit{n}-dodecane flames, respectively. These four paraffin fuels are on the same scale, which is located on the right side of the figure. An \textit{iso}-contour of 20\% of maximum signal of \textit{n}-dodecane flame is shown on the 2-D plots to distinguish the spatial extent of the LIF signal from the small aromatics.

Figure 5-4 (a) shows that in the \textit{m}-xylene/\textit{n}-dodecane flame, small aromatics are present at the tube exit because \textit{m}-xylene itself is a one-ring aromatic and fluoresces in the 320-380 nm bandwidth. The small aromatics LIF signal initially shows a trend of decreasing intensity and then increases in the downstream direction. Initially, the total number of moles increases primarily due to \textit{n}-dodecane decomposition. This increase in total number of moles results in a decrease in mole fraction of \textit{m}-xylene. The decrease in mole fraction of \textit{m}-xylene leads to a decrease in the LIF signal because the LIF signal is proportional to mole fraction. Additionally, the initial decrease in LIF signal could be due to the diffusion of \textit{m}-xylene and consumption reactions of \textit{m}-xylene to form other one ring products like toluene, which has lower absorption cross-section compared to \textit{m}-xylene. Further downstream, the signal increases again as other one and two ring aromatics are formed. The small aromatics LIF signal decreases further downstream as the process of oxidation and conversion to large aromatics dominates over the production of the small aromatics, as seen in Fig. 5-5 (a), which shows the large aromatics. In the \textit{m}-xylene/\textit{n}-dodecane mixture, the large aromatics LIF signal is first detected at 3-4 mm HAB in the annular region of the flame and then along the centerline at 5-6 mm HAB. The LIF signal from large aromatics first increases as the formation processes are dominant and then decreases as the aromatics are oxidized, convert to larger PAHs, or contribute to soot growth.
Figure 5-4 Two-dimensional small aromatics obtained at $\phi_{\text{jet}}=24$ for (a) $m$-xylene/$n$-dodecane (scale on left side); (b) $n$-dodecane (scale on right side); (c) $n$-heptane/$n$-dodecane (scale on right side); (d) iso-octane/$n$-dodecane (scale on right side); (e) methylcyclohexane/$n$-dodecane (scale on right side).

Figure 5-5 Two-dimensional large aromatics obtained at $\phi_{\text{jet}}=24$ for (a) $m$-xylene/$n$-dodecane (scale on left side); (b) $n$-dodecane (scale on right side); (c) $n$-heptane/$n$-dodecane (scale on right side); (d) iso-octane/$n$-dodecane (scale on right side); (e) methylcyclohexane/$n$-dodecane (scale on right side).

through PAH condensation. Figure 5-4 (a) and Figure 5-5 (a) show that for the $m$-xylene fuel, the peak small and large aromatics LIF signal is higher in the annular region as compared to
along the flame centerline. Previous studies, for example, [187, 188] of the effects of temperature on LIF for aromatic species have shown that the LIF signal intensity decreases with an increase in the temperature. These studies highlight the need to consider the local flame temperature while interpreting the aromatic-LIF signal on annular region and centerline. However, due to the lack of knowledge of different aromatic species present in the flame, local temperature, and effect of temperature on the LIF signal for all these aromatic species, any adjustments to account for the effects of temperature on the LIF signal were not possible.

Figure 5-4 (b)-(e) shows that the small aromatics spatial development is quite similar for the four paraffin fuels although the peak LIF signal varies from approximately 11300 counts to 16700 counts for n-heptane/n-dodecane and methylcyclohexane/n-dodecane flames, respectively. The small aromatics LIF signal is first detected in the annular region of the flame at 3-4 mm HAB, and appears along the flame centerline at 5-6 mm HAB. Along any streamline, the LIF signal first increases and at locations farther downstream, the signal of small aromatics decreases due to their oxidation and conversion to the large aromatics, as can also be seen in Fig. 5-5 (b)-(e). Figure 5-5 (b)-(e) shows that the spatial development of the large aromatics for the paraffin fuels is similar to the m-xylene/n-dodecane flame in Fig. 5-5 (a). The large aromatics appear at 6-7 mm HAB in the annular region of the flame for all the paraffin fuels and then appear along the flame centerline at 14-15 mm HAB. Similar to the m-xylene/n-dodecane flame, the peak small and large aromatics LIF signal in the annular region is higher as compared to the paraffin-fuel flame centerlines.

Although the overall spatial distribution of aromatics species is similar among the paraffinic fuels, the LIF images show differences in peak LIF signal levels. For small aromatics, the relative peak signal levels are C_{12}: 1.00, C_{7}: 0.85, i-C_{8}: 1.23, and MCH 1.25. For large
aromatics, the relative peak signal levels are $C_{12}$: 1.00, $C_7$: 0.97, i-$C_8$: 1.25, and MCH 1.25. The methylcyclohexane/$n$-dodecane and $iso$-octane/$n$-dodecane flames produce similar levels and both have higher level of small and large aromatics as compared to the two $n$-alkane fuels. The level of small aromatics in the pure $n$-dodecane flame is higher as compared to the $n$-heptane/$n$-dodecane flame. However, within the measurement uncertainty, the level of peak large aromatics is similar in both the pure $n$-dodecane and $n$-heptane/$n$-dodecane fuels.

Figure 5-6 shows the comparison of the 2-D LIF signals at the $\phi_{\text{jet}} = 6$ condition obtained for small aromatics. An iso-contour of 20% of maximum counts of $n$-dodecane flame is shown on the 2-D plots to compare the spatial extent of presence of the small aromatics for all the fuels. The spatial distribution of small aromatics in $m$-xylene/$n$-dodecane flame is similar to the small aromatics development at $\phi_{\text{jet}} = 24$, shown in Figure 5-4 (a). However, peak LIF signal level for $\phi_{\text{jet}} = 6$ is reduced by a factor of approximately 3.8 from the $\phi_{\text{jet}} = 24$ flame. As in the higher equivalence ratio case, the signal from small aromatics is present at the tube exit is from the $m$-xylene. Further downstream, the small aromatics LIF intensity decreases, then increases again as one and two-ring aromatics are formed. The peak level of aromatics LIF signal appears in an annular region rather than near the centerline of the flame.

Figure 5-6 (b)-(e) shows that the spatial distribution of small aromatics is similar for the paraffin fuels; the scale for these images is located on the right of the figure. The small aromatics first appear in the annular region at 4-5 mm HAB and form at positions closer to the flame centerline at higher heights above the burner exit. For the paraffin fuels, the peak levels of LIF signal from small aromatics appear in a conical region about the centerline as opposed to the annular region in which the small aromatics peaked for the $m$-xylene fuel, shown in Fig. 5-6 (a). Within the measurement uncertainty, the peak LIF signal of small aromatics is same
Figure 5-6 Two-dimensional small aromatics obtained at $\phi_{\text{jet}}=6$ for (a) $m$-xylene/$n$-dodecane (scale on left side); (b) $n$-dodecane (scale on right side); (c) $n$-heptane/$n$-dodecane (scale on right side); (d) iso-octane/$n$-dodecane (scale on right side); (e) methylcyclohexane/$n$-dodecane (scale on right side).

for all paraffin fuels, peaking at 7000 counts at approximately 25 mm HAB for all the paraffin fuels. It is likely that the PAH-LIF technique is unable to distinguish among the paraffin fuels due to low signal-to-noise ratio at this $\phi_{\text{jet}}$. The 2-D LIF signals from large aromatic species at the $\phi_{\text{jet}}=6$ condition for the paraffin fuels have low signal-to-noise ratio and hence, are neither reported nor discussed here. The $m$-xylene/$n$-dodecane 2-D large aromatics distribution is discussed in Section 5.6.

Previous work that provides insights into the effects of fuel structure on reactions that form the first and second aromatic rings in the flames with non-premixed fuel jets is summarized in Wang et al. [145]. The similar chemistry explains the trends observed in the flames with partially-premixed fuel. Therefore, only the key points of that discussion are summarized here. The reduction of aromatic species in $n$-heptane/$n$-dodecane compared to pure $n$-dodecane is due to the slower rate of reaction of the $n$-heptane. The increased formation of aromatic species
for the iso-octane/n-dodecane flame is likely due to the formation of C3-species from iso-butene and propene, which result from the reaction of iso-octane. In the methylcyclohexane/n-dodecane flame, reaction pathways are present that increase the formation of C3 and C4-species that are important for the formation of the first aromatic ring. In contrast to the paraffin fuels, m-xylene fuel has direct pathways to the formation of two-ring aromatics without the necessity of forming the first aromatic ring.

5.4 Soot
While the LIF images show the qualitative differences in soot formation processes driven by changes in fuel molecular structure, the LII imaging provides quantitative information about soot volume fraction in the flames and the impact that fuel molecular structure has on soot at various jet equivalence ratios. Figure 5-7 shows the 2-D soot volume fraction distribution for all the fuels at $\phi_{jet} = 24$. In order to show the 2-D spatial soot structure amongst various fuels distinctly, the m-xylene flame and paraffinic fuels are plotted on different scales. For the m-xylene fuel, the maximum value on the scale is 16 ppm, shown on the left side of the figure, and the paraffinic fuels are plotted on a scale with a maximum of 6 ppm, shown on the right side of the figure. An iso-contour of 1 ppm is shown on the 2-D plots for all the flames, to distinguish the spatial extent of presence of the LII for all the fuels on both scales. As discussed in the Chapter 3, variation in laser intensity across the sheet resulted in “banding” of the LII images; the variation associated with the banding is within the measurement uncertainty of ±15%.

Figure 5-7 (a) shows that the soot in the m-xylene/n-dodecane flame has a distinct spatial development as compared to the paraffin fuels, shown in Fig. 5-7 (b)-(e). First, the soot formed in the m-xylene flame is not completely oxidized, and hence, the flame tip does not close. The
soot is completely oxidized in all the paraffin fuels. Additionally, the \textit{m}-xylene flame shows LII signal from soot at 7 mm HAB in the annular region of the flame, as compared to 12-14 mm HAB for the paraffin fuels. This difference in the height at which LII is first detected is a result of accelerated aromatic formation caused by the presence of \textit{m}-xylene. This first appearance of LII signal at lower HAB in a fuel with an aromatic component as compared to a fuel having no aromatic component is also reported by other researchers [118].

Figure 5-7 (b)-(e) shows that the 2-D spatial distribution of soot for the paraffin fuels is quite similar. The LII signal is first detected at a height of 12-14 mm HAB in the annular region of the flame for all the paraffin fuels. Further downstream, the LIF signal is detected along the flame centerline at 20-22 mm HAB for all the paraffin fuels. This trend of first appearance of soot in the annular region of the flame and then along the centerline further downstream is consistent with previous published work in co-flow flames [20]. Quantitatively, the peak soot volume fraction in \textit{m}-xylene flame is a factor of three higher as compared to all the paraffin fuels. The \textit{iso}-octane/\textit{n}-dodecane and methylcyclohexane/\textit{n}-dodecane flames produce very similar amounts of soot, which are higher than the soot volume fraction in the pure \textit{n}-dodecane flame, while the \textit{n}-heptane/\textit{n}-dodecane flame produces slightly lower amount of soot as compared to the pure \textit{n}-dodecane flame.

Figure 5-8 shows the 2-D soot volume fraction for all the fuels at $\phi_{\text{jet}} = 6$. An iso-contour of 1 ppm is shown on the 2-D plots for all the flames. The spatial development of soot is similar in all the fuels, with LII appearing first in the annular region of the flame and appearing along the flame centerline further downstream. Figure 5-8 (a) shows that in the \textit{m}-xylene flame the LII signal is first detected in the annular region at 10 mm HAB, as compared to 18-20 mm HAB for the paraffin fuels. The \textit{m}-xylene flame has a larger spatial extent of soot to a height of 53
Figure 5.7 Two-dimensional soot volume fraction obtained at $\phi_{\text{jet}} = 24$ for (a) $m$-xylene/$n$-dodecane (scale on left side); (b) $n$-dodecane (scale on right side); (c) $n$-heptane/$n$-dodecane (scale on right side); (d) iso-octane/$n$-dodecane (scale on right side); (e) methylcyclohexane/$n$-dodecane (scale on right side).

Figure 5.8 Two-dimensional soot volume fraction obtained at $\phi_{\text{jet}} = 6$ for (a) $m$-xylene/$n$-dodecane (scale on left side); (b) $n$-dodecane (scale on right side); (c) $n$-heptane/$n$-dodecane (scale on right side); (d) iso-octane/$n$-dodecane (scale on right side); (e) methylcyclohexane/$n$-dodecane (scale on right side).
mm HAB, in contrast to the paraffin fuels, which have no soot beyond 45 mm HAB. The larger extent of soot in the \( m \)-xylene flame is because peak soot produced in the \( m \)-xylene flame is approximately three times larger than the paraffin fuels, and hence, would require more distance or time to completely oxidize. The study by Arana et al. [87] in ethylene flames reported beyond \( \phi_{\text{jet}} = 24 \), where flame heights decrease with increase in premixing, the flame heights are limited by oxidizer diffusion. The local oxidation rate would depend on the local temperature, species concentration and the soot nanostructure. The comparison of Fig. 5-7 and Fig. 5-8 shows that the increased premixing results in reduced soot levels in the \( \phi_{\text{jet}} = 6 \) flames as compared to the corresponding \( \phi_{\text{jet}} = 24 \) flames; the spatial extent of LII is also reduced for \( \phi_{\text{jet}} = 6 \) flames. The most drastic change is evident in the \( m \)-xylene flame at \( \phi_{\text{jet}} = 6 \); Figure 5-7 (a) and Figure 5-8 (a) show complete oxidation of all soot produced and the flame is closed tip for the lower jet equivalence ratio flame.

5.5 Effects of Chemical Structure

Figures 5-9 (a) and (b) summarize the results for peak soot volume fraction anywhere in the flame and peak volume fraction along the centerline; the two plots use the same ordinate scale so that the lengths of the bars have the same meaning in both graphs. Figure 5-9 includes results for the non-premixed flames discussed in Wang et al. [145]. The data show that the same relative trends in soot among the five fuels exist at all three jet equivalence ratios, with \( m \)-xylene producing the highest soot volume fractions, followed by \textit{iso}-octane and methylcyclohexane, and finally by \textit{n}-dodecane and \textit{n}-heptane. Numerical simulations for the five fuels in a homogenous reaction at 1600 K indicate all the fuels produce similar amounts of acetylene, within 20%. As such, the differences in the amount of soot produced in the \( m \)-xylene flames compared to the paraffin flames can be attributed to increased concentrations of
aromatic species that enhance soot growth and also lead to greater numbers of incipient soot particles.

Figure 5-9 Peak soot volume fractions: (a) over entire flame; (b) along the centerline. Dividing the maximum soot volume fractions by the maximum soot volume fraction for the base fuel, \( n \)-dodecane, reveals that, within experimental uncertainty, the ratios are constant for each fuel across the three experimental conditions. The ratios are presented in Table 5-2. Regardless of the jet equivalence ratio, the \( m \)-xylene fuel produces a peak soot level three times that of \( n \)-dodecane fuel. The ratio of the integrated soot volume fraction for \( m \)-xylene/\( n \)-
dodecane and \( n \)-dodecane flame are 3.0, 3.0, and 5.6 for non-premixed, \( \phi_{\text{jet}} = 24 \), and \( \phi_{\text{jet}} = 6 \) conditions, respectively. At non-premixed and \( \phi_{\text{jet}} = 24 \) conditions, LII measurements are available only until 57 mm HAB. Therefore, the actual ratio obtained by an integrating sensor would be higher than the ratio obtained from the LII measurements because flame height of the \( m \)-xylene\( / n \)-dodecane flame is longer than 57 mm due to the smoking nature of the flame. At the \( \phi_{\text{jet}} = 6 \) condition, the ratio of the integrated soot volume fraction is higher than the ratio of the peak soot volume fraction on account of larger spatial presence of the soot volume fraction in the \( m \)-xylene\( / n \)-dodecane flame.

<table>
<thead>
<tr>
<th></th>
<th>m-X</th>
<th>C12</th>
<th>C7</th>
<th>i-C8</th>
<th>MCH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-premixed</td>
<td>3.1</td>
<td>1.0</td>
<td>0.9</td>
<td>1.2</td>
<td>1.3</td>
</tr>
<tr>
<td>( \phi_{\text{jet}} = 24 )</td>
<td>3.3</td>
<td>1.0</td>
<td>0.9</td>
<td>1.2</td>
<td>1.1</td>
</tr>
<tr>
<td>( \phi_{\text{jet}} = 6 )</td>
<td>2.7</td>
<td>1.0</td>
<td>0.9</td>
<td>1.2</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Table 5-2 Ratio of Max Soot Volume Fraction to Max for \( n \)-dodecane along the centerline

<table>
<thead>
<tr>
<th></th>
<th>m-X</th>
<th>C12</th>
<th>C7</th>
<th>i-C8</th>
<th>MCH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-premixed</td>
<td>1.6</td>
<td>1.0</td>
<td>0.9</td>
<td>1.0</td>
<td>1.1</td>
</tr>
<tr>
<td>( \phi_{\text{jet}} = 24 )</td>
<td>1.9</td>
<td>1.0</td>
<td>0.9</td>
<td>1.2</td>
<td>1.1</td>
</tr>
<tr>
<td>( \phi_{\text{jet}} = 6 )</td>
<td>2.7</td>
<td>1.0</td>
<td>0.9</td>
<td>1.2</td>
<td>1.1</td>
</tr>
</tbody>
</table>

For the paraffin fuels, the \( iso \)-octane and methylcyclohexane have peak soot levels approximately 20% higher than \( n \)-dodecane, and the \( n \)-heptane fuel produces approximately 10% lower peak soot levels. The data shows that regardless of the amount of air mixed into the
fuel jet, within measurement uncertainty, the effect of fuel structure on peak soot volume fraction is consistent. The consistent relationship among peak soot volume fractions for the five fuels exists even though the structure of the \textit{m}-xylene flame changes from smoking to non-smoking between $\phi_{\text{jet}} = 24$ and $\phi_{\text{jet}} = 6$.

Interestingly, normalizing the peak soot volume fractions along the centerline by that of \textit{n}-dodecane shows that the effects of fuel structure are also consistent for all fuels, except for the $\phi_{\text{jet}} = 6 \text{\textit{m}-xylene flame}$; the normalized volume fractions are 1.6, 1.9 and 2.7 at $\phi_{\text{jet}} = \text{Inf}$, 24 and 6. The ratios are presented in Table 5-3. As will be discussed in more detail in the next section, the \textit{m}-xylene flame shifts from smoking at $\phi_{\text{jet}} = 24$ to non-smoking at $\phi_{\text{jet}} = 6$. This change is accompanied by substantial changes in the spatial distribution of soot as well as aromatic species. The changes in the spatial distribution of aromatic species may be the reason that the \textit{m}-xylene $\phi_{\text{jet}} = 6$ flame deviates from the others in terms of fuel effects on maximum soot levels along the centerline.

The peak soot volume fraction on the flame centerline and in the whole domain reduces for all five fuels at $\phi_{\text{jet}} = 24$ and $\phi_{\text{jet}} = 6$ as compared to the non-premixed flames for all five fuels. The reduction in peak soot with premixing of air into the fuel can be due to several effects, as identified in previous studies [86, 198, 199]. First, the decrease in the soot precursors/large aromatics with premixing, discussed in Section 5.3, would result in the decrease in the soot nucleation rate. Furthermore, the reduction in the level of PAH formed due to premixing would result in decrease in the soot growth by PAH condensation. Additionally, the residence time in the flame reduces as flame length decreases with the increase in premixing, as can be seen in Fig. 5-1, thereby reducing the time for soot growth [200, 201].
In order to determine if the fuel structure altered the relationship between the amount of large aromatics in a flame and the peak amount of soot produced, the peak soot volume fraction was plotted against the peak in LIF from large aromatic species. The \( m \)-xylene flame results are not plotted because the peak LIF signal location lies in a region with different temperature and species compared to the location of peak LIF for the paraffin fuels. As discussed in Section 5.3, the local conditions can have a substantial impact on the LIF signals. The LIF from large aromatics at \( \phi_{\text{jet}} = 6 \) had poor signal to noise ratio, so only data from the non-premixed and \( \phi_{\text{jet}}=24 \) flames are included in the Fig. 5-10. The data show a linear relationship, as was found in ethylene premixed flames [22], where the linear relationship was interpreted as an indication that the aromatic species were a substantial source of carbon for soot growth.

![Figure 5-10 Correlation between peak soot volume fraction and peak large aromatic LIF signal (R²=0.9772).](image)

Figure 5-10 Correlation between peak soot volume fraction and peak large aromatic LIF signal (\( R^2=0.9772 \)).
5.6 Effect of premixing

Figure 5-11 (a) compares the radial profiles at 5 mm HAB for $n$-heptane fuel at three different jet equivalence ratios – infinite (non-premixed), 24, and 6. As air is added to the fuel jet, the centerline temperature decreases, and the peak temperature increases. Figure 5-11 (b) compares the centerline profiles for $n$-heptane fuel at three different jet equivalence ratios – infinite (non-premixed), 24 and 6. As air is added to the fuel jet, the centerline temperature decreases as compared to the non-premixed flame until approximately 12 mm HAB. At further downstream location, the temperature is higher in the $\phi_{jet} = 6$ flame, as compared to the non-premixed and $\phi_{jet} = 24$ flame. McEnally and Pfefferle [186] noted similar trends in their work on partially-premixed methane flames. Their experiments included species as well as temperature measurements. McEnally and Pfefferle interpreted species profiles near the burner surface as indicating that radial species transport was reduced due to premixing, and they extend this observation to conclude that radial heat transfer is also reduced. The mechanism for the reduced radial transport was postulated to be caused by reduced convection between the flame front and the centerline.

Figure 5-11 Trends in (a) radial temperature profiles for $n$-heptane fuel at 5mm HAB; (b) Centerline temperature as premixed air increases.
The spatial distribution of small aromatics and large aromatics in non-premixed flames, from Wang et al. [145], and $\phi_{jet} = 24$ flames is quite similar. A comparison of Figure 5-4 (b)-(e) and Figure 5-6 (b)-(e) shows that the spatial development of the small aromatics for the paraffin fuels changes when more air is premixed with the fuel. First, in the $\phi_{jet} = 24$ flames, shown in Figure 5-4 (b)-(e), the peak in the small aromatics LIF signal occurs in the annular region of the flame. However, for the $\phi_{jet} = 6$ flames, shown in Figure 5-6 (b)-(e), the peak of the small aromatics LIF occurs on the flame centerline. However, the $m$-xylene/$n$-dodecane flame shows similar spatial development of small aromatics in $\phi_{jet} = 24$ and $\phi_{jet} = 6$ flames; the peak in the small aromatics LIF signal occur in the annular region. Additionally, the formation of the small and large aromatics is at higher HAB along the centerline at $\phi_{jet} = 6$. The shift in the first appearance of aromatics at higher HAB with more premixing was observed in previous premixed flame studies involving methane and ethylene fuels [22, 186]. Finally, the peak LIF signal of small and large aromatics in the $\phi_{jet} = 6$ flame is lower as compared to the corresponding $\phi_{jet} = 24$ flames.

The reduction in signal from small aromatic species and detection of small aromatics at higher HAB and hence, large aromatics, in the $\phi_{jet} = 6$ flames as compared to the corresponding $\phi_{jet} = 24$ flames is due to a combination of chemical, dilution, and thermal effects. Figure 5-11 (b) shows that the temperature in lower part of flame until 12 mm HAB is lower in $\phi_{jet} = 6$ flames as compared to the corresponding $\phi_{jet} = 24$ flames due to the air dilution effect. The chemical kinetic rate of the formation of the first ring is reduced in $\phi_{jet} = 6$ flames as compared to the $\phi_{jet} = 24$ flames as a result of the lower temperature and dilution effect. However, aromatic and soot production is not just a function of temperature, but also residence time, which is driven by flow velocity inside the flame.
At the exit of the tube burner, the flow field is dominated by convection as opposed to buoyancy due to the mass flow from the tube. As such, the residence time until approximately 20 mm HAB is less in $\phi_{jet} = 6$ as compared to the $\phi_{jet} = 24$ flame due to higher tube exit velocity since the mass flow rate in the $\phi_{jet} = 6$ case is higher. The shorter residence time until approximately 20 mm HAB in the $\phi_{jet} = 6$ flames can shift the formation of the first aromatic ring at higher HAB as compared to $\phi_{jet} = 24$ flames. Further downstream, however, both the $\phi_{jet} = 24$ and $\phi_{jet} = 6$ flames are buoyancy driven, meaning that the flow velocities are similar for both flames after approximately 20 mm HAB [21].

Furthermore, the higher level of premixing causes the carbon in the fuel to oxidize more, and hence, less carbon is available for ring formation. The presence of higher level of oxidizer would result in oxidative attack on the aromatics that are produced, and further hamper the growth of larger aromatics [31].

Figure 5-12 (a), (b) and (c) show the spatial distributions of soot, large and small aromatic species of $m$-xylene flames for non-premixed, $\phi_{jet} = 24$ and $\phi_{jet} = 6$ flames. The left half of each image is scaled to the peak soot/signal level of each flame so that the spatial distribution is clear. The right half of each image is plotted on the same color scale as that of the non-premixed flame so that changes in absolute signal level are clear. Results for a non-smoking, non-premixed $m$-xylene with 0.48 slpm of nitrogen are also shown in Fig. 5-12 and are discussed below.

Comparison of the spatial distribution of soot between the non-premixed and $\phi_{jet} = 24$ fuel jets, Fig. 5-12 (a), shows that they are very similar in structure up to a height of approximately 40 mm above the burner. Above 40 mm HAB, the peak soot volume fraction at each HAB for the non-premixed jet remains near the maximum soot volume fraction of 17 ppm (red) and lies
Figure 5-12 Spatial distributions of (a) soot; (b) large aromatics; and (c) small aromatic species of \( m \)-xylene flames for non-premixed, \( \phi_{jet} = 24 \) and \( \phi_{jet} = 6 \). The left half of each image is scaled to the peak soot/signal level; the right half of each image is plotted on the same color scale as the non-premixed flame at 0.2 slpm \( N_2 \). The scale and contour levels are shown in Table 5-4. Results for a non-smoking, non-premixed \( m \)-xylene 0.48 slpm \( N_2 \) are also shown.
Table 5-4 Scale and contour levels for small aromatics, large aromatics and soot in Figure 5-12.

<table>
<thead>
<tr>
<th></th>
<th>Small max on scale [counts]</th>
<th>Small contour [counts]</th>
<th>Large max on scale [counts]</th>
<th>Large contour [counts]</th>
<th>Soot max on scale [ppm]</th>
<th>Soot contour [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \phi_{\text{jet}} = \text{Inf} - 0.2N_2 )</td>
<td>170000</td>
<td>4200</td>
<td>75000</td>
<td>4200</td>
<td>18</td>
<td>1</td>
</tr>
<tr>
<td>( \phi_{\text{jet}} = 24 ) -0.2N_2</td>
<td>95000</td>
<td>4200</td>
<td>50000</td>
<td>4200</td>
<td>16</td>
<td>1</td>
</tr>
<tr>
<td>( \phi_{\text{jet}} = 6 ) -0.2N_2</td>
<td>35000</td>
<td>4200</td>
<td>16000</td>
<td>4200</td>
<td>8</td>
<td>1</td>
</tr>
<tr>
<td>( \phi_{\text{jet}} = \text{Inf} - 0.48N_2 )</td>
<td>107000</td>
<td>4200</td>
<td>28000</td>
<td>4200</td>
<td>8</td>
<td>1</td>
</tr>
</tbody>
</table>

Figure 5-13 Radial plots of soot volume fraction Top row: (a) \( m \)-xylene, \( \phi_{\text{jet}}=\text{Inf} \) flame, (b) \( m \)-xylene, \( \phi_{\text{jet}}=24 \) flame, (c) \( m \)-xylene, \( \phi_{\text{jet}}=6 \) flame, Bottom row: (d) \( \text{iso-octane}, \phi_{\text{jet}}=\text{Inf} \) flame, (e) \( \text{iso-octane}, \phi_{\text{jet}}=\text{Inf} \) flame, (f) \( \text{iso-octane}, \phi_{\text{jet}}=\text{Inf} \) flame.

near the edges of the flame. For the \( \phi_{\text{jet}} = 24 \) jet flame shown in Fig. 5-12 (a) and Fig. 5-13 (b) however, the peak soot at each HAB has decreased to levels below the maximum soot volume fraction of 14 ppm and the soot volume fraction is relative constant at 7 ppm along the radius.
above 50 mm HAB. Comparing the aromatic species for the two flames, Fig. 5-12 (b) and (c), shows that the overall structure remains very similar but that the signal from aromatic species present decreases substantially as indicated by the shift from red-yellow to light green in the right-side images for small and large aromatic species.

When the amount of air in the fuel jet is increased to achieve $\phi_{\text{jet}} = 6$, the flame becomes non-smoking and the amount of peak soot drops by a factor of approximately two from the $\phi_{\text{jet}} = 24$ flame. For the $\phi_{\text{jet}} = 6$ fuel jet shown in Fig. 5-12 (a) and Fig. 5-13 (c), the maximum soot concentration is distributed across the most of the flame compared to the peak occurring in the annular region near the flame sheet for the $\phi_{\text{jet}} = 24$ and the non-premixed jet flames. The maximum height along the centerline of the LIF from small aromatic species, Fig. 5-12 (c), is reduced from 30-35 mm in $\phi_{\text{jet}} = 24$ flame to approximately 25 mm in $\phi_{\text{jet}} = 6$ flame. The spatial extent of detectable LIF from large aromatic species changes much more than that of the LIF from small aromatic species. At $\phi_{\text{jet}} = 6$, the first detectable signal appears at approximately 10 mm above the burner and ends at approximately 25 mm. For the non-premixed and $\phi_{\text{jet}} = 24$ flame, the corresponding heights are approximately 5 mm and 35 mm.

In m-xylene flame, the shift from smoking to non-smoking results in a shift from a soot field that is characterized by large soot volume fractions near the flame front to a soot field that is more uniform across the cross-section of the flame. This shift is evident in the data in Fig. 5-9 and Fig. 5-13 (a)-(c). For the smoking m-xylene flames, the peak soot volume fractions are approximately twice the peak volume fractions along the centerline of the flame. For the non-smoking m-xylene flame at $\phi_{\text{jet}} = 6$, the maximum soot volume fraction is equal to the maximum along the centerline within experimental uncertainty. In addition, the effect of premixing on peak soot in m-xylene flame is evident in flame annular region, where peak soot decreases
from 17 ppm to 7.5 ppm. However, the peak soot volume fraction on flame centerline decreases marginally from 8.5 ppm to 7.2 ppm. This is evident in Fig. 5-9.

A shift in the nature of the soot field from one that has clear peaks in an annular region off the centerline to more uniform field is also evident for two of the paraffin fuels, i-C₈ and MCH. This shift can be seen by comparing the soot images, but it is also evident in Fig. 5-9. When the peak across the entire flame (Fig. 5-9a) is larger than that along the centerline (Fig. 5-9b), the soot field has an annular structure – this structure is evident in the non-premixed iso-octane and methylcyclohexane flames. This structure change is illustrated for iso-octane flame in Fig. 5-13 (d)-(f). When the peak soot in the entire domain is close to that along the centerline, the soot field is uniform across the cross-section of the flame. Previous studies in ethylene co-flow flame have also reported the transition in peak soot volume fraction from the annular region to flame centerline. The study by Santoro et al. [20] observed the transition of the peak soot location from an annular region to the centerline when the fuel jet velocity was changed. The study by Smooke et al. [201] reported a similar transition when the fuel jet was diluted with different levels of nitrogen; the authors concluded the transition of peak soot volume fraction from centerline to annular region arises, as fuel fraction increases, due to the change in the relative importance of soot inception and growth processes along with the increase in the soot residence time in the annular region. In the current study, the transition in the location of peak soot volume fraction with air addition to the fuel jet may be due to a combination of dilution and chemical effects of oxygen. To the best of authors’ knowledge, no prior studies have reported results involving this transition behavior due to premixing in higher molecular weight fuels.
Fuel structure appears to affect the jet equivalence ratio at which the transition from annular to uniform soot field occurs. For the \textit{m}-xylene fuel, the transition of soot distribution from annular to a more uniform distribution happens somewhere between $\phi_{\text{jet}}=24$ and 6. For the \textit{i}-C$_8$ and MCH fuels, the transition occurs somewhere between the non-premixed flame and $\phi_{\text{jet}}=24$. The two lowest sooting fuels, C$_{12}$ and C$_7$, do not show peak soot in the wings even in the non-premixed flames. Thus, the data suggest that the key factor in determining the $\phi_{\text{jet}}$ at which the transition occurs is the peak amount of soot in the non-premixed flame. The greater the amount of soot in the annular region, the more air must be premixed before the annular peak is reduced to levels similar to the centerline.

The effects of oxygen addition on the \textit{m}-xylene flame structure can be seen from a comparison of the $\phi_{\text{jet}}=6$ flame and a non-smoking, non-premixed flame that was achieved by increasing the nitrogen flow rate until an incipient sooting condition was achieved. Results for non-smoking, non-premixed \textit{m}-xylene are also shown in Fig. 5-12 (scale and contour levels for this figure are shown in Table 5-4); this flame has a nitrogen flow rate of 0.48 slpm compared to the 0.2 slpm that was the standard operating condition for the vaporizer system. Table 5-5 compares composition of the fuel jet of these two flames in terms of moles/mole of fuel as well as the mole fraction of fuel. The total number of moles per mole of fuel and the fuel mole fraction are within 5\% for the two flames. Even though the total volumetric flow rates are within 5\%, the oxygen for the $\phi_{\text{jet}}=6$ condition reduces the height of the flame substantially, from 70 mm to 50 mm. This difference in height is evident in the soot field, as well as the spatial extent of LIF from large and small aromatic species. The soot field is uniform in both $\phi_{\text{jet}} = 6 - 0.2N_2$ and non-premixed-0.48N$_2$ flames, as compared to the non-premixed-0.2N$_2$ flame that has peak soot in the narrow annular region.
Table 5-5 Comparison of composition of the fuel jet of \( m \)-xylene flames: \( \phi_{\text{jet}} = 6 - 0.2N_2 \) flame and a non-smoking non-premixed flame with 0.48\( N_2 \) flame.

<table>
<thead>
<tr>
<th></th>
<th>Fuel (mole/min)</th>
<th>( O_2 ) (mole/min)</th>
<th>( N_2 ) (mole/min)</th>
<th>Total (mole/min)</th>
<th>Fuel mole fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \phi_{\text{jet}} = 6 ) 0.2 slpm ( N_2 )</td>
<td>1.0</td>
<td>2.6</td>
<td>18.0</td>
<td>21.6</td>
<td>0.0462</td>
</tr>
<tr>
<td>Non-premixed 0.48 slpm ( N_2 )</td>
<td>1.0</td>
<td>0.0</td>
<td>20.1</td>
<td>21.1</td>
<td>0.0473</td>
</tr>
</tbody>
</table>

Furthermore, Fig. 5-12 (a) shows in the \( \phi_{\text{jet}} = 6 - 0.2N_2 \) flame, 1 ppm of soot is detected at 22 mm HAB on flame centerline, closer to the tube exit compared to 35 mm HAB in non-premixed, 0.48 slpm flame. However, the peak soot for the 0.48 slpm non-premixed fuel jet is 7 ppm, similar to 7.6 ppm for \( \phi_{\text{jet}} = 6 \) with the standard nitrogen flow rate. The reason for peak soot to be similar in both the flames, in spite of higher level of peak LIF signal in 0.48 slpm, non-premixed flame, may be due to higher temperature in the \( \phi_{\text{jet}} = 6 - 0.2N_2 \) flame in lower parts of the flame. The temperature measurements on flame centerline until 20 mm HAB, Fig. 5-14, indicate that the temperature difference between the two flames increases along the downstream location from approximately 90 K at tube exit to 260 K at 19 mm HAB. This higher temperature in \( \phi_{\text{jet}} = 6 - 0.2N_2 \) flame can increase the soot formation processes, thereby leading to earlier detection of LII, shown in Fig. 5-12 (a); the peak soot volume fraction of 7.6 ppm is at approximately 35 mm HAB in \( \phi_{\text{jet}} = 6 - 0.2N_2 \) flame whereas peak soot of 7 ppm is at 50 mm HAB in non-premixed-0.48\( N_2 \) flame.
Figure 5-14 Comparison of centerline temperature of $m$-xylene, $\phi_{\text{jet}} = 6$, 0.2 slpm flame and $m$-xylene, non-premixed, 0.48 slpm flame.
Chapter 6 Experimental and numerical investigation of effects of premixing on soot processes in iso-octane co-flow flames.

Chapter 6 expands on Chapters 4 and 5, which focused on the effects of fuel molecular structure on emissions. One of the key results was that iso-octane/n-dodecane and methycyclohexane/n-dodecane fuel blends had the highest sooting propensity amongst several paraffin fuels: n-heptane/n-dodecane, n-dodecane and n-hexadecane/n-dodecane [145, 146, 202]. The iso-octane/n-dodecane and methycyclohexane/n-dodecane fuels also displayed an interesting feature with premixing, where the location of the peak soot transitioned from the annular region to the centerline as the level of premixing increased. The transition occurs at jet equivalence ratios (ϕ_{jet}) between infinity (non-premixed) and 24. In the present chapter, the physical and chemical processes responsible for this trend in peak soot are considered in iso-octane flames at a range of jet equivalence ratios, using both experimental and numerical methods. iso-Octane is an important molecule to study because it is a primary reference fuel, and it is used to represent iso-alkane components of real fuels in surrogate fuel formations [7, 109].

The goal of this work is to understand the processes controlling the transition of the location of peak soot in a laminar, co-flow flame for a high-hydrocarbon fuel that is representative of fuel components in real transportation fuels and the relative roles of gas-phase vs. condensed-phase processes in controlling the soot distribution. To derive this understanding, this work uses a combination of experimental measurements and numerical methods with detailed chemistry and soot models. The numerical work was performed by Dr. Xuan’s group at Penn State. The author is responsible for undertaking the data analysis and data reduction of the numerical results, provided by Dr. Xuan, to interpret the experimental results.
6.1 Experimental Conditions

The experimental matrix is provided in Table 6-1. The flames studied are non-premixed and partially-premixed flames. The carbon flow rate of fuel is kept constant for all the flames at 0.0111 mol/min, to be consistent with our previous work [145]. The vaporized fuel is carried from the vaporization chamber to the tube exit using a 0.2 slpm stream of nitrogen. The coflow air is set at 4 scfm. The purity level of iso-octane used in the experiment is > 99%.

Table 6-1 Matrix of fuel mixtures

<table>
<thead>
<tr>
<th>Liquid Fuel flow rate (ml/min)</th>
<th>Equivalence ratio ($\phi_{jet}$)</th>
<th>Carbon flow rate (mol/min)</th>
<th>Study</th>
<th>Model boundary condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.23</td>
<td>Inf</td>
<td>0.0111</td>
<td>Exp + Num</td>
<td>9.06</td>
</tr>
<tr>
<td>24</td>
<td></td>
<td></td>
<td>Exp + Num</td>
<td>12.39</td>
</tr>
<tr>
<td>15</td>
<td></td>
<td></td>
<td>Exp</td>
<td>-</td>
</tr>
<tr>
<td>12</td>
<td></td>
<td></td>
<td>Exp + Num</td>
<td>15.64</td>
</tr>
<tr>
<td>9</td>
<td></td>
<td></td>
<td>Exp</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td>Exp + Num</td>
<td>22.16</td>
</tr>
</tbody>
</table>

6.2 Simulation description

6.2.1 Simulation Framework

The flow solver used in this work is the NGA code [203]. The equations for conservation of mass, momentum, species, and energy are solved using a finite difference formulation in cylindrical coordinates. The BQUICK scheme is used for solving the discretized species and temperature equations. This scheme ensures that the transported scalars remain within their physical bounds [204]. A recently-developed computationally-efficient, semi-implicit,
iterative method is used for the time integration of the chemical source terms in the transport
equations of gas-phase species. This method has been shown to be free of lagging errors, as
efficient as an explicit time-integration per time step, and capable of using large, stable time-
step sizes [205]. These numerical methods guarantee globally second-order accuracy in both
space and time [206].

The detailed chemistry model employed in the current work contains 185 species and 1903
reactions (forward and backward reactions counted separately), and takes into account all
major pathways of polycyclic aromatic hydrocarbons (PAH) formation [206]. This chemical
model has been extensively validated for multiple fuels [207], including the one used in this
study. This model has been used in multiple configurations, including laminar and turbulent
flames [208, 209].

6.2.2. Soot Model

The soot model employed in the current study is taken from Ref. [137], which is a simplified
version of that presented in Ref. [138]. Soot particles are considered as fractal aggregates and
geometrically described based on the total volume, \( V \), and total surface area, \( S \). The population
of the soot particles is statistically described using a bi-variate soot Number Density Function
(NDF), \( n(V; S) \), and is approximated by two delta functions, following previous work [20]. The
evolution of soot is determined by transporting key soot moments

\[
M_{x,y} = \iint n(V, S)V^xS^ydVdS
\]

of the soot NDF using the following transport equation
\[
\frac{\partial M_{x,y}}{\partial t} + \nabla \cdot (u^* M_{x,y}) = \dot{\omega}_{x,y}
\]

Where

\[
u^* = u - 0.556(\nu/T)\nabla T
\]

is the velocity vector accounting for thermophoresis effects [139], \(\nu\) is fluid kinematic viscosity, and \(\dot{\omega}_{x,y}\) accounts for the various contributions from soot nucleation, condensation, surface growth, and oxidation [138].

6.3 Flame heights

Figure 6-1 shows the experimental and numerical results of the soot volume fraction obtained for iso-octane flames at \(\phi_{jet} = \text{Inf}, 24, 12\) and 6 conditions. The numerical study is carried out for these four flame conditions as they represent the observed sooting behavior and therefore, results for \(\phi_{jet} = 15\) and 9 were not calculated in the present study. In the experimental results, the flame heights, as defined by the visible flame images, are approximately 65 mm, 58 mm, 55 mm, and 50 mm, for \(\phi_{jet} = \text{Inf}, 24, 12,\) and 6 conditions, respectively. The flame height uncertainty is ± 2 mm. In the simulation, the flame height is equivalent to the distance from the tube exit to the tip of the \(f_v = 0.1\) ppm isocontour. The flame heights from the simulation are 58 mm, 49 mm, 48 mm, and 43 mm for \(\phi_{jet} = \text{Inf}, 24, 12,\) and 6 conditions, respectively. In both the experimental and numerical studies, the flame heights decrease with increased premixing of the fuel jet, consistent with previous work [146]. Similar to the experiment, the flame height in the simulation decreases by approximately 25% from the \(\phi_{jet} = \text{Inf}\) to the \(\phi_{jet} = 6\) flame. However, the flame heights are under-predicted by 10-15% in the simulation as compared to the experiment. Possible reasons for the mismatch may be uncertainties in the
boundary conditions characterized in the experiment, the chemical kinetic model, or the soot model.

Figure 6-1 Two-dimensional images of the $f_v$ [ppm] for $\phi_{\text{jet}}$ of (a, b) Inf, (c, d) 24, (e, f) 12, and (g, h) 6.

6.4 Effect of air addition on soot volume fraction distribution

Figure 6-1 shows that the soot is first detected in the annular region and then develops towards the flame centerline at higher heights above the burner (HAB) for both non-premixed and premixed flames; this trend of soot development is consistent with previous results [20]. However, the location of the maximum $f_v$ changes significantly with premixing. In the non-premixed flame, Fig. 6-1 (a) shows that the location of peak soot is in the annular region; the peak $f_v$ is approximately 40% higher in annular region as compared to the centerline. In the $\phi_{\text{jet}} = 24$ flame, the peak $f_v$ is approximately 20% higher in the annular region as compared to the centerline. With the increase in premixing, the location of peak $f_v$ shifts from the flame annular region to the flame centerline. Figures 6-1 (e) and 6-1 (g) shows that the soot field is relatively
uniform in the mid-section of the flame, with a peak $f_v$ of approximately 6 ppm and 5 ppm in the $\phi_{jet} = 12$ and 6 flames, respectively.

Comparison of the numerical and experimental results shows that the simulation captures the spatial trends of the soot field. Figures 6-1 (b) and 6-1 (d) show that in the $\phi_{jet} = \text{Inf}$ and 24 flames, the peak $f_v$ location is in the annular region, and transitions to the centerline as the equivalence ratio is reduced. In the non-premixed flame, the peak $f_v$ is 65% higher in the annular region as compared to the centerline. In the $\phi_{jet} = 6$ flame, the peak $f_v$ is near the centerline, consistent with the experimental results. The qualitative trend of transition of peak $f_v$ from the annular region to the centerline is identical to the previous studies in ethylene flames [20, 201].

Figure 6-2 shows the comparison of peak $f_v$ against $1/\phi_{jet}$ in the whole domain and on centerline in the experiment and simulation for all the flames. In both experiment and simulation, the peak $f_v$ decreases with premixing. The peak $f_v$ in the domain decreases by 60% and 80% from $\phi_{jet} = \text{Inf}$ to $\phi_{jet} = 6$ in experiment and simulation, respectively. The peak centerline $f_v$ decreases by 33% and 45% from $\phi_{jet} = \text{Inf}$ to $\phi_{jet} = 6$ in experiment and simulation, respectively. The model predicts the percentage decrease in peak $f_v$ due to premixing to be higher in the annular region as compared to the centerline, as in the experiment. On the centerline, the peak $f_v$ shows a decreasing linear trend with increased premixing; this trend is captured well in the simulation. However, the model over-predicts the percentage decrease in peak $f_v$ due to premixing by approximately 20%. Quantitatively, the peak $f_v$ in the simulation is lower by a factor of 1.3-2.8 as compared to the experiment. A similar level of accuracy by numerical models have been reported in co-flow flame studies [210, 211].
6.5 Numerical investigation of effects of premixing on soot evolution processes

In order to gain insight into the physical and chemical processes that drive the shift in the peak \( f_v \) location from the annular region to the centerline, the nucleation, surface growth, PAH condensation, and oxidation processes amongst the four flames are compared. The details on the models used for these processes can be found in Ref. [138].

6.5.1 Soot nucleation

Figure 6-3 shows the spatial distribution of PAH dimer concentration (left half of each image) and soot nucleation rate (right half of each image) for the four flames. The maximum values of the scale are shown on the top of each figure. Comparison of Figs. 6-3 (a)-(d) shows that the peak intensity of the nucleation rate shifts from the annular region in the \( \phi_{jet} = \text{Inf} \) flame to the centerline in the \( \phi_{jet} = 6 \) flame. This shift in the location of peak nucleation rate is different than the results of the ethylene flame study by Smooke et al. [201]. In the ethylene flame, the
authors observed a shift in the soot field, similar to current study, but they did not see a shift in the peak inception rate, which only occurred along the centerline at all nitrogen dilution rates.

Figure 6-3 Spatial distribution of the PAH dimer concentration (left half of each image) and nucleation rate \( \left[ \times 10^{-6} \right] \) [1/s] (right half of each image) for \( \phi_{\text{jet}} \): (a) Inf, (b) 24, (c) 12, and (d) 6. The maximum value of the scale are shown on the top of each figures.

In the current soot model, the soot nucleation rate is dependent on the local temperature and dimer concentration [138], i.e. \( \dot{\omega}_{\text{nuc}} \propto [T]^{0.5} [\text{DIMER}]^2 \). Therefore, the shift in the location of peak nucleation rate with premixing could be due to the change in the PAH dimer spatial distribution and/or temperature field. Table 6-2 reports the peak nucleation, condensation, and surface growth rates along two streamlines: one that passes through maximum \( f_s \) in the domain and another on the centerline. At the locations of peak soot nucleation, condensation, and surface growth, the value of the various parameters that affect the soot sub-mechanisms are also reported in Table 6-2.
Table 6-2 Maximum value of the parameters affecting nucleation, condensation and surface growth over two streamlines: passes through the centerline and the maximum $f_v$ location.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Max $f_v$ location streamline</th>
<th>Centerline streamline</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\phi_{jet} = \text{Inf}$</td>
<td>$\phi_{jet} = 6$</td>
</tr>
<tr>
<td>Residence time (ms)</td>
<td>115</td>
<td>60</td>
</tr>
<tr>
<td>Nucleation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\omega_{nucl}$</td>
<td>5.11E-04</td>
<td>3.33E-04</td>
</tr>
<tr>
<td>T (K)</td>
<td>1530</td>
<td>1580</td>
</tr>
<tr>
<td>[DIMER]</td>
<td>6.01E-02</td>
<td>7.03E-03</td>
</tr>
<tr>
<td>Condensation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\omega_{cond}$</td>
<td>5.78E-04</td>
<td>7.89E-05</td>
</tr>
<tr>
<td>T (K)</td>
<td>1570</td>
<td>1670</td>
</tr>
<tr>
<td>[DIMER]</td>
<td>7.16E-02</td>
<td>1.36E-02</td>
</tr>
<tr>
<td>Number Density (1/cm$^3$)</td>
<td>9.40E+15</td>
<td>1.66E+15</td>
</tr>
<tr>
<td>Surface growth</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\omega_{surf}$</td>
<td>2.00E-04</td>
<td>6.21E-05</td>
</tr>
<tr>
<td>k4</td>
<td>3.79E-03</td>
<td>4.66E-03</td>
</tr>
<tr>
<td>[C2H2]</td>
<td>1.05E+04</td>
<td>1.45E+04</td>
</tr>
<tr>
<td>$r/(1+r)$</td>
<td>3.75E-03</td>
<td>6.49E-03</td>
</tr>
<tr>
<td>Number of active sites (P)</td>
<td>1.640</td>
<td>0.522</td>
</tr>
</tbody>
</table>

At the peak nucleation location, the temperature increases by approximately 50 K in the $\phi_{jet} = 6$ flame as compared to the $\phi_{jet} = \text{Inf}$ flame. Due to the square root dependence of nucleation rate on the temperature, the temperature increase doesn’t have significant effect on the nucleation rate. However, the dimer concentration decreases by a factor of eight in the $\phi_{jet} = 6$ flame as compared to the $\phi_{jet} = \text{Inf}$ flame. The net result is that the dimer concentration has a
dominant effect on the nucleation rate in these flames. Figure 6-3 shows the PAH dimer concentration, which is obtained by using techniques described in Ref. [138]. The comparison of spatial distribution of PAH dimers shows that the location of peak concentration of PAH dimer is in the annular region and near centerline in $\phi_{\text{jet}} = \text{Inf}$ and 6 flames, respectively. These differences in the PAH dimer distribution among the four flame results in the shift in the location of peak nucleation rate from annular region to centerline due to premixing. Furthermore, the concentration of PAH species decreases with increased premixing, leading to a decrease in the dimer concentration, and therefore, the nucleation rate from the $\phi_{\text{jet}} = \text{Inf}$ to the $\phi_{\text{jet}} = 6$ flame. The shift in peak PAH dimer location and decrease in the PAH concentration with premixing is consistent with the observed trends in the PAH-LIF measurements in our previous work [146].

Simulations in a closed homogeneous reactor model are used to explore the effects of air addition on the iso-octane pyrolysis at constant temperature (1500 K) and pressure (1 atm). Under both non-premixed and partially-premixed conditions ($\phi_{\text{jet}} = 6$), the simulations show that propargyl recombination is the dominant pathway to the formation of A1 (benzene). The rate of formation of benzene is reduced with premixing due to a reduction in propargyl radical mole fraction. The reduction in propargyl radical could be the result of dilution and/or oxidation of $\text{C}_3\text{H}_3$ or the radicals that form $\text{C}_3\text{H}_3$ by $\text{O}_2/\text{OH}$.

6.5.2 Soot growth: PAH condensation and surface reaction

Figure 6-4 shows the comparison of soot growth rate due to PAH condensation (left half of each image) and the HACA mechanism (right half of each image) for the four flames. The soot growth rates in Fig. 6-4 (a)-(d) show that with increasing premixing, the peak soot growth rate due to both PAH condensation and the HACA mechanism shifts from the annular region in the
$\phi_{jet} = \text{Inf flame to the centerline in the } \phi_{jet} = 6 \text{ flame. Additionally, similar to the soot nucleation rate, the peak growth rates due to PAH condensation and the HACA mechanism decrease by approximately a factor of seven and three, respectively, as premixing is increased.}

**Figure 6-4** Spatial distribution of the PAH condensation rate [1/s] (left half of each image) and soot surface growth rate [1/s] (right half of each image) for $\phi_{jet}$: (a) Inf, (b) 24, (c) 12, and (d) 6. The maximum value of the scale are shown on the top of each figures.

The condensation and surface growth terms, which are modeled according to Ref. [138], are given by,

\[
\dot{\omega}_{\text{cond}} \propto [T]^{0.5}[\text{DIMER}] 
\]

\[
\dot{\omega}_{\text{surf}} \propto k_4[C_2H_2]P(r/1 + r) 
\]

where $k_4$, $[C_2H_2]$, $P$, and $r$ are the per-site rate coefficient for acetylene addition, the concentration of acetylene, number of active site on the soot surface, and the ratio of radical to neutral sites on the particle surface, respectively. $r$ is given by
\[ r = \frac{k_{1f}[H] + k_{2f}[OH] + k_{3f}}{k_{1b}[H_2] + k_{2b}[H_2O] + k_{3b}[H] + k_4[C_2H_2]} \]

The various rate constants can be found in [20].

The PAH condensation rate depends on the local temperature, PAH dimer concentration, and soot number density. Table 6-2 shows that with premixing, the temperature increases by 100 K, which could result in an increase in the PAH condensation rate in the \( \phi_{jet} = 6 \) flame as compared to the \( \phi_{jet} = \text{Inf} \) flame. However, dimer concentration and soot number density decreases by a factor of five with premixing. The condensation rate decreases with premixing as a result of the decrease in dimer concentration and soot number density. The dimer concentration decreases with premixing as a result of the decrease in PAH formation in the flame. The soot number density decreases with premixing as a result of the decrease in nucleation rate. The decrease in PAH condensation, in turn, further hampers soot growth. Table 6-2 shows that the ratio of dimer concentration and soot number density, from \( \phi_{jet} = \text{Inf} \) to \( \phi_{jet} = 6 \), decreases by approximately a factor of five and two in the whole domain and on centerline, respectively. The higher reduction of dimer concentration and soot number density in the whole domain results in greater reduction of the condensation rate in the annular region as compared to the centerline.

Table 6-2 shows that several key parameters for surface growth increase with premixing, including \( k_4 \), \( C_2H_2 \) concentration, and the ratio of radical to neutral sites on the particle surface. However, the total number of active sites on the soot surface decreases by a factor of three from \( \phi_{jet} = \text{Inf} \) to \( \phi_{jet} = 6 \). The decrease in the total number of active sites on the soot surface offsets the increase in \( k_4 \), the acetylene concentration, and the ratio of radical to neutral sites on the particle surface in the \( \phi_{jet} = 6 \) flame as compared to the \( \phi_{jet} = \text{Inf} \) flame. Consequently,
the peak soot growth rate due to the HACA mechanism decreases with premixing. Table 6-2
also shows that the surface growth rate decreases by a greater magnitude in the annular region
as compared to the centerline. This greater reduction in soot growth rate leads to a higher
percentage decrease of the peak $f_v$ in the annular region as compared to the centerline, as
discussed in Section 6.4.

Simulations also indicate that the peak location of oxidation shifts from the annular region in
the $\phi_{\text{jet}} = \text{Inf}$ flame to the centerline in the $\phi_{\text{jet}} = 6$ flame. This shift in location of peak oxidation
rate is expected since the oxidation processes occur in the region containing maximum soot.

6.5.3 Residence time

The total soot produced in a flame is not just a function of the soot production rates, but also
the residence time of the soot in the flame. Since the flames are buoyancy driven, the velocities
are similar in these flames beyond the exit of the tube [21]. Therefore, the residence time
depends on the flame height. Figure 6-1 shows that the flame height decreases due to
premixing. The residence time is calculated by measuring the time for the soot $f_v$ to fall below
the cut-off of 0.1 ppm along the two streamlines, along the flame centerline and the maximum
$f_v$ location. Table 6-2 shows that the residence time is similar along the two streamlines for
both flames. As a result, the total residence time available for soot processes decreases by
approximately 50 ms in the $\phi_{\text{jet}} = 6$ flame as compared to the $\phi_{\text{jet}} = \text{Inf}$ flame. The longer
residence time, along with faster soot production processes, result in higher soot growth in the
non-premixed flame.
Chapter 7 Effect of aromatic fuels and premixing on aromatic species and soot distributions in laminar, co-flow flames

This chapter focuses on the effect of single-ring aromatic fuel structure on the distribution of the aromatics and soot in a co-flow, laminar flame at atmospheric pressure. This chapter advances findings from Chapters 4 and 5, which focused on the effect of n-alkane, iso-alkane, cycloalkane, and one-ring aromatic fuels on the distribution of aromatics and soot. This chapter discusses temperature, aromatic species, and soot results for non-premixed flame and at a jet equivalence ratio ($\phi_{\text{jet}}$) of 6. Additionally, the effects of nitrogen dilution on soot volume fraction are also presented. Furthermore, CHEMKIN simulations are used to understand the differences in the pathways of fuel decomposition and formation of soot precursors for the four aromatic fuels.
7.1 Visible flame images

Figure 7-1 shows the visible flame images of the five fuels obtained using a digital camera at the same camera operating parameters. Each image shows, from left to right, the \( n \)-dodecane (C12), \( n \)-propylbenzene/\( n \)-dodecane (PB), toluene/\( n \)-dodecane (TOL), \( m \)-xylene/\( n \)-dodecane (mX), and 1,3,5-trimethylbenzene/\( n \)-dodecane (TMB) flames. The \( n \)-dodecane flame height, obtained from the visible flame image, is approximately 57 mm. In non-smoking flames, the flame tip has a fluctuation of \( \pm 2 \) mm. Figure 7-1 (a) shows that in non-premixed flames, the addition of the four aromatic fuels to the \( n \)-dodecane, while maintaining the total carbon flow rate, causes the flame to have an open tip that emits soot. The visible flame image for partially-premixed flames at the \( \phi_{\text{jet}} = 6 \) condition is shown in Fig. 7-1 (b). At the \( \phi_{\text{jet}} = 6 \) condition, the aromatic flames have a closed tip and all soot that is produced is oxidized. The aromatic flames, however, have a longer visible flame length compared to the \( n \)-dodecane flame, consistent with our previous work in the \( m \)-xylene/\( n \)-dodecane flame [145, 146]. The flame images are also obtained at long exposure time; these images show that in both non-premixed and premixed flames, there is a gap of approximately 1 mm between the tube exit and blue region of the flame.
Figure 7-1 Visible flame images of five fuels: $n$-dodecane flame, $n$-propylbenzene/$n$-dodecane flame, toluene/$n$-dodecane flame, $m$-xylene/$n$-dodecane flame, and 1,3,5-trimethylbenzene/$n$-dodecane flame: (a) $\phi_{\text{jet}} = \text{Inf}$ (non-premixed); and (b) $\phi_{\text{jet}} = 6$

**7.2 Comparison of the temperature field**

Figure 7-2 shows the radial (at 5 mm HAB) and centerline (until 20 mm HAB) temperature profiles for the five fuels at the non-premixed condition. While no soot deposition on the thermocouple bead is observed at distances upstream of 20 mm HAB, soot deposition downstream of this location affects temperature measurements; therefore, the temperature
beyond this point is not measured. The trend in centerline and radial temperature profiles is identical to previous work [145, 146]. For the five fuels, Fig. 7-2 shows that the temperature field is similar, within the measurement uncertainty of \( \pm 100\text{K} \). The uncertainty in spatial location of thermocouple bead is estimated to be \( \pm 0.5 \text{ mm} \). However, the temperature field downstream of 20 mm HAB is expected to be different on account of different levels of soot amongst the five fuels [184]. The radial temperature measurement at 5 mm HAB and along the flame centerline until 18 mm HAB in the \( \phi_{\text{jet}} = 6 \) flames, Fig. 7-3, show similar trends as the non-premixed flames. The five fuels have similar temperatures in the fuel pyrolysis zone at each \( \phi_{\text{jet}} \).

**Figure 7-2 Corrected temperature measurement for \( \phi_{\text{jet}} = \text{Inf} \) flame:** (a) Radial at 5 mm HAB; (b) Centerline until 20 mm HAB.
Figure 7-3 Corrected temperature measurement for $\phi_{\text{jet}} = 6$ flame: (a) Radial at 5 mm HAB; (b) Centerline until 18 mm HAB.

7.3 Small and large aromatics spatial distribution

The similarity in the temperature field in the fuel pyrolysis zone among the five fuels and the similar boundary conditions at a particular $\phi_{\text{jet}}$ indicate that the differences visible in the small and large aromatics amongst the five fuels are likely due to chemical, not thermal, effects. The pyrolysis of the four aromatic fuel mixtures is studied using numerical simulation in a homogenous reactor at constant temperature (1600 K) and pressure (1 atm) to compare the initial pathways of fuel consumption for the four fuels. The published aromatic fuels chemistry from Malewicki et al. [212] is used for these simulations.

The pyrolysis of the four aromatic fuel mixtures is studied using a homogenous reactor simulation at constant temperature (1600 K) and pressure (1 atm) to compare the initial pathways of fuel consumption for the four fuels. The published aromatic fuels chemistry from Malewicki et al. [212] is used for these simulations. Based on the work done on the $m$-xylene fuel chemistry in the SERDP program [11], one modification is implemented in the Malewicki mechanism. The reaction:
m-Xylene + C₂H₄ = Methyl-Styrene + CH₄ \hspace{1cm} 3.00E+45 \hspace{1cm} -8.65 \hspace{1cm} 42422

is replaced with following two elementary reactions:

C₆H₄CH₃ + C₂H₄ = Methyl-Styrene + H \hspace{1cm} 1.50E+45 \hspace{1cm} -8.65 \hspace{1cm} 42401

m-Xylene + C₂H₃ = Methyl-Styrene + CH₃ \hspace{1cm} 13931.5 \hspace{1cm} 2.581 \hspace{1cm} 5048

Further details of the above modifications are discussed in the SERDP report [11]. The modified mechanism does not impact the chemical pathways, shown in Figures 7-4 and 7-5, for \textit{n}-propylbenzene, toluene, and 1,3,5-trimethylbenzene binary fuel mixtures. The simulations are run at both non-premixed and rich-premixed ($\phi_{\text{jet}} = 6$) conditions. The key inputs to the reaction model are presented in Table 7-1.

\textbf{Table 7-1 Initial conditions for the CHEMKIN closed homogeneous reactor simulation. (Temperature and pressure are kept constant. Surface temperature same as gas temperature)}

<table>
<thead>
<tr>
<th>Fuel mixture Second component</th>
<th>Aromatic fuel mole fraction (%)</th>
<th>Initial Temperature (K)</th>
<th>Initial Pressure (atm)</th>
<th>Initial Equivalence ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textit{n}-propylbenzene (PB)</td>
<td>35.4</td>
<td></td>
<td></td>
<td>Non-premixed and $\phi_{\text{jet}} = 6$</td>
</tr>
<tr>
<td>toluene (TL)</td>
<td>41.3</td>
<td>1600</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>\textit{m}-xylene (mX)</td>
<td>38.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,3,5-trimethylbenzene (TMB)</td>
<td>35.4</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 7-4 shows the comparison of the fuel consumption pathways for the four aromatic fuels, at \(t=0\) sec, under non-premixed conditions.
Figure 7-4 Comparison of fuel consumption pathways for the four aromatic fuel mixtures in a homogeneous reactor at constant temperature (1600 K) and pressure (1 atm) at t=0 sec for non-premixed flame: (a) PB flame; (b) TL flame; (c) mX flame; (d) TMB flame.

Figure 7-5 shows the comparison of the absolute rate of production or consumption for the four aromatic fuels, at t=1E-7 sec, under non-premixed conditions. Time equal to 1E-7 sec is selected for analyzing the fuel consumption pathways because approximately 40-50% of n-dodecane has decomposed at this time. Therefore, radicals are available from n-dodecane decomposition that could impact the growth or consumption of the parent aromatic fuel or the aromatic radicals that are formed initially from the thermal decomposition of the aromatic fuel.
Figure 7-5 Comparison of reaction pathway analysis of aromatic fuel consumption for the four fuels in a homogeneous reactor at constant temperature (1600 K) and pressure (1 atm) at t=1E-7 sec for non-premixed flame: (a) n-propylbenzene flame; (b) toluene flame; (c) m-xylene flame; (d) 1,3,5-trimethylbenzene flame.
The numerical simulation shows that, initially, $n$-propylbenzene can form benzyl radicals by C-C bond fission due to thermal decomposition. Furthermore, once chain-carrying radicals are available from $n$-dodecane decomposition, $n$-propylbenzene can also undergo H-abstraction by H or CH$_3$ radicals to form 1-phenyl-1-propyl radical, which subsequently forms styrene. Additionally, $n$-propylbenzene can undergo H-abstraction by H radicals to form 1-phenyl-2-propyl and 3-phenyl-1-propyl radicals that can consequently form C$_6$H$_5$C$_3$H$_5$-2 and benzyl radicals, respectively. The toluene mixture pyrolysis demonstrates that toluene is primarily consumed by C-H bond fission or H-abstraction by H radical to form benzyl radical. Additionally, the simulation shows that toluene can also react with H radicals to form C$_8$H$_6$CH$_3$ or benzene and a methyl radical. The comparison of the normalized mole fraction of toluene and $n$-propylbenzene shows that the consumption of $n$-propylbenzene is faster than that of toluene. The relative trend of consumption of the two fuels is consistent with previous work involving $n$-propylbenzene and toluene [67]; the weaker C-C bond in $n$-propylbenzene as compared to the C-H bond in the methyl side chain in toluene results in faster consumption of $n$-propylbenzene.

The $m$-xylene fuel mixture pyrolysis simulation shows that $m$-xylene primarily forms $m$-xylyl radical by C-H fission. Once $n$-dodecane undergoes decomposition, $m$-xylene undergoes H abstraction by the CH$_3$ or H radical to form $m$-xylyl. The 1,3,5-trimethylbenzene fuel simulation demonstrates that it forms C$_9$H$_{11}$ by C-H bond fission from the methyl side chain, or H-abstraction by H or CH$_3$ radicals. 1,3,5-trimethylbenzene can also react with a H radical to form $m$-xylene and a CH$_3$ radical. These simulations show that the four aromatic fuels are consumed through different reaction pathways at different rates, which result in differences in the initial pool of aromatic radicals.
The aromatics-LIF signal collected in each wavelength band, for small and large aromatics [145], is emitted from a number of different species. The previous work involving fluorescence of aromatic species showed that different aromatic molecules can have significantly different absorption cross-sections and fluorescence quantum yields [213, 214]. Due to the differences in the initial pool of aromatic radicals formed from the parent aromatic fuels, combined with incomplete knowledge of the effects of temperature on fluorescence quantum yield and absorption cross-section for the aromatic species, we are unable to calibrate the aromatic-LIF signal to obtain quantitative information about the gas phase species. Therefore, small and large aromatic results are presented on a normalized scale of 0-1, where each data set is normalized by the corresponding peak value of the LIF signal. If the peak LIF signal is located at the tube exit due to excitation of the fuel molecules, the peak LIF signal from the downstream location is selected as the value to normalize the data set. Therefore, the primary information gained from the aromatic-LIF measurement is the spatial development of aromatics and how this spatial distribution changes with fuel molecular structure. Moreover, the LIF measurements provide information about the effect of premixing the fuel jet on the spatial distribution of aromatics, which in turn can affect soot inception and soot growth through PAH condensation.

Figure 7-6 shows the 2-D spatial distribution of small aromatics for the five fuels, each presented on a normalized scale of zero to one. Therefore, the data can only be viewed qualitatively, not quantitatively. An iso-contour of 20% of the peak LIF signal of the n-dodecane flame, equivalent to 4200 counts, is shown on all the 2D LIF-images to illustrate the spatial extent of the LIF signal. Figure 7-6 shows that the signal strength is higher on the left side of the image as compared to the right side of the image. This LIF-signal intensity
difference on left and right half of the flame is caused by laser fluence attenuation due to absorption by PAHs as the laser beam traverses through the flame from the left to the right side of the image. Figure 7-6 (b)-(e) shows the presence of LIF signal at the tube exit, although the intensity of the LIF signal for the four flames is different. The LIF signal is present at the tube exit because the fuel molecules, \( n \)-propylbenzene, toluene, \( m \)-xylene, and 1,3,5-trimethylbenzene, are themselves single-ring aromatic species, and they fluoresce in the wavelength band in which the small aromatics LIF signal is collected. Furthermore, Fig. 7-2 (b) shows the temperature at the tube exit is similar, 700 K, for all the flames. Therefore, the difference in the intensity of LIF signal in the four aromatic flames at the tube exit is likely due to differences in the mole fraction of the aromatic species and their absorption coefficient at 266 nm [214].

A comparison of the spatial distribution of small aromatics in the \( n \)-dodecane flame, in Fig. 7-6 (a), relative to that in the four aromatic flames, in Fig. 7-6 (b)-(e), shows that the presence of an aromatic component in the fuel changes the spatial extent of the small aromatics for the four aromatic flames as compared to the \( n \)-dodecane flame. Furthermore, beyond the cone region at the tube exit, the 2-D small aromatics LIF structure is quite similar; the peak LIF signal occurs in the annular region at 5-10 mm HAB in the aromatic fuels and at 10-20 mm HAB in the \( n \)-dodecane flame. The higher LIF signal intensity at lower HAB in the aromatic flames as compared to the \( n \)-dodecane fuel is due to the accelerated path to the formation of one and two ring aromatics from a fuel that contains one ring aromatics. Previous studies involving \( m \)-xylene [215, 216], \( n \)-propylbenzene [110, 122, 217], 1,3,5-trimethylbenzene [112, 113], and toluene [122, 218, 219] have shown direct pathways to polycyclic aromatic hydrocarbons from the initial fuel ring.
Figure 7-6 Two dimensional LIF image for small aromatics [normalized counts] for $\phi_{\text{jet}} = \text{Inf}$: (a) $n$-dodecane flame; (b) $n$-propylbenzene flame; (c) toluene flame; (d) $m$-xylene flame; (e) 1,3,5-trimethylbenzene flame.

Figure 7-7 Two dimensional LIF image for large aromatics [normalized counts] for $\phi_{\text{jet}} = \text{Inf}$: (a) $n$-dodecane flame; (b) $n$-propylbenzene flame; (c) toluene flame; (d) $m$-xylene flame; (e) 1,3,5-trimethylbenzene flame.
The comparison of the small aromatics for the four aromatics fuels, Fig. 7-6 (b)-(e), shows that the spatial distribution of small aromatics is similar for the four aromatic fuels. Downstream of the LIF signal from fuel florescence, the LIF signal intensity decreases. The initial decrease in the LIF signal is due to the decrease in the mole fraction of the aromatic fuel, since the total number of moles increases as a result of the \( n \)-dodecane decomposition. Furthermore, the diffusion of the aromatic fuel and formation of new aromatic species with different quantum yields as compared to the parent fuel may also result in the initial decrease in the LIF signal. Further downstream, the LIF signal increases as new one and two ring aromatics are formed. Comparison of the trend of the LIF signal from the \( n \)-dodecane and aromatic fuels on the centerline streamline shows that in the aromatic fuels, the LIF signal starts to increase at approximately 5 mm HAB; this HAB is similar to the height above the tube exit where the LIF signal is first detected in the \( n \)-dodecane flame. Therefore, the increase in LIF signal in the aromatic fuels is because of formation of one and two ring species from the decomposition products of \( n \)-dodecane. The radicals from \( n \)-dodecane decomposition may contribute to the growth of other one and two ring aromatics from one ring radicals like benzyl, \( m \)-xyllyl, styrene, and others, which are formed from parent aromatic fuels. Further downstream, the LIF signal decreases again as these small aromatics form larger PAHs, are oxidized, or are consumed via soot growth.

The large aromatics are shown in Fig. 7-7; each of the five figures have been normalized by the corresponding peak value of the LIF signal and all use a normalized color scale of zero to one. The five figures can only be compared qualitatively. The 2-D spatial distribution of large aromatics for the \( n \)-dodecane flame and the four aromatic flames is similar, although the large aromatics in the \( n \)-dodecane flame are shifted downstream from those in the aromatic-fueled
flames; the peak LIF signal intensity occurs in the flame annular region as compared to on the flame centerline for all five fuels. In spite of the similarities in the 2-D structure between the \textit{n}-dodecane and four aromatic flames, there are some differences that are evident from Fig. 7-7. In aromatic fuels, the LIF signal is detected over a larger spatial extent, from approximately 3 mm to 40 mm HAB, as compared to 8 mm to 35 mm HAB for the \textit{n}-dodecane flame. The earlier detection of large aromatics LIF signal in a flame with an aromatic fuel component as compared to the \textit{n}-dodecane flame is expected, as the aromatic fuels contain a single ring aromatic, and so the growth to large PAHs is accelerated. Along the centerline streamline, the LIF signal increases first due to dominant PAH formation processes and then decreases at further downstream locations as aromatics are oxidized, form larger PAH, or contribute to soot growth through PAH condensation.

At the partially-premixed condition, the small and large aromatics 2-D spatial distribution for the $\phi_{\text{jet}} = 6$ flames are presented in Figs. 7-8 and 7-9. The LIF signals from the flames presented in Figs. 7-8 and 7-9 have been normalized by the corresponding peak value. A comparison of the small aromatics of the \textit{n}-dodecane flame, in Fig. 7-8 (a), to the aromatics flame shown in Fig. 7-8 (b)-(e), shows that addition of an aromatic component to \textit{n}-dodecane results in a change in the spatial distribution of small aromatics. The \textit{n}-dodecane flame has peak LIF signal in a region close to the flame centerline at 20-25 mm HAB. However, the aromatic fuel has a peak LIF signal in the flame annular region between 7 mm and 22 mm HAB. Similar to the aromatic distribution in the non-premixed flames, Fig. 7-8 (b)-(e) shows that the small aromatic distribution is similar for the four aromatics fuels in the premixed flames.

The large aromatic spatial distribution for the \textit{n}-dodecane, $\phi_{\text{jet}} = 6$ flame shown in Fig. 7-9 (a) has a low signal-to-noise ratio due to decreasing concentration of large aromatics; the LIF
Figure 7-8 Two dimensional LIF image for small aromatics [Normalized counts] for $\phi_{jet} = 6$: (a) $n$-dodecane flame; (b) $n$-propyl benzene flame; (c) toluene flame; (d) $m$-xylene flame; (e) 1,3,5-trimethyl benzene flame.

Figure 7-9 Two dimensional LIF image for large aromatics [Normalized counts] for $\phi_{jet} = 6$: (a) $n$-dodecane flame; (b) $n$-propyl benzene flame; (c) toluene flame; (d) $m$-xylene flame; (e) 1,3,5-trimethyl benzene flame.
signal is comparable to the noise at 30-40 mm HAB. A comparison of the large aromatics in
the aromatic fuel in Fig. 7-9 (b)-(e) and n-dodecane fuel in Fig. 7-9 (a) shows that the spatial
distribution is similar, in spite of the differences in the small aromatics. The peak LIF signal is
located near the flame centerline at 20-25 mm HAB.

The discussion until now has focused on the effects of the addition of aromatic fuels and
premixing on the spatial development of the aromatic species, which provide important
information on the distribution of gas-phase species. The 2-D spatial distribution of the small
and large aromatics amongst the four aromatic fuels, within the measurement uncertainty, is
quite similar at a particular $\phi_{jet}$. Furthermore, premixing the fuel jet results in substantial
changes in the 2-D spatial distribution of the aromatic-LIF measurements in the aromatic fuels.
The peak LIF intensity of small and large aromatics decreases as a result of premixing.
Additionally, the first location of detection of large aromatics shifts to higher HAB due to
premixing. The decrease and shift in first location of detection of large aromatics to higher
HAB due to premixing is the result of a combination of chemical, dilution, and thermal effects,
which are discussed in detail in Chapter 5.

7.4 Soot volume fraction distribution

This section discusses the effects of aromatic fuel addition to n-dodecane and premixing on
the 2-D distribution of soot. Figure 7-10 shows the 2-D $f_v$ obtained using LII for the five fuels.
The n-dodecane flame, shown in Fig. 7-10 (a), is on a scale of 8 ppm, while the four aromatic
flames, shown in Fig. 7-10 (b)-(e), are on a scale of 18 ppm. An iso-contour of 1 ppm is shown
on each of the five figures to compare the spatial extent of the $f_v$. Figs. 7-10 and 7-11 show
banding of the LII images since each 2-D LII image is compiled by stitching three or four
flame images at different HAB; variation in the laser intensity across the laser sheet also
contributes to banding in the images. A comparison of Fig. 7-10 (a) with Fig. 7-10 (b)-(e) shows that the 2-D structure of \( f_v \) for the four aromatic fuels is similar, but is substantially different to that of the \( n \)-dodecane flame.

In the four aromatic fuels, shown in Fig. 7-10 (b)-(e), the first location of detection of LII signal in both the annular region and along the centerline is quite similar. Here, the LII signal is first detected at approximately 6 mm HAB as compared to 12 mm HAB for the \( n \)-dodecane flame. The earlier detection of LII signal in the aromatic flames is expected, as addition of an aromatic fuel to \( n \)-dodecane results in earlier formation of large aromatics, as discussed in Section 7.3, which would result in soot inception at lower HAB. The first detection of LII signal at similar HAB for the four aromatic fuels is consistent with the large aromatics-LIF results. The LIF signal from large aromatics is also first detected at similar HAB for the four aromatic fuels. Furthermore, the four aromatic flames emit smoke, \( i.e., \) the soot produced is not oxidized completely. This could be because peak \( f_v \) in the aromatic flames is higher, by a factor of 2.6-3.9, as compared to the \( n \)-dodecane flame. In co-flow ethylene diffusion flames [184], the peak centerline temperature decreased by approximately 150 K due to the increase in peak \( f_v \) from 6 ppm to 18 ppm. In the current study, the higher peak \( f_v \) in the aromatic flames lowers the local flame temperature due to soot radiation cooling, thereby reducing the soot oxidation rate [20].

Numerical simulation of fuel pyrolysis in a homogeneous reactor at a constant temperature of 1600 K using aromatic fuels chemistry from Malewicki et al. [212] is conducted in order to identify chemical effects of the five fuels on the key species involved in the soot formation processes. The results from the homogeneous reactor are not meant to directly simulate the flames. To stay as consistent as possible in analyzing the chemistry across the test fuels,
Figure 7-10 Two dimensional LII image for $f_v$ [ppm] for $\phi_{jet} = \text{Inf}$: (a) $n$-dodecane flame; (b) $n$-propylbenzene flame; (c) toluene flame; (d) $m$-xylene flame; (e) 1,3,5-trimethylbenzene flame. Note scale of $n$-dodecane is on left while for the four aromatic fuels scale is on right. The dotted line is an iso-contour of 1 ppm.

Figure 7-11 Two dimensional LII image for $f_v$ [ppm] for $\phi_{jet} = 6$: (a) $n$-dodecane flame; (b) $n$-propylbenzene flame; (c) toluene flame; (d) $m$-xylene flame; (e) 1,3,5-trimethylbenzene flame. Note scale of $n$-dodecane is on left while for the four aromatic fuels scale is on right. The dotted line is an iso-contour of 1 ppm.
we were looking for a single mechanism that had chemistry for \( n \)-dodecane, \( n \)-propylbenzene, toluene, \( m \)-xylene, and 1,3,5-trimethylbenzene. Malewicki et al. [212] is the only mechanism that has all five fuels and therefore, this mechanism was used. Fig. 7-12 shows that the peak acetylene concentration is higher in the \( n \)-dodecane flame than for the four aromatic fuels. Therefore, the increase in the peak \( f_v \) in aromatic fuels as compared to \( n \)-dodecane is due to an increase in aromatic species, as discussed in Section 7.3, which would result in increase in soot inception and soot growth due to PAH condensation. Additionally, Fig. 7-10 shows that for the \( n \)-dodecane flame, the peak \( f_v \) has a similar magnitude in the annular region and as on centerline. However, for aromatic fuels, the peak \( f_v \) at each HAB occurs in a narrow annular region. The peak \( f_v \) is higher in the annular region by approximately a factor of two as compared to the peak \( f_v \) on the centerline, which indicates that aromatic chemistry tends to have a greater influence on soot in the annular region as compared to the centerline. The higher percentage increase of peak \( f_v \) in the annular region as compared to the centerline could be due to enhanced aromatics production as well as higher temperature in the annular region.
Figure 7-12 Comparison of acetylene mole fraction for the four aromatic fuel mixtures in a homogeneous reactor at constant temperature (1600 K) and pressure (1 atm) (a) non-premixed condition; (b) partially-premixed condition ($\Phi_{\text{jet}} = 6$).

Figure 7-11 shows the 2-D spatial $f_v$ at the $\Phi_{\text{jet}} = 6$ condition. The $n$-dodecane result is on a scale of 3 ppm, while the aromatic flame results are on a scale of 9 ppm. The addition of air to the fuel jet substantially changes the soot field for the aromatic fuels. In contrast to the non-premixed flames, the premixed aromatic flames do not emit soot. Additionally, the $n$-dodecane and aromatic fuel flames have similar $f_v$ distributions; the soot field is more uniform across the cross-section with the peak $f_v$ location closer to the centerline. Similar to the non-premixed cases, LII signal is first detected at lower HAB in the aromatic flames as compared to the $n$-dodecane flame. Furthermore, the aromatic fuels have a larger spatial extent of LII, from approximately 10 to 50 mm HAB as compared to 18 to 45 mm HAB in the $n$-dodecane flame. The large spatial extent of LII in the aromatic flames is likely a result of earlier formation of soot in aromatic fuels, spurred by accelerated growth of aromatic species. Subsequently, the large peak $f_v$ in aromatic fuel flames needs more time, or height, for soot oxidation. The peak $f_v$ in aromatic fuels is a factor of 2.4-3.0 higher as compared to the $n$-dodecane flame.
The comparison of the $f_v$ spatial distribution for aromatic fuels in Fig. 7-10 and Fig. 7-11 shows that the addition of air to fuel causes the peak $f_v$ location to shift from the annular region in the non-premixed flames to a more uniform distribution near the centerline in the $\phi_{jet} = 6$ flames. This shift in peak $f_v$ location with premixing is identical to the trend in the location of the peak large aromatics LIF signal, observed in Fig. 7-7 and Fig. 7-9. In the non-premixed flames, Fig. 7-7 (b)-(e) shows that the peak LIF signal is located in the annular region at 6-20 mm HAB, while in $\phi_{jet} = 6$ flames, Fig. 7-9 (b)-(e) shows that the peak LIF signal is located closer to the centerline at 20-25 mm HAB. It is likely that the transition of peak LIF signal from annular to centerline due to premixing results in an increase in soot inception and soot growth due to PAH condensation on the centerline as compared to the annular region. As a result, the peak $f_v$ location transitions from the annular region to the centerline. A transition of peak $f_v$ location from the annular region to the flame centerline has also been reported in ethylene flames [20, 184]. In ethylene flames, Smooke et al. [184] observed the peak $f_v$ location shifted from the centerline to the annular region with decreasing nitrogen dilution of the fuel jet. Numerical simulation of the flames by the same authors show that the change in the soot field is due to the increase in soot residence time in the annular region and variations in the relative importance of soot inception and growth processes. In the current work, the transition behavior of the soot field is observed due to the addition of air, which has both the chemical/dilution effects of oxygen and the dilution effects of nitrogen.

### 7.5 Effect of fuel structure and premixing on peak soot volume fraction

Figure 7-13 shows the comparison of peak $f_v$ in the whole domain for the five fuels and on the centerline for three $\phi_{jet}$ at two nitrogen ($N_2$) flow rates, 0.2 slpm and 0.48 slpm. The data for peak $f_v$ is not reported for $n$-dodecane, 0.48$N_2$ flames since they were not studied in the
previous program [145, 146]. The 95% confidence interval (CI) for the peak $f_v$ in the annular region of the smoking flame, discussed in Appendix F, is ±15%, while the 95% CI for the peak $f_v$ in non-smoking flames and peak $f_v$ on centerline of smoking flames is ±4%.

![Figure 7-13](image)

**Figure 7-13 Effect of fuel structure on peak $f_v$ [ppm] in (a) whole domain; (b) centerline. Error bars show ±15% measurement uncertainty.**

In the current study, the fuel jet dilution level is increased from standard burner operation at 0.2 slpm to 0.48 slpm N$_2$ flow rate for the four aromatic fuels. The 0.48 slpm N$_2$ dilution level was selected to be consistent with our previous work involving the $m$-xylene/$n$-dodecane fuel [145, 146], in which 0.48 slpm N$_2$ flow rate resulted in a non-smoking flame for the $m$-xylene/$n$-dodecane fuel. At 0.48 slpm N$_2$ flow rate, all non-premixed and premixed aromatic fuel flames except the 1,3,5-trimethylbenzene/$n$-dodecane, non-premixed flame have a closed tip i.e., all soot that is produced is oxidized. The soot emission in the 1,3,5-trimethylbenzene/$n$-dodecane flame could be a result of higher peak $f_v$ produced in the 1,3,5-trimethylbenzene/$n$-dodecane flame as compared to other aromatic fuels, as is evident in Fig. 7-13.
Figure 7-13 (a) shows that the \(n\)-propylbenzene/\(n\)-dodecane, toluene/\(n\)-dodecane, and \(m\)-xylene/\(n\)-dodecane fuels, within the measurement uncertainty, have similar peak \(f_v\) except at the \(\phi_{\text{jet}}=\text{Inf}-0.2\text{N}_2\) condition; at this condition, the toluene/\(n\)-dodecane flame shows higher peak \(f_v\) as compared to the \(m\)-xylene/\(n\)-dodecane flame. Furthermore, the 1,3,5-trimethylbenzene/\(n\)-dodecane flame has a higher peak \(f_v\) as compared to the \(n\)-propylbenzene/\(n\)-dodecane, toluene/\(n\)-dodecane, and \(m\)-xylene/\(n\)-dodecane flames at all six flame conditions. In the smoking flames, the peak \(f_v\) is located in a narrow annular region of 0.5 mm at each HAB. Due to a high gradient of \(f_v\) in this 0.5 mm, the 95% confidence interval of the LII measurement is greater in the annular region as compared to the centerline. This higher measurement uncertainty in the annular region of smoking flames may be a reason for differences in peak \(f_v\) in the toluene/\(n\)-dodecane and \(m\)-xylene/\(n\)-dodecane flame at the \(\phi_{\text{jet}}=\text{Inf}-0.2\text{N}_2\) condition, which is not evident in the non-smoking flames.

In addition, Fig. 7-13 (b) shows that on centerline, the peak \(f_v\) is similar in the \(n\)-propylbenzene/\(n\)-dodecane, toluene/\(n\)-dodecane, and \(m\)-xylene/\(n\)-dodecane flames for all six flame conditions. 1,3,5-trimethylbenzene/\(n\)-dodecane flames produce higher peak \(f_v\) as compared to the other three aromatic fuels. However, at the two premixing levels of the fuel jet, the differences in the peak \(f_v\) among the aromatic flames, at a given \(\phi_{\text{jet}}\), are small in comparison to the resolution of the experiment. To the best of the authors’ knowledge, this effect of premixing on \(f_v\) for these aromatic fuels has not been reported earlier, and therefore, provides a new dataset to test chemical models for four aromatic fuels under different levels of dilution, at both non-premixed and partially-premixed conditions.

The relative sooting tendency of the four aromatic fuels is different in the present study as compared to the YSI values reported in McEnally and Pfefferle [67]. The differences in the
sooting tendency of the aromatic fuels between YSI and present study could be a result of differences in the chemistry in the two studies. In YSI, the aromatic fuels react in the chemical and thermal fields of a methane flame, while in the current study, the chemical and thermal fields are from a \( n \)-dodecane flame. The differences in the chemistry of methane and \( n \)-dodecane flames can create differences in the local flame conditions, particularly species, which can impact soot formation processes. Additionally, in YSI, small dopant levels are added to the methane flame, while in the current work, nearly 25% by volume of the fuel comes from the aromatics; therefore, the second fuel can significantly impact the local flame conditions. Conturso et al. [120] has also reported differences in the sooting tendency of ethylene/aromatic fuel mixtures and YSI values.

Numerical simulation of fuel pyrolysis, using the chemical mechanism from Malewicki et al. [212] in a homogeneous reactor at constant temperature and pressure, is used to compare the pyrene mole fraction amongst the four aromatic fuel mixtures. The pyrene mole fraction is compared because pyrene dimerization is used as the nucleation reaction in several soot models [176, 177]. The simulations are performed at constant temperature to isolate the chemical effects of the initial fuel mixture on the pyrene mole fraction. These simulations in Fig. 7-14 (a) show that the pyrene mole fraction is similar for the \( n \)-propylbenzene/\( n \)-dodecane, toluene/\( n \)-dodecane, and \( m \)-xylene/\( n \)-dodecane fuels, while the pyrene mole fraction is considerably higher in the 1,3,5-trimethylbenzene/\( n \)-dodecane fuel.

Figure 7-15 shows that in 1,3,5-trimethylbenzene, a higher mole fraction of methylnaphthalene (A3CH\( \_3 \)) is initially produced as compared to the other three aromatic fuels. The higher level of A3CH\( \_3 \) results in higher pyrene (A4) production in the 1,3,5-trimethylbenzene fuel as compared to the \( n \)-propylbenzene, toluene, and \( m \)-xylene fuels; A3CH\( \_3 \) can form from
DIMERS196 (1-(phenylmethyl)-3,5-dimethylbenzene) through the pathway described in Gudiyella et al. [113]. Here, DIMERS196 can form from the reaction of the 1,3,5-trimethylbenzyl radical and benzene, followed by H atom removal. Figure 7-14 shows that the trend in pyrene mole fraction amongst the four aromatic fuels is consistent under both non-premixed and premixed conditions, $\phi_{jet} = 6$. Furthermore, comparison of the pyrene mole fraction in Fig. 7-14 (a) and (b) shows that the peak concentration of pyrene decreases with premixing, which would result in a decrease in soot nucleation rate.

Figure 7-14 Comparison of pyrene (A4) mole fraction for the four aromatic fuel mixtures in a homogeneous reactor at constant temperature (1600 K) and pressure (1 atm) (a) non-premixed condition; (b) partially-premixed condition ($\phi_{jet} = 6$).
Figure 7-15 Comparison of methylanthracene (A3CH₃) mole fraction for the four aromatic fuel mixtures in a homogeneous reactor at constant temperature (1600 K) and pressure (1 atm) (a) non-premixed condition; (b) rich premixed condition (ϕjet =6).

For the four aromatic fuels, Fig. 7-13 (a) shows that premixing the fuel jet tends to reduce the peak $f_v$ at both nitrogen flow rates. The percentage reduction in the peak $f_v$ in the 0.2N₂ and 0.48N₂ flames is approximately 55-60% and 30-40%, respectively. The reduction in the peak $f_v$ with premixing can be due to a combination of chemical, dilution, and residence time effects, as identified in previous studies [86, 198, 199].
Chapter 8 Effect of fuel volatility on emissions

In practical devices like gas turbine engines, the physical properties of the fuel have a dominant impact on the engine’s performance. Experiments in a model gas turbine combustor help to understand the fuel volatility effect on emissions in a more realistic combustion device. This chapter starts with a brief description of the combustor facility, the fuel injector, and the air/fuel delivery system. The operating procedure and conditions for the present study are discussed next. Following that, the results for the visible flame height, temperature measurements, aromatic species distributions, and soot distributions from the laminar flame configuration are presented. Finally, the soot results obtained for a baseline fuel, JP8 (POSF 5699), and the two fuel mixtures are discussed. One of the outcomes of this work is to connect the laminar flame response to those in a more realistic configuration to understand the applicability of the results in the Santoro burner with pre-vaporized liquid fuels to configurations where the fuel is not pre-vaporized.

8.1 Model gas turbine combustor

The schematic of the model gas turbine combustor is shown in Figure 8-1. It consists of two sections: the inner section where the combustion occurs and the outer co-flow section for regenerative cooling.
Figure 8-1 Schematic of model gas turbine combustor [134].

The compressed air from the air delivery system enters the outer co-flow section of the combustor. The passage through this section pre-heats the air thereby cooling the quartz window on the combustor chamber and removing the heat from the exhaust steam. The preheated air then enters an electric heater, where it can be heated to a maximum temperature of 800 K. The heated air enters the combustion chamber after passing through a 7.39 mm inlet venture and a 45° flat vane swirler. The schematic of the air swirler is shown in Figure 8-2. The geometric based swirl number based on the equation 5-1, given by Beer and Chigier [220] is 0.69.

\[
S_n = \frac{2}{3} \left[ 1 - \frac{(D_h / D_n)^3}{1 - (D_h / D_n)^2} \right] \tan \varphi
\]

8-1

where, \(D_h\) and \(D_n\) are the hub diameter and nozzle outer diameter, respectively, and \(\varphi\) is the swirl vane angle. It is used to impart angular momentum to the air stream which helps to improve fuel-air mixing. The premixed fuel-air mixture then flows into the 45 mm diameter, 307mm long combustion chamber.
The combustion products exit the combustor through a choked nozzle. The choked inlet and outlet helps to isolate the impact of combustion instabilities on inlet air or fuel flow rate and avoid the pressure oscillations from the exit section to propagate to the combustion. The exit nozzle is maintain at a temperature of 400° F using air and water nozzles. Two quartz windows of 12.5 mm in diameter are installed at the exit of the combustor to provide optical access for laser extinction technique. The quartz windows are purged with nitrogen gas to maintain the temperature of the windows and prevent soot deposition on them.

The liquid fuel injector used in this study is the same as used in Iyer et al [147]. It consists of two concentric stainless-steel tubes. The liquid fuel under pressure from the fuel delivery system enters the inner tube of the injector and is forced out through the 0.005” diameter, 12 radial injector holes. The injection point is 37mm upstream of the dump plane.

A part of the primary cooled air is diverted to flow through the annular region surrounding the inside tube of the injector to prevent the fuel from vaporizing inside the inner tube. The annulus is tapered at the end to create a shearing force to break the liquid fuel into small droplets. A stainless steel bluff body is attached at the end of the injector for flame anchoring. The tip of
this bluff body is coated with zirconium oxide to act as a thermal barrier. The fuel droplets are vaporized by the energy from the heated air.

![Diagram of fuel injector](image)

**Figure 8-3 Schematic diagram of the fuel injector [134].**

The air supply system of the combustor is shown in Figure 8-4. The air from the compressor is dried and filtered to remove the moisture and oil before it passes through the metering system. An adjustable dome loader valve controls the air pressure upstream of the venturi. The air mass flowrate is adjusted by selecting one or more of the venturis. The temperature and pressure are monitored upstream of the critical venture orifices. A jewel orifice (#5 in Figure 8-4) supplies the cold air to the injector to prevent the fuel from vaporizing before the injector.

Figure 8-5 shows the schematic layout of the liquid fuel delivery system. The liquid fuel is stored in three tanks of combined capacity of 48 liters. The liquid fuel is pressurized at 3.5MPa using Helium. The fuel flow rate is metered using an electronically controlled variable-area, cavitating, needle valve (Whitey, Model SS 21RS4) and a Hoffer turbine flowmeter (model MF 1/2x30B). A trickle flow is provided to maintain a minimum pressure in the liquid fuel line to prevent the oxidizer or combustion products from entering the injector.
Figure 8-4 Air delivery system [134].

Figure 8-5 Liquid fuel delivery system [134].
8.2 Model gas turbine combustor diagnostics

The line-of-sight soot volume fraction at the exit of the combustor is determined using laser extinction technique. The laser extinction optical setup is shown in Figure 8-6. The laser extinction measurements are obtained using a Coherent Innova 70 (2W) argon ion laser at a 514.5 nm wavelength. The laser input is 0.5 W and the beam is modulated at 1000 Hz using a mechanical chopper. A beam splitter (30%:70%) is used to deflect and monitor the incident laser beam ($I_0$) by a PIN-10D silicon photodiode. A neutral density filter (NDF) is used before this photodiode to reduce the beam intensity to levels so that the photodiode operates in its linear region.

![Figure 8-6 Laser extinction setup for dump combustor][221]

The beam directed towards the combustor section is passed through a collimator to obtain a parallel beam in the extinction section. The total path length through the combustor is 45 mm. The transmitted power, $I$, is measured using a similar photodiode. An aperture is used before the photodiode to eliminate the back reflections. The output signals from both photodiodes are
converted to voltages using a trans-impedance amplifier and then fed into a lock-in amplifier to reduce the noise from the surrounding environment. The data are collected by a National Instruments data acquisition system (NI-PCI-6110) at a sampling rate of 100 samples/sec for 4 sec.

8.3 Operating conditions

The model combustor is capable of running both gaseous and liquid fuels. Initially, natural gas is used to establish a steady state combustion environment in the combustor. Then, liquid fuel is introduced at a low flow rate through the injector. The flow of natural gas is then decreased gradually and that of liquid fuel increased simultaneously. The natural gas is shut off completely to achieve a steady state liquid fuel flame.

The fuel matrix, shown in Table 8-1, is comprised of two binary mixtures: \( n \)-heptane/\( n \)-dodecane, and \( n \)-hexadecane/\( n \)-dodecane, a high boiling point fuel; \( n \)-hexadecane has a boiling point of 287˚C as compared to 216˚C for \( n \)-dodecane and 98˚C for \( n \)-heptane. The two binary mixtures are chosen such that the carbon fraction of \( n \)-dodecane and the added hydrocarbon is constant.

<table>
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<th>Table 8-1 Fuel Matrix</th>
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The flames investigated are non-premixed (jet equivalence ratio $\phi_{\text{jet}} = \text{Inf}$) and rich premixed ($\phi_{\text{jet}} = 24$ and $6$). The total carbon flow rate is held constant for all the flames at 0.011 mole/min.

The carbon flow rate is defined as the summation of the product of each component flow rate and the corresponding number of carbon atoms. The carbon flow rate is fixed to match carbon flow from the base flame, a 75% $n$-dodecane and 25% $m$-xylene mixture [145]. The flow rate of nitrogen, 0.2 slpm, is used to carry the vaporized fuel to obtain a stable flame.

The effect of fuel volatility on soot emissions, for the fuels listed in Table 8-1, is investigated in a model gas turbine combustor. This experiment replicates the complexity of bulk mixing, turbulent mixing, and spray as is present in a real combustor operating on liquid fuels. The combustor has been used in previous studies on combustion instability, soot, and emissions [149, 222]. In addition to the two binary fuel mixtures, JP-8 (POSF 5699) fuel is tested to compare the results obtained in this study to previous published data [222], which involved testing of soot emission from JP-8 under the same experimental conditions. The experimental conditions for the model gas turbine combustor are outlined in Table 8-2. The air mass flow rate and inlet temperature are kept constant at 32 g/s and 560±10K for all the fuels tested. The inlet air temperature is measured at the location upstream of the critical venturi.

The soot production can be impacted by the fuel droplet size and droplet evaporation time. The initial droplet size depends on the type of injector used [133]. For a particular size droplet, the droplet evaporation time would depend on the initial temperature of the droplet and the adiabatic flame temperature. A higher inlet temperature would increase the adiabatic flame temperature, which would result in faster droplet evaporation. The faster evaporation results in more premixed combustion, leading to less soot production. The inlet air temperature is held constant for all the fuels in order to make the comparison between different fuels possible. The
adiabatic temperature of both fuels $n$-heptane and $n$-hexadecane is quite similar, close to 2265 K [223]. Hence, the flame temperature is expected to be similar for both the fuels at a particular equivalence ratio. The global equivalence ratio ($\phi_{\text{global}}$) is varied from 0.9 to 1.8 by changing the fuel flow rate. An exit nozzle of 10.2 mm diameter is used to choke the flow to create a mean chamber pressure of 0.51 MPa. The combustor chamber pressure is held steady at 5 atm, within measurement uncertainty, for $\phi_{\text{global}}$ from 0.9 to 1.8. The flames are both statically and dynamically stable under these operating conditions. The fuels used had purity of > 99% and 95% for the jet flame experiment and the model combustor, respectively.

| Table 8-2 Experimental conditions for model gas turbine combustor. |
|---------------------------------|-----------------|
| Air mass flow rate              | 32 g/s          |
| Inlet air temperature           | 560 K±10 K      |
| Injector                        | MP, 12 hole, 0.005” diameter |
| Swirl angle                     | 45˚             |
| Chamber Pressure                | 0.51MPa (5 atm) |
| Chamber Length                  | 307 mm          |

8.4 Laminar flame: visible flame heights

Figure 8-7 shows the visible flame images for all the flames obtained using a Canon camera at same operating settings (ISO=80, f-stop, and exposure time). From left to right, the flames are $C_7 \phi_{\text{jet}} = \text{Inf flame}$, $C_{16} \phi_{\text{jet}} = \text{Inf flame}$, $C_7 \phi_{\text{jet}} = 24$ flame, $C_{16} \phi_{\text{jet}} = 24$ flame, $C_7 \phi_{\text{jet}} = 6$ flame, and $C_{16} \phi_{\text{jet}} = 6$ flame.
In this work, the flame height is defined as the distance from the tube exit to the flame tip. The flame tip is obtained from the visible flame images, shown in Fig. 8-7. The flame tip has a fluctuation of ± 2 mm over the duration of the experiment. At a particular $\phi_{\text{jet}}$, within measurement uncertainty, the flame heights are similar for both the fuels. As the level of premixing is increased, the flame height decreases. The flame heights decrease by approximately 18% for both the fuels from the $\phi_{\text{jet}} = \text{Inf}$ condition to $\phi_{\text{jet}} = 6$ condition. In these six buoyancy driven flames, the similar flame height, at a particular $\phi_{\text{jet}}$, indicates that the residence time in the flame for soot formation and oxidation is similar for the two fuels, if the soot nucleation is at similar height above burner (HAB).

8.5 Laminar flame: development of aromatics

Figure 8-8 shows the 2-D spatial development of small aromatics for the two fuels at three different $\phi_{\text{jet}}$. In all the 2-D LIF and soot volume fraction figures comparing the six flames, parts (a), (b), (c), (d), (e) and (f) show the 2-D profiles for $C_7 \phi_{\text{jet}} = \text{Inf}$ flame, $C_{16} \phi_{\text{jet}} = \text{Inf}$ flame, $C_7 \phi_{\text{jet}} = 24$ flame, $C_{16} \phi_{\text{jet}} = 24$ flame, $C_7 \phi_{\text{jet}} = 6$ flame, and $C_{16} \phi_{\text{jet}} = 6$ flame, respectively. The minimum and maximum value of the scale are shown on the top of each
figures, for example, [0 27000], [0 15000], and [0 6] means the lowest value of the scale is 0; and 27000, 15000, and 6 corresponds to the maximum value of the scale. At a particular $\phi_{\text{jet}}$, the 2-D profiles are plotted on the same scale for the two fuels. However, the scale is different for the three $\phi_{\text{jet}}$ to show the effect of premixing on the spatial development of small aromatics, large aromatics, and soot distinctly.

In Figure 8-8, an iso-contour of approximately 15% of the peak LIF count is shown in white on the 2-D plots for the three $\phi_{\text{jet}}$ to distinguish the spatial extent of the small aromatics for the two fuels. Figure 8-8 (a) and (b) show that the spatial distribution of the small aromatics is similar for both the fuels under non-premixed condition; however, the peak small aromatics LIF count is approximately 35% higher in the C$_{16}$ fuel as compared to the C$_{7}$ fuel. The first location of the detection of small aromatic LIF signal is similar for both the fuels; the small aromatics LIF signal is visible in the flame annular region at approximately 3 mm HAB and at 6 mm HAB on the flame centerline. The LIF signal from small aromatics initially increases as the one and two ring aromatic species formation processes are dominant. Further downstream, the signal peaks and then decreases as the small aromatics consumption processes through oxidation or formation of larger aromatics are dominant.

Figure 8-8 (c) and (d) shows that for the $\phi_{\text{jet}} = 24$ condition, the spatial distribution of small aromatics is similar for the two fuels; the small aromatics LIF signal is first detected in the annular region at lower HAB at approximately 4 mm HAB as compared to 7 mm HAB on the flame centerline. Similar to the $\phi_{\text{jet}} = \text{Inf}$ flame, the peak small aromatics LIF count is higher in the C$_{16}$ flame as compared to the C$_{7}$ flame by approximately 30%. The small aromatics spatial distribution for the two fuels at the $\phi_{\text{jet}} = 24$ condition is similar to the $\phi_{\text{jet}} = \text{Inf}$ condition.
Figure 8-8 Two-dimensional small aromatics [counts] obtained for: (a) $C_7\ \phi_{\text{jet}}=\text{Inf}$; (b) $C_{16}\ \phi_{\text{jet}}=\text{Inf}$; (c) $C_7\ \phi_{\text{jet}}=24$; (d) $C_{16}\ \phi_{\text{jet}}=24$; (e) $C_7\ \phi_{\text{jet}}=6$; (f) $C_{16}\ \phi_{\text{jet}}=6$.

Figure 8-9 Two-dimensional large aromatics [counts] obtained for: (a) $C_7\ \phi_{\text{jet}}=\text{Inf}$; (b) $C_{16}\ \phi_{\text{jet}}=\text{Inf}$; (c) $C_7\ \phi_{\text{jet}}=24$; (d) $C_{16}\ \phi_{\text{jet}}=24$; (e) $C_7\ \phi_{\text{jet}}=6$; (f) $C_{16}\ \phi_{\text{jet}}=6$.

However, for the two fuels, the peak count of small aromatics decreases at $\phi_{\text{jet}} = 24$ as compared to the corresponding $\phi_{\text{jet}} = \text{Inf}$ flame.

With increased level of air addition to the fuel, at $\phi_{\text{jet}} = 6$ shown in Figure 8-8 (e) and (f), the spatial distributions and the peak level of small aromatics are similar in both the fuels. It is possible that the LIF technique is unable to resolve the differences in the level of small
aromatics in the two fuels at the $\phi_{\text{jet}} = 6$ condition because of low signal-to-noise ratio. In addition to the decrease in the peak LIF count of small aromatics in the $\phi_{\text{jet}} = 6$ flame as compared to the $\phi_{\text{jet}} = 24$ flame, substantial differences are visible in the spatial distribution of small aromatics in the $\phi_{\text{jet}} = 6$ as compared to the $\phi_{\text{jet}} = \text{Inf}$ and 24 flames. First, in the $\phi_{\text{jet}} = \text{Inf}$ and 24 flames, the peak small aromatics LIF count is higher in the annular region than on the centerline. However, in the $\phi_{\text{jet}} = 6$ flames, the peak LIF count of small aromatics is near the centerline at 20-25 mm HAB. Furthermore, with the increase in the premixing, the location where small aromatics LIF signal is first detected on the flame centerline shifts to higher HAB; this location is approximately 6 mm HAB for $\phi_{\text{jet}} = \text{Inf}$ and 24 flames, and 10 mm HAB for $\phi_{\text{jet}} = 6$ flame. This shift in the location and reduction in small aromatics with more premixing could be due to a combination of dilution, chemical, thermal, residence time of small aromatics, and LIF signal quenching due to oxygen, as discussed in detail in Makwana et al. [146].

The differences evident in the peak level of small aromatics of the two fuels can be due to differences in temperature in the flame and/or chemical effects of the fuel. The comparison of radial temperature measurement at 5 mm HAB, shown in Fig. 8-10 (a)-(c), and the centerline temperature measurement until 20 mm HAB, shown in Fig. 8-10 (d)-(f), for the two fuels and three $\phi_{\text{jet}}$ indicate that within measurement uncertainty, the temperature is similar for the two fuels at a given $\phi_{\text{jet}}$. Therefore, in a similar temperature field, the difference in the peak level of small aromatics of the two fuels at a particular $\phi_{\text{jet}}$ is likely due to the chemical effect of the fuel breakdown process and growth to the one and two ring aromatics.
A detailed chemical mechanism developed as part of the program [11] was used to compare the pyrolysis of the pure \(n\)-dodecane and the \(n\)-heptane/\(n\)-dodecane fuel blend. In addition, the LLNL high temperature \(n\)-alkane mechanism [224] was used to compare the pyrolysis of the \(C_{16}\) and \(C_7\) fuels. Figure 8-11 shows the consumption of \(n\)-heptane, \(n\)-dodecane, and \(n\)-hexadecane in a pyrolysis simulation under homogeneous reactor conditions at a constant temperature and pressure of 1600 K and 1 atm. These simulations show that \(n\)-dodecane and \(n\)-hexadecane decompose more quickly than \(n\)-heptane. The faster decomposition of \(n\)-hexadecane results in higher concentrations of reaction products, including the \(C_3/C_4\) species that form the first aromatic ring. For example, Fig. 8-12 shows the comparison of the mole fraction of \(C_3H_3\) and \(C_4H_6\) species for the \(C_7\) and \(C_{16}\) fuel mixtures in a pyrolysis (with no air in reactants) simulation under homogeneous reactor condition at constant temperature (1600 K) and pressure (1 atm) using CHEMKIN. These simulations show that the peak mole fraction
of $\text{C}_3\text{H}_3$ and $\text{C}_4\text{H}_6$ is higher in $\text{C}_{16}$ fuel mixture as compared to the $\text{C}_7$ fuel mixture. The $\text{C}_3\text{H}_3$ radical can lead to benzene formation through a self-addition reaction [16]. The $\text{C}_4\text{H}_6$ can form $i$-$\text{C}_4\text{H}_5$ or $n$-$\text{C}_4\text{H}_5$, which can form benzene through pathways described in [16]. The homogeneous reactor simulation with addition of air to the fuel ($\phi_{\text{jet}} = 24$ and 6) under the same temperature and pressure conditions shows that the $n$-hexadecane decomposes faster than $n$-heptane even under premixed conditions.

![Figure 8-11](image)

**Figure 8-11** Comparison of the consumption of $n$-dodecane, $n$-heptane and $n$-hexadecane in a pyrolysis simulation under homogeneous reactor condition at constant temperature ($T=1600$ K) and pressure (1 atm) using CHEMKIN.
Figure 8-12 Comparison of C₃H₃ and C₄H₆ mole fraction for C₇ and C₁₆ fuel mixtures in a pyrolysis simulation under homogeneous reactor condition at constant temperature (T=1600 K) and pressure (1 atm) using CHEMKIN.

To complete the discussion of the LIF results, Fig. 8-9 shows the 2-D spatial development of large aromatics for the two fuels at three \( \phi_{\text{jet}} \). Figure 8-9 (e) and (f) includes LII signal at 30-35 mm HAB, which is comparable to the LIF signal at 20-25 mm HAB. The LII signal appears because the laser beam intensity could not be lowered further than 585\( \mu \text{J} \), as doing so would reduce the LIF signal-to-noise ratio in other flame conditions. As a result of the low signal levels, no conclusions can be drawn about the large aromatics in the \( \phi_{\text{jet}} = 6 \) flames.

Figure 8-9 (a) and (b) show that the spatial distribution of large aromatics is similar for C₁₆ and C₇ non-premixed flames; the large aromatics LIF signal is first detected at approximately 6 mm HAB and 11 mm HAB in the annular region and on the flame centerline, respectively. Similar to the small aromatics shown in Fig. 8-8 (a) and (b), the peak LIF count of large aromatics is higher in the flame annular region as compared to the centerline. Quantitatively, the peak large aromatic LIF count is similar, within measurement uncertainty, for both the fuel...
mixtures. Figure 8-9 (c) and (d) show that the spatial distribution of large aromatics for $\phi_{\text{jet}} = 24$ flames is similar to the $\phi_{\text{jet}} = \text{Inf}$ flames, shown in Fig. 8-9 (a) and (b). Within experimental uncertainty, the peak LIF count of large aromatics is similar for both the fuels. Similar to small aromatics discussed earlier, the peak LIF count of large aromatics decrease as compared to the non-premixed flame with the increase in air addition to fuel jet for both C$_{16}$ and C$_{7}$ fuels. As expected, for each flame condition, the HAB where large aromatics LIF signal is first detected is at higher HAB as compared to the location at which small aromatics LIF signal is first detected because large aromatics form from the small aromatics. The spatial or temporal development of small aromatics to large aromatics is discussed in detail in [146].

8.6 Laminar flame: soot volume fraction

Figure 8-13 shows the 2-D spatial development of soot volume fraction for the two fuels at three $\phi_{\text{jet}}$. An iso-contour of approximately 10% of peak soot volume fraction is shown to illustrate the spatial extent of LII signal and compare the results at three $\phi_{\text{jet}}$. The horizontal stripes visible in the images are an artifact from variation in the local fluence of the laser sheet. Figure 8-13 shows that the LII is first detected in the flame annular region, and further downstream, the soot field develops towards the flame centerline for all six flames. The spatial development of soot in this co-flow flame is consistent with the previous published literature on non-premixed and partially premixed flames [20].

With the increase in premixing level, the spatial extent of the LII signal reduces for both the fuels; the LII signal is detected until approximately 58 mm, 54 mm, and 45 mm HAB for the $\phi_{\text{jet}} = \text{Inf}, 24,$ and 6 flames, respectively. Furthermore, the location at which the LII signal is first detected in the annular region shifts further downstream with increased premixing for both
the fuels; the LII signal is first detected at approximately 12 mm, 15 mm, and 20 mm HAB in the flame annular region for the $\phi_{\text{jet}} = \text{Inf}$, 24, and 6 flames, respectively. Quantitatively, the peak soot volume fraction is slightly higher in the C$_{16}$ flame as compared to the C$_7$ flame for both non-premixed and rich premixed flames. Even though the differences in the soot volume fraction amongst the two fuels at a particular $\phi_{\text{jet}}$ is within the measurement uncertainty, the trend of slightly higher soot volume fraction in the C$_{16}$ flames as compared to the corresponding C$_7$ flames is repeatable. The trend of increase in soot volume fraction with increase in the carbon number in the $n$-alkane family is consistent with previous work [59, 60]; the threshold sooting index (TSI), a global sooting parameter, showed a trend of increasing TSI with increase in the carbon number of the $n$-alkane fuels.

The peak soot volume fraction is lower for the two fuels at the $\phi_{\text{jet}} = 24$ and 6 conditions as compared to the non-premixed flame. The percentage reduction in peak soot volume fraction is similar for both the fuels; the peak soot volume fraction reduces by approximately 18% and 50% for the $\phi_{\text{jet}} = 24$ and 6 flames, as compared to the non-premixed flames.
In order to understand the spatial location of peak soot volume fraction, the soot volume fraction on a streamline that passes through the flame center and maximum soot volume fraction along the downstream direction are plotted. Figure 8-14 (a), (b), and (c) show the comparison of the centerline soot volume fraction for the two fuels at $\phi_{\text{jet}} = \text{Inf}$, 24, and 6 flames, respectively. For all the three $\phi_{\text{jet}}$, the soot volume fraction increases initially due to dominant soot growth processes, reaches a peak, and then decreases at higher HAB as oxidation processes are dominant.

![Figure 8-14](image_url)

**Figure 8-14** Centerline comparison for C\textsubscript{16} and C\textsubscript{7} fuels: Soot volume fraction for (a) $\phi_{\text{jet}}$=Inf; (b) $\phi_{\text{jet}}$=24; (c) $\phi_{\text{jet}}$=6. Maximum soot volume fraction for (d) $\phi_{\text{jet}}$=Inf; (e) $\phi_{\text{jet}}$=24; (f) $\phi_{\text{jet}}$=6. Note: Plots are 1 mm moving average.

Figure 8-14 (d), (e), and (f) show the maximum soot volume fraction for the $\phi_{\text{jet}} =$ Inf, 24, and 6 flames, respectively, for the two fuels. At a particular HAB, higher value of maximum soot volume fraction as compared to the centerline soot volume fraction, indicates the peak soot volume location is in the flame annular region. The C\textsubscript{16} and C\textsubscript{7} $\phi_{\text{jet}}$ = Inf flames have a peak soot volume fraction of approximately 5 ppm, in both the flame annular region and on the
centerline. Similar to the non-premixed flames, the $C_{16}$ and $C_{7}$ $\phi_{jet} = 24$ flames have a peak soot volume fraction of approximately 4 ppm, in both the flame annular region and on the centerline. In contrast to the $\phi_{jet} = \text{Inf}$ and 24 flames, Fig. 8-14 (c) and (f) show that the $\phi_{jet} = 6$ flames have peak soot volume fraction of approximately 2.7 ppm on the flame centerline for both the fuels.

The LII measurements in the jet flames using pre-vaporized fuels shows that the $C_{16}$ fuel result in slightly higher peak soot volume fractions as compared to the $C_{7}$ fuel under both non-premixed and rich premixed conditions. With a nearly identical temperature field and soot residence time, the differences in the soot volume fraction between the two fuels are most likely due to the chemical effect of the fuel. In the laminar flame experiment, both fuels were pre-vaporized, whereas in a model combustor, both the differences in chemical structure and fuel volatility may impact the combustor soot emissions. In order to understand the effect of the fuel volatility of the two fuels: $n$-heptane and $n$-hexadecane, which varies by 189º C, on soot emission, the fuel mixtures are tested in a model combustor.

8.7 Soot emissions from the model gas turbine combustor

Figure 8-15 shows the comparison of line-of-sight soot volume fraction results as a function of $\phi_{global}$ for the two binary mixtures and JP-8 fuel. $\phi_{global}$ is defined as the ratio of inlet fuel-to-air ratio. The plot shows result from two different experiments for each of the three fuels. Each experiment is comprised of three or four sweeps in $\phi_{global}$ from 0.9 to 1.8 and then again from 1.8 to 0.9 in increments of 0.1. The uncertainty in the equivalence ratio is estimated to be $\pm 2.6\%$ [222]. The line-of-sight soot volume fraction at the exit of the combustor provides an estimate of the net soot produced in the combustor.
The soot emission increases with the increase in the $\phi_{\text{global}}$ for all the three fuels; this result is reflected in the laminar flame studies, where higher $\phi_{\text{jet}}$ results in higher peak soot volume fraction. Additionally, the increase in $\phi_{\text{global}}$ would result in lower adiabatic flame temperature, thereby leading to slower droplet evaporation. The slower evaporation rate may result in relatively bigger size droplets, at $\phi_{\text{global}} = 1.8$ as compared to at 1.0, to convect to the flame front, thereby increasing soot formation due to fuel rich regions. The comparison of soot volume fraction amongst the three fuels shows that the net soot produced by the two binary mixtures is substantially less as compared to the JP-8 fuel in the range of $\phi_{\text{global}}$ from 1.0 to 1.8. At $\phi_{\text{global}} = 1.8$, the soot emission from JP-8 is approximately 6 ppm, nearly a factor of six higher than the soot emission from the two fuel mixtures, which emit approximately 1 ppm of soot. Furthermore, for the two $n$-alkane fuels, the $\phi_{\text{global}}$ at which measurable amount of soot using the LE technique is first detected is at a richer $\phi_{\text{global}}$ of approximately 1.4 as compared...
to at approximately $\phi_{\text{global}} = 1.2$ for the JP-8 fuel. Additionally, the factor by which the soot volume fraction is higher in JP-8 fuel as compared to the two fuel mixtures, increases with the increase in $\phi_{\text{global}}$ from 1.4 to 1.8. Within experimental uncertainty, the C$_{16}$ and C$_{7}$ fuels have a similar amount of net soot production for $\phi_{\text{global}}$ of 1.0 to 1.8.

The JP-8 fuel emits more soot as compared to the two binary fuel mixtures because JP-8 contains a range of aromatic species, 20% by mass [225]; the aromatic components in a fuel can result in a higher soot production as compared to a fuel that has no aromatic content. The higher soot production in a fuel containing aromatic species is consistent with our recent study done in jet flames [146]. In the non-premixed flames, replacing 25% volume fraction of n-dodecane with m-xylene, thereby maintaining constant carbon flow rate, resulted in an increase in the peak soot volume fraction by approximately three times the amount produced in the n-dodecane flame. Furthermore, the m-xylene/n-dodecane flame emits smoke since the soot produced is not completely oxidized. This increase in soot production is because the m-xylene reacts to form radicals such as m-xylyl that react to form two-ring PAH, thereby accelerating the formation of larger aromatic species that are involved in formation of incipient soot particles. The faster production of PAH also leads to higher concentrations of these species, which increases the amount of soot mass through condensation processes.

The hypothesis of this study was that fuels with different boiling points would affect the fuel droplet vaporization processes, and that a fuel with a higher boiling point would produce higher levels of soot. However, Fig. 8-15 shows that soot emission from both the C$_{16}$ and C$_{7}$ fuels is quite similar in the gas turbine combustor. It is possible that the current design of the injector and combustor results in the complete vaporization of the fuel droplets before the combustion zone. If the fuel droplets are vaporized before the combustion zone, the impact of fuel boiling
point on soot emission may not be evident in the current experiment, just as it was not in the pre-vaporized laminar flame. In future, the fuel-air mixing and droplet size measurements need to be done to better interpret the results. The chemical effect of the fuel molecular weight on soot is expected to remain. However, the experiment in jet flames show that the chemistry has relatively small effect on the peak soot volume fraction, which cannot be resolved by the LE technique applied on the model gas turbine combustor.
Chapter 9 Conclusions and Future Work

9.1 Accomplishments and conclusions

The broad impact of this study was to better understand how integration of alternative fuels in the fuel supply chain would impact the emission characteristics of combustion devices. In particular, the study was designed to investigate how the chemical structure of the fuel impacts polycyclic aromatic hydrocarbons and soot formation in jet flames. Another objective of the study was to understand how fuel volatility impacts soot emission in a model gas turbine combustor.

A fuel test matrix was designed to investigate the effect of molecular structure and fuel volatility on emissions. The fuel test matrix included five fuels. \( n \)-Dodecane was used as the base fuel and was used to check consistency of the burner and results for all the experiments. In addition to \( n \)-dodecane fuel, four binary fuel mixtures were prepared by mixing \( n \)-dodecane with \( m \)-xylene, \( n \)-heptane, \( iso \)-octane, and methylcyclohexane. These four hydrocarbons represent the four major hydrocarbon classes found in alternative fuels: aromatic, normal paraffin, branched paraffin, and cyclo-paraffin. Additionally, in order to investigate effects of fuel volatility on soot emissions, binary mixture of \( n \)-dodecane with \( n \)-hexadecane was added to the test matrix. To investigate the effect of aromatic fuel molecular structure on soot precursors and soot, four single-ring aromatic fuels, \( n \)-propylbenzene, toluene, \( m \)-xylene, and 1,3,5-trimethylbenzene, were also studied. These fuels were chosen to understand the role of the number of methyl groups and the lengthening of the aliphatic chain on the aromatic ring in aromatic and soot formation.

A previously built jet flame burner system was re-designed during the course of this work to improve the reliability and durability of the vaporizer system. The new design enabled rapid
switching between the base flame and the binary mixture, which made it possible to troubleshoot and maintain operational consistency from day-to-day. In jet flames stabilized on this burner, the laser extinction technique has been successfully applied to obtain the soot volume fraction. Two-dimensional soot volume fraction measurement were obtained using the LII technique and calibrated using the laser extinction measurements. Qualitative 2-D aromatic species measurements for two size ranges of aromatics were obtained using planar-LIF. CHEMKIN simulations, using published fuel chemical mechanism, have been used to interpret the aromatic LIF results and understand differences in the pathways to soot precursors for different fuel molecular structures. Additionally, temperature measurements in the non-sooting part of the flame were obtained using a custom-built micro-thermocouple. The experimental results obtained in this work provide a comprehensive benchmark data set to validate the gas-phase kinetics for the formation of aromatic species and soot. The experimental data for different fuel molecular structures in the same experimental configuration is important for validation of comprehensive gas kinetics models that are being developed for high molecular weight fuels.

Furthermore, the research involved close coordination with two simulation groups, Dr. Xuan at Penn State and Dr. Katta at ISSI, to validate and improve the capability of the simulation models to capture soot formation in high molecular weight fuels. The computational simulation of the effects of premixing on soot formation processes, performed by Dr. Xuan’s group at Penn State, are presented in this work. Finally, a model gas turbine combustor has been successfully operated with liquid fuel and a laser extinction technique was applied to obtain the soot volume fraction leaving the combustor. The major conclusions from this work are discussed in the sub-sections below.
9.2.1 Effect of fuel composition and premixing on soot and aromatic species distributions in laminar, co-flow flames

The experimental results, from the four major hydrocarbon classes, demonstrate the substantial impact of aromatic species on peak levels of aromatic species and soot. The results also show that addition of the aromatic species changes the structure of the flame from non-smoking to smoking. Quantitatively, the reduction in peak soot when replacing the carbon in the \textit{m}-xylene with \textit{n}-heptane is a factor of approximately three. In addition, the spatial distribution of the aromatic species is substantially changed. The trends in peak small aromatics, large aromatics, and soot volume fraction are consistent amongst the four molecular structures: \textit{m}-xylene produces the highest, followed by methylcyclohexane and \textit{iso}-octane, and \textit{n}-heptane the least.

In premixed flames ($\phi_{\text{jet}} = 24$ and 6), normalizing the maximum soot volume fraction by the maximum for the \textit{n}-dodecane base fuel uncovered that the effect of fuel structure on maximum soot volume fraction is independent of the equivalence ratio of the fuel jet. A similar analysis for maximum soot along the centerline revealed a similar independence from equivalence ratio of the fuel jet, except for the $\phi_{\text{jet}} = 6$ \textit{m}-xylene flame. The data in this study demonstrate that the presence of an aromatic compound in the fuel leads to the largest effects on aromatic species and soot compared to the paraffin fuels that were studied.

For $\phi_{\text{jet}} = 24$, the flame with the \textit{m}-xylene fuel is smoking and has distinctly different in flame structure and spatial distribution of soot than the paraffinic fuels; in fact, it is quite similar to the non-premixed flame. For $\phi_{\text{jet}} = 6$, the \textit{m}-xylene flame is no longer smoking and its overall structure is similar to that for the paraffin fuels, albeit with higher levels of soot and LIF signals. In the \textit{m}-xylene flame, the transition from smoking to non-smoking is accompanied by a shift from a soot field that has an annular structure to one with a more uniform spatial
distribution of soot. This shift is accompanied by a movement of the peak soot volume fraction from a location near the flame from to the centerline of the flame. The iso-octane/n-dodecane and methylcyclohexane/n-dodecane fuels show a similar transition between the non-premixed and $\phi_{jet} = 24$ conditions. In paraffinic fuels, the data of peak soot volume fraction versus amount of large aromatics show a linear relationship; the linear relationship shows an indication that the aromatic species are a substantial source of carbon for soot growth in these flames.

Numerical simulations, performed by Dr. Xuan, were undertaken to investigate the physical and chemical processes responsible for the shift in the peak soot volume fraction location from the flame annular region to the centerline by considering iso-octane flames at a range of jet equivalence ratios. Numerical simulations capture the shift in peak soot location due to premixing. Similar to the soot volume fraction, the peak rate of soot nucleation, condensation, and surface growth processes shift from the annular region towards the centerline with premixing. The soot residence time also decreases in the flame due to premixing. The change in location of peak rates of soot formation processes, along with the decrease in the residence time, result in changes in the soot volume fraction spatial distribution.

The simulation shows that the location of peak PAH dimer concentration shifts from the annular region in the $\phi_{jet} = \text{Inf}$ flame to the centerline in the $\phi_{jet} = 6$ flame. This change in PAH dimer distribution results in a shift in the region where soot nucleation and PAH condensation rates peak. Additionally, PAH dimer concentration decreases with increased premixing, leading to a decrease in the soot nucleation rate. The reduction in soot nucleation rate, in turn, reduces soot number density, and therefore, soot surface area available for soot growth processes due to surface reactions and PAH condensation. Furthermore, the reduction in PAH
dimer concentration due to premixing also results in a reduction of soot growth due to PAH condensation.

9.2.2 Effect of aromatic fuel molecular structure on soot and aromatic species distributions in laminar, co-flow flames

The results of the four aromatic fuels, \textit{n}-propylbenzene/\textit{n}-dodecane, toluene/\textit{n}-dodecane, \textit{m}-xylene/\textit{n}-dodecane, and 1,3,5-trimethylbenzene/\textit{n}-dodecane, show that under non-premixed conditions, the addition of aromatic fuel to \textit{n}-dodecane results in substantial changes in the 2-D distribution of soot. Comparison of the four aromatic flames with \textit{n}-dodecane shows that aromatic chemistry tends to have a larger effect on the production of soot in the flame annular region as compared to the centerline. As a result, the \( f_v \) peaks in a narrow annular region in the aromatic flames as compared to a uniform soot distribution across the cross-section in the \textit{n}-dodecane flame. At the \( \Phi_{\text{jet}} = 6 \) condition, the aromatic fuels and \textit{n}-dodecane have a similar distribution of soot; however, the peak soot volume fraction and spatial extent of the LII signal is greater in the aromatic flames as compared to the \textit{n}-dodecane flame.

The comparison of the four aromatic fuels indicates that at a particular \( \Phi_{\text{jet}} \), the location of first detection of large aromatics LIF signal, and hence, LII signal, is found be at a similar heights above the tube exit. Quantitatively, LII results show that the \textit{n}-propylbenzene/\textit{n}-dodecane, toluene/\textit{n}-dodecane, and \textit{m}-xylene/\textit{n}-dodecane flames, within measurement uncertainty, produce similar levels of peak soot, while 1,3,5-trimethylbenzene/\textit{n}-dodecane produces a higher level of peak soot. Furthermore, the relative trend of peak soot amongst the four aromatic fuels is found to be the same for both non-premixed (\( \Phi_{\text{jet}} = \text{Inf} \)) and rich-premixed (\( \Phi_{\text{jet}} = 24 \) and 6) conditions.
9.2.3 Effect of fuel volatility on soot emission

The effect of fuel volatility on soot emissions was tested in a model gas turbine combustor; three fuels were studied: \( n \)-heptane/\( n \)-dodecane, \( n \)-hexadecane/\( n \)-dodecane, and JP-8. The laser extinction (LE) measurements indicate that the change in the fuel volatility did not affect the soot emissions in the model combustor operating at \( \phi_{\text{global}} = 1.0 \) to 1.8. The absence of the impact of fuel volatility on soot emission could be due to unique design of the injector and combustor and hence, it is recommended to test the fuel matrix in other types of combustors.

The JP-8 fuel has significantly higher soot emission as compared to the two fuel mixtures. In addition, the LE technique first detects soot emission approximately at richer \( \phi_{\text{global}} = 1.4 \) for the \( n \)-alkane fuel mixtures as compared to first detection at \( \phi_{\text{global}} = 1.2 \) for the JP-8 fuel. The JP-8 fuel emits more soot as compared to the two binary fuel mixtures because JP-8 contains a range of aromatic species, 20% by mass [29]; the aromatic components in a fuel can result in a higher soot production as compared to a fuel that has no aromatic content. The higher soot production in a fuel containing aromatic species is consistent with the study done in the jet flames.

The two binary fuel mixtures, \( n \)-heptane/\( n \)-dodecane and \( n \)-hexadecane/\( n \)-dodecane, flames were also tested in co-flow flame under non-premixed and rich premixed conditions to simulate the fuel rich conditions present in the primary zone of the combustor. This experiment aids in understanding the chemical impact of the two fuel mixtures on aromatics and soot volume fraction. The LII measurement shows that the \( n \)-hexadecane/\( n \)-dodecane fuel produces slightly higher peak soot volume fraction as compared to the \( n \)-heptane/\( n \)-dodecane fuel at all three \( \phi_{\text{jet}} \). However, the difference in soot volume fraction between the two fuels is within the measurement uncertainty of ±15%. Additionally, the \( n \)-hexadecane/\( n \)-dodecane produces approximately 35% higher peak level of small aromatics as compared to the \( n \)-heptane/\( n \)-dodecane/\( n \)-dodecane.
dodecane fuel at $\phi_{\text{jet}} = \text{Inf}$ and 24. For both non-premixed and premixed flames, the peak large aromatics level is similar for the two fuel mixtures, within the measurement uncertainty. The addition of air results in the decrease in the peak level of small aromatics, large aromatics, and soot volume fraction in $\phi_{\text{jet}} = 24$ and 6, as compared to in $\phi_{\text{jet}} = \text{Inf}$, for both the fuels.

9.2 Future work

To aid in the continuous development of numerical models, it is necessary to have spatially resolved measurements for species, temperature, and soot from a flame. While the current work has developed the benchmark flames and obtained soot, aromatics species, and temperature measurements for high molecular weight fuels on a modified version of the Santoro burner, there is a need to obtain additional measurements that would further help to validate and improve the next generation numerical models. In particular, particle size measurements and soot nanostructure using HRTEM in the jet flames would provide valuable information to evaluate the relative effect of the fuel composition on soot growth versus soot inception. Additionally, in the current study, the temperature measurements were obtained in the non-sooting regions of the flame. Similar to the 2-D LIF and LII measurements, spatially resolved temperature measurements in the sooting part of the flames would be important, particularly for the smoking flames. The higher level of soot in the aromatics flames can significantly affect the flame temperature on account of soot radiation; the temperature measurements in such flames would aid to validate the radiation models as well.

Attempts were made in the current work to obtain species measurements using the Triple Quadrupole Mass Spectrum (TQMS). However, the measurements were unsuccessful due to repeated failure of the components of the TQMS. Mass spectrometer measurements of key species in the jet flames can provide valuable information on how the different fuel molecular
structure and premixing impacts the soot precursor species. The data obtained for PAH and HAP can be used to validate and calibrate the chemical kinetic models and also, interpret spatially resolved aromatic LIF results.

The experimental aromatic LIF and fuel pyrolysis simulation results obtained for the aromatic fuels demonstrate that the aromatic fuels are consumed through different reaction pathways at different rates resulting in differences in the initial pool of aromatic radicals. Due to the differences in the initial pool of aromatic radicals, combined with incomplete knowledge of the effects of temperature on fluorescence quantum yield and absorption cross-section for the aromatic species, the aromatic LIF signal from fuels containing aromatic component cannot be used to obtain quantitative information about the gas phase species. The combined analysis of the CHEMKIN simulations and aromatic LIF results highlight a need to undertake a combined experimental and numerical study to interpret and quantify the aromatic LIF results better than the qualitative distribution in the flame.

The study on laminar co-flow flames helps to understand the effect of molecular structure on emissions in a steady flame and to isolate the chemical effects of the fuel structure on emissions. However, practical combustion devices are unsteady, three-dimensional, and turbulent. Hence, it is important to understand the coupling between the chemistry and unsteady flow, particularly turbulence. In turbulent flames, one encounters wider variations in residence time, local equivalence ratio, and temperature history than are present in a laminar flame. In addition, turbulent flames have varying strain rate and scalar dissipation rates. However, it is difficult to quantify this complex fluid-chemical coupling in either experimental or numerical study because of high levels of unsteadiness, and large ranges of time scales and spatial gradients. Instead, an intermediary step to investigate laminar jet flames with acoustic
forcing at a range of frequencies and amplitudes to quantify the unsteadiness in terms of timescales (acoustic periods) and analyze their effect the soot development would a good next step. This approach would offer a more quantifiable interaction of the flow field and soot chemistry and help understand the effect of periodic oscillation and vortex structure on the emissions from the high molecular weight fuels.

Finally, the hypothesis of the study in the model gas turbine combustor was that fuels with different volatility would affect the fuel droplet vaporization processes, and that a fuel with a higher boiling point would emit higher levels of soot. However, in the current setup, it is possible that the current design of the injector results in the complete vaporization of the fuel droplets before the combustion zone. If the fuel droplets are vaporized before the combustion zone, the impact of fuel boiling point on soot emission may not be evident in the current experiment, just as it was not in the pre-vaporized laminar flame. Therefore, in order to better interpret the results obtained from the model gas turbine combustor, the fuel-air mixing and droplet size measurements would be valuable.
Appendix A Burner boundary conditions

The temperature boundary condition, shown in Fig. S1 (a), was obtained using a K-type thermocouple with no flame. The fuel flow rate was that of the base \( n \)-dodecane flame. The boundary conditions are similar for the five fuels since the fuel flow rates are quite similar. The spatial location of the thermocouple bead is approximately 1 mm above the fuel tube exit. The estimated uncertainty in the temperature measurement is \( \pm 5^\circ \text{C} \).

The velocity boundary condition, shown in Fig. S1 (b), was obtained using an anemometer (Kanomax model 6006) at room temperature of 298 K without fuel. The fuel volumetric flow rate was replicated by flowing air equivalent to the flow rate that would be obtained when 0.211 slpm of \( n \)-dodecane is vaporized. The velocity measurements shown in Fig. S1 (b) are corrected for the actual temperature at the tube exit using the ideal gas assumption. The uncertainty in the velocity measurements by the anemometer is \( \pm 5\% \) or 0.015 m/s, whichever is greater. The spatial location of the anemometer sensor is approximately 4 mm above the fuel tube exit. The uncertainty in the spatial location of the thermocouple bead and anemometer probe is \( \pm 0.5 \) mm.
Figure S1 Boundary conditions for 0.2N2: Non-premixed, $\phi_{\text{jet}} = 24$, $\phi_{\text{jet}} = 6$ flames and 0.48N2: Non-premixed flame (a) Temperature measurements; (b) Velocity measurement.
Appendix B Gas chromatography results of re-condensed fuel from the tube exit

Figures S2 and S3 show the gas chromatography (GC) analysis of re-condensed fuel from the tube exit for \( n \)-dodecane and \( n \)-hexadecane fuels, respectively. The analysis was performed for both non-premixed and rich-premixed conditions. The GC analysis demonstrates no fuel pyrolysis to occur within the burner tubing system.

Figure S2 GC analysis of re-condensed \( n \)-dodecane fuel from the tube exit.
Figure S3 GC analysis of re-condensed $n$-hexadecane fuel from the tube exit.
Appendix C Spectral response curves for filters used for LIF.

Figure S4 Spectral response curve for small aromatics filters. (Source: http://www.schott.com/d/advanced_optics/c7ef378d-ea1b-4c36-9cd1-79a379804dca/1.4/schott-optical-filter-diagram-december-2012-eng.pdf)
Figure S5 Spectral response curve for large aromatics filter. (Source: https://www.andovercorp.com/products/bandpass-filters/standard/500-599nm/)
Appendix D Radiation correction for thermocouple measurements.

The conduction along the thermocouple wires has been neglected. An energy balance at the thermocouple bead under steady state conditions would be

\[ A_{TC} h (T_g - T_{TC}) = \sigma \varepsilon (T_{TC}^4 - T_b^4) A_{TC} \]  

(1)

where \( A_{TC} \) is surface area of thermocouple bead.; \( h \) is the heat transfer coefficient between gas and thermocouple wire; \( T_g \) is gas temperature; \( T_{TC} \) is measured thermocouple bead temperature; \( T_b \) is wall/background temperature; \( \sigma \) is Stephan-Boltzman constant; and \( \varepsilon \) is thermocouple emissivity. The radiation term is estimated by considering thermocouple as gray-emitting surface enclosed in large, isothermal diffuse-gray surface. For relatively cold surrounding, \( T_b^4 \ll T_{TC}^4 \), then equation (1) becomes:

\[ T_g - T_{TC} = \Delta T = \frac{\sigma \varepsilon d}{k Nu} T_{TC}^4 \]  

(2)

The emissivity for Pt/Pt-13% Rh is taken from Bradley and Entwistle [153]. The conductivity, density and viscosity of the gas are taken as that of nitrogen. The bead is considered spherical of diameter 254 \( \mu \)m. The Nusselt number for a sphere is estimated by a correlation from Eckert and Drank [152]. The velocities typically ranges from 30-250 cm/sec inside the flame [21] and a value of 60 cm/sec is considered, in this work for the radiation correction.
Appendix E Aromatics LIF analysis.

The relative level of peak small aromatics for the paraffin fuels is calculated by normalizing the peak LIF signal of small aromatics in a particular fuel with the peak LIF signal of small aromatics in the \( n \)-dodecane fuel. In order to determine the peak LIF signal of small aromatics, first the maximum LIF signal at each HAB is plotted against the HAB. Then, a 9-point moving average profile is calculated using the smooth function of the MATLAB. The peak count from the 9 point averaged profile is defined as the maximum LIF signal for each fuel. The 9-point averaging did not have any significant impact on the overall shape of the profile, as shown in Fig. S6 for the i-C8 and MCH fuels.

Figure S6 Comparison of the raw and averaged LIF signal versus HAB for: (a) small aromatics i-C8 fuel; (b) small aromatics MCH fuel; (c) large aromatics i-C8 fuel; (d) large aromatics MCH fuel.
Appendix F 95% Confidence Interval (CI) for soot volume fraction.

The general form of confidence interval (CI) is given by

\[
\bar{x} \pm Z \left( \frac{\sigma}{\sqrt{n}} \right)
\]  

(3)

where,

\(\bar{x}\) is the sample mean.

\(Z=1.96\) is the 95% Z-value from the normal distribution table.

\(\sigma\) is the sample standard deviation.

\(n\) is the number of images collected, which is varied from 30 to 100 depending on the signal to noise level in a particular flame.

Figures S7 and S8 show the percentage value of the total 95% confidence interval (CI) as compared to the mean \(f_v\) for the 0.2N\(_2\) and 0.48N\(_2\) flames, respectively. The analysis is presented for the highest smoking fuel mixture \(i.e., 1,3,5\)-trimethylbenzene/\(n\)-dodecane. The value presented in Figures S7 and S8 is given by

\[
\frac{2 \cdot Z \left( \frac{\sigma}{\sqrt{n}} \right)}{\bar{x}} \cdot 100
\]  

(4)

In the smoking flames, Figure S7 shows that the 95% confidence interval (CI) for the \(f_v\) in the annular and center region is \(\pm 15\%\) and \(\pm 4\%\) of the mean \(f_v\), respectively. Additionally, in the non-smoking flames, Figures S7 and S8 show that there is higher measurement uncertainty in the flame-tip, consistent with observed fluctuation of \(\pm 2\) mm in the flame-tip location. Figure S8 (a) shows that soot emits from flame tip in the 1,3,5-trimethylbenzene \(\phi_{jet} = \text{Inf-0.48N}_2\)
flame as a result of higher peak $f_v$ produced in the 1,3,5-trimethylbenzene flame as compared to other aromatic fuels.

**Figure S7** Two dimensional total 95% confidence interval [% of the mean] for soot volume fraction for TMB fuel, 0.2slpm N$_2$ flow: (a) Non-premixed; (b) $\phi_{jet}$ = 24; (c) $\phi_{jet}$ = 6.

**Figure S8** Two dimensional total 95% confidence interval [% of the mean] for soot volume fraction for 1,3,5-trimethylbenzene, 0.48slpm N$_2$ flow: (a) Non-premixed; (b) $\phi_{jet}$ = 24; (c) $\phi_{jet}$ = 6.
Appendix G Fortran code of Fourier inversion

This code is used to topographically invert the line of sight light extinction measurements to yield local soot extinction coefficients.

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
   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)
      enddo
   endif
20 CONTINUE
```
THETA_J = (J-1) * PIN
COSTHTAJ = COS(THETA_J) / XPOS
SINTHTAJ = SIN(THETA_J) / 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.LT.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 H JP-8 fuel composition

JP-8 fuel composition used in the current work.

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<th>Mole fraction</th>
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References


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