The thesis of Zepeng Li is approved by the examination committee

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ABSTRACT

Effect of Dimethyl Ether Mixing on Soot Size Distribution in Premixed Ethylene Flame

Zepeng Li

As a byproduct of incomplete combustion, soot attracts increasing attentions as extensive researches exploring serious health and environmental effects from soot particles. Soot emission reduction requires a comprehensive understanding of the mechanism for polycyclic aromatic hydrocarbons and of soot formation and aging processes. Therefore, advanced experimental techniques and numerical simulations have been conducted to investigate this procedure.

In order to investigate the effects of dimethyl ether (DME) mixing on soot particle size distribution functions (PSDFs), DME was mixed in premixed ethylene/oxygen/argon flat flames at the equivalence ratio of 2.0 with a range of mixing ratio from 0% to 30% of the total carbon fed. Two series of atmospheric pressure flames were tested in which cold gas velocity was varied to obtain different flame temperatures.

The evolution of PSDFs along the centerline of the flame was determined by burner stabilized stagnation probe and scanning mobility particle sizer (SMPS) techniques, yielding the PSDFs for various separation distances above the burner surface. Meanwhile, the flame temperature profiles were carefully measured by a thermocouple and the comparison to that of simulated laminar premixed burner-stabilized stagnation flame was satisfactory. Additionally, to understand the chemical role of DME mixing
in soot properties, characterization measurements were conducted on soot samples using thermo-gravimetric analysis (TGA) and elemental analysis (EA).

Results of the evolution of PSDFs and soot volume fraction showed that adding DME into ethylene flame could reduce soot yield significantly. The addition of DME led to the decrease of both the soot nucleation rate and the particle mass growth rate. To explain the possible mechanism for the observation, numerical simulations were performed. Although DME addition resulted in the slight increase of methyl radicals from pyrolysis, the decrease in acetylene and propargyl radicals inhibited the production of polycyclic aromatic hydrocarbons. At the same time, the addition of DME gave rise to the increase of the flame temperatures, which favored the production of OH radicals. The incremental concentration of OH radicals promoted the oxidation rate of soot particles. Additionally, soot samples from flames with higher DME mixing ratios showed higher O/C, H/C mass ratios and thus better oxidation characteristics.

In summary, the addition of DME reduces soot emission in two ways: on the one hand, it inhibits soot nucleation and mass/size growth, then the production of soot particles decreases; on the other hand, it promotes soot oxidation process by increasing the concentration of OH radicals and improving the oxidation behavior of the soot particles, then more particles are oxidized. Both of them are responsible for the reduction of soot emissions at the presence of DME.
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Chapter 1

Introduction

1.1 Motivation and Objectives

Combustion of fossil fuels or biomass provides energy for industrial or individual usage. However, the pollutant emissions from this process, such as $NO_x$, Peroxyacetyl Nitrate (PAN) and particles, is hazardous to environment and human health. As the byproduct of incomplete combustion, soot attracts increasing attentions as many studies have exposed the reduction of combustion efficiency and serious health and environmental effects from soot particles. To some extent, soot particles are responsible for the climate change on a global scale. As for the global warming issue, it is widely recognized that the contribution of soot particles is estimated to be second to that of $CO_2$, and the absorption of solar energy by soot will affect global radiation balance. Furthermore, acting as the cloud condensation nuclei (CCN) and ice nuclei (CN), aerosols such as soot have a critical impact on the precipitation. Additionally, the risk of respiratory, cardiovascular and allergic diseases for human beings increases as well due to growing emissions of small particles.

Above all, sound actions for inhibiting the formation or enhancing the oxidation of small particles are essential to reduce the emission of PAHs and soot particles from combustion, and this requires sufficient understanding in the mechanism of the above processes. Regarding that adding oxygenates is a potential way for reducing soot.
Therefore, this concern motivates the thesis research on the effect of dimethyl ether on soot formation and oxidation processes in laboratory scale, which aims to provide some information of the application of the oxygenated fuel that is similar to dimethyl ether.

1.2 Research Background

1.2.1 Soot Formation and Oxidation Process

The formation process of polycyclic aromatic hydrocarbons (PAHs) and soot particles has attracted vast attentions in combustion research area. The study of soot formation and its hazard extends to theoretical, computational and experimental aspects and overspreads various subjects such as physics, chemistry and biology. Figure 1.1 shows a conceptual picture for soot formation in homogeneous mixtures. In general, the formation of soot particles in premixed flames consists four main processes based on the current understanding [1 5 6 7 8 9].

- Formation of soot precursors. It happens in the molecular zone and among the key gas precursors such as polyacetylenes and ionic species and polycyclic aromatic hydrocarbons (PAHs), PAHs are regarded as the most important precursors in soot formation. The generation of PAHs from fuels is a very complex process, thus primary focus is on the formation of the first aromatic ring. After the pyrolysis of fuel molecules, small radicals and species react with each other to produce benzene, where odd-carbon-chemistry play a critical role. The aromatics start to grow via hydrogen-abstraction-\(C_2H_2\)-addition (HACA) reactions, species like acetylene \(C_2H_2\) and propargyl \(C_3H_3\) are main contributors in these reactions.
• Nucleation of soot particles from PAHs. Soot particle inception is a transition step where gas-phase species become solid particles. Nascent soot can be sampled by burner stabilized stagnation probe technique then the size distributions can be detected with scanning mobility particle sizer system. Moreover, the advanced technique of auto-sampling reveals a method for nascent soot collection which contributes to the morphology analysis of soot particulate with transmission electron microscopy.

• The growth of particulate via surface reactions. In this process, nucleation kinetics determines the number of soot while coagulation determines the evolution of the particle number density. In the meantime, the accumulation of the mass of particles is controlled primarily by the processes of particulate surface reactions, growth and oxidation. It was highlighted that acetylene was the principal gaseous species in soot surface reaction in premixed laminar flames from experimental studies.

Figure 1.1: A simple diagram for soot formation in premixed flames [1]
Coagulations of particles. Once formed, soot particles tend to collide to form larger particles. After coagulation, incipient spherical particles will be transformed into a fractal shape such as botryoidal chains.

To reduce the emission of PAHs and soot particles into the environment, we can either inhibit the formation process or enhance the oxidation process. The most popular strategy for the reduction of particulate emissions is using a diesel particulate filter (DPF) \([10, 11, 12, 13, 14]\) to capture particles in the exhaust pipelines. However, the DPF should be refreshed intermittently since the trapped particulate matter in the inlet channels would clog the DPF. Frequent regeneration of the filters is not practical, so the removal of the trapped particulate matter on the DPF is usually achieved by oxidative reactions. Hence, the efficiency of oxidation of soot has a crucial effect on the replacing frequency of the filters.

Observations showed the combustion process could influence soot characteristics thereby influencing the oxidation rate. Studies in this area have ranged from shock tubes to in-situ flames, either of the systems has specific advantages as well as limitations in terms of time, temperature and chemical environments \([15]\). Moreover, testament of various types of carbon have also conducted on their oxidation properties, such as combustion soot, commercial carbon black, and amorphous carbon. Results showed that the oxidation rate could vary by factors of 6 to 20 relative to the rate of Nagle Strickland-Constable for graphite oxidation \([16]\). In addition, as the edge sites were much more active than the sites in the basal plane of a graphene layer, the particulate with more populated edge sites showed better reactivity \([10]\). Also, soot from the inception and post-oxidation region of fuel-rich premixed laminar flames showed a close relationship between soot oxidation reactivity and particle characteristics, such as soot morphology, H/C and O/C atomic or mass ratios \([17]\).

Since the popularity of alternative fuels recently, more researchers have focused on the influence of fuel formulation or fuel additives on soot characteristics and emission
quantity. Song et al. [14] suggested that specific compounds in the fuel might produce soot with favorable oxidation behavior. They found that the oxidation rate of soot from soybean-derived biodiesel was five times higher than that from Fischer-Tropsch diesel fuel, where the relative oxygen content on soot surface was an important factor for the oxidation rate. Vander et al. [15] illustrated that soot produced from benzene, ethanol and acetylene flames had different nano-structural order and oxidative reactivity, and soot derived from benzene was more reactive than soot from acetylene. Moreover, adding oxygenated functional groups resulted in the higher oxidation rate [10, 14].

Therefore, fuel additives and operation conditions have a significant influence on soot formation. For a given set of flame conditions, the size, structure, concentration, elemental contents and surface functional groups of soot particles depend on the fuel composition, which further affect the corresponding soot oxidizability.

1.2.2 Dimethyl Ether Studies

Produced from contemporary biomass through chemical or biological reactions, the biofuels like biodiesel or bioethanol attract vast attention on the research of practical and environment-friendly alternative fuels. Alternative fuels, or fuel additives, have been developed and practically utilized from the last several decades for the sake of the reduction of particles and $NO_x$ emissions. In advantage of the low auto-ignition temperature due to a high cetane number and low particulate emissions, dimethyl ether (DME, $CH_3OCH_3$) is evaluated as one of the most promising fuel additives or alternative fuels. However, many physical properties of DME requires improvements to the internal structures of diesel engine, for instance, the low viscosity, lubricity, combustion enthalpy and boiling point [18]. Therefore, usage of DME/diesel oil mixtures for CI engines and vehicles was more practical than using pure DME, owing to that it was able to avoid many specific problems of diesel engines feeding
Evidence from different laboratory studies was added to the effect of DME mixing on soot formation. Sirignano [20] found that addition of DME could slow down soot formation in premixed configurations, especially for small nanoparticles. However, the production of soot precursors was not so sensitive to DME addition. Wu and coworkers [2, 3] compared the emission tendency for PAHs production between DME and ethanol in Figure 1.2 and Figure 1.3. They supposed that the carbon from fuels had two destinations, CO and PAHs. From the carbon flux diagrams, up to 31.3% of carbon in DME was converted to species that contributed to PAHs generation, while up to 54.5% of carbon in ethanol contributing to PAHs generation. Thus, more carbon was removed from the pathway to produce soot particles in DME fuels.

However, a synergistic effect of DME mixing in counterflow flames was found by Yoon et al. [21]. In their work, DME addition enhanced the formation of PAHs and soot particles when ethylene doped with a small amount of DME (such as 14% or so).
Figure 1.3: Carbon flux diagram for ethanol in Ethanol-added-ethylene-flame at the equivalence ratio of 2.34; percentage indicates the ratio of carbon from DME flowing to the corresponding species [3].

It was clarified by chemical analysis, which showed that the increase of $CH_3$ concentration exceeded the decrease of $C_2H_2$ concentration to a large extent in counterflow flames in case of the small amount of DME addition. As the consequence, the synergistic effect enhanced the formation of PAHs and soot particles in ethylene/DME mixture flames.

1.3 Work Frame

This thesis work focuses on the investigation of the effect of dimethyl ether (DME) mixing on soot particle size distribution functions (PSDFs) in premixed ethylene flame. To analyze the experimental observations, flame temperature profiles and soot particle oxidation behaviors coupled with chemical analysis were considered.

The flame configurations are described below. DME was mixed in premixed
ethylene/oxygen/argon flames at the equivalence ratio of 2.0 stabilized on the McKenna Burner, with the DME mixing ratios ranging from 0% to 30% of the total carbon fed. Two series of atmospheric pressure flames were tested, in which Flame Series A had the cold gas velocity at 6cm/s while Flame Series B had the cold gas velocity at 8cm/s. This comparison was expected to clarify the role of flame temperatures in the soot formation and oxidation. According to the target and flame configurations, the measurements involved in this work are listed below.

- The flame temperature profiles for flames with different DME mixing ratios were carefully measured by a thermocouple using the rapid-insertion technique. In the meanwhile, computed flame temperatures were compared with the experimental data to add more creditability to the measurement and in turn to testify the feasibility of the kinetic model for chemical analysis.

- Soot size distribution functions were determined by burner stabilized stagnation probe and scanning mobility particle sizer (SMPS) technique described in section 2.4. The variations of PSDF's of soot particles were expected to show some relationship regarding the DME mixing ratios and the separation distances between burner surface and stagnation plate.

- Characterization measurements were conducted on soot samples using thermogravimetric analysis and elemental analysis to understand the chemical role of DME mixing in soot oxidation behaviors.

- Numerical simulations for the distributions of some crucial radicals or intermediates in our operational flames were employed to illustrate the effect of DME on soot formation process.
Chapter 2

Experimental Technique and Numerical Simulation

2.1 Introduction

Considerable variations in size, concentration, morphology and chemical composition of soot particles, or other aerosols (liquid or solid phase particulates) in the atmosphere, makes it a great challenge to quantify all of these characteristics by one single instrument. For this reason, a comprehensive profile of soot formation in both temporal and spatial scales requires employing multiple measurement methodologies simultaneously.

In this thesis, the McKenna Flat Flame Burner was adopted to produce the one-dimensional premixed flame. A type-R thermocouple coated with silica was applied to measure flame temperature profile. Meanwhile, scanning mobility particle sizer with an online sampling tubular probe were utilized to acquire soot particle size distribution functions (PSDFs). Then the Thermo-gravimetric Analysis (TGA) characterized soot oxidation properties and Elemental Analysis (EA) illustrated C/H/O element composition of soot samples. In addition to the processes above, numerical simulations were carried out to analyze species distribution of these flames in order to explain experimental results.
This chapter gives detailed descriptions of experimental setup and techniques as well as numerical simulations using CHEMKIN PRO Software.

### 2.2 Burner-Stabilized Stagnation Flames

McKenna Burner is commonly used to produce well-characterized standard flames, which provides temperature and species concentration to study on hydrocarbon fuels combustion targeting at emission control and optical techniques calibration. Laminar premixed flat flames were stabilized on the 6cm-diameter bronze water-cooled porous sintered matrix with a sintered bronze shroud ring and a stainless steel outer housing (Figure 2.1). A stagnation plate with a tubular sample probe embedded inside was configured to define flame boundary conditions and to collect soot samples from flames (Figure 2.2). Both of the burner and the stagnation plate were cooled by water. Probe sampling was an inherently intrusive measurement and the extent of probe perturbation had been estimated [5].

![Figure 2.1: Sectional view of the McKenna flat flame burner](image)
The evenly distributed mixture of fuel and oxidizer was introduced from burner surface, and through a concentric porous shroud ring, all flames were isolated from ambient air by a nitrogen flow shield to avoid secondary flames. Figure 2.3 shows the configuration of a typical one-dimensional Burner-Stabilized Stagnation (BSS) ethylene flame with the composition of the unburned reactants of 16% (mol) ethylene and 24% (mol) oxygen in nitrogen. The equivalence ratio of the reactants was 2.0 and the cold gas velocity was 6 cm/s (298 K & 1 atm). In this thesis, the cold gas velocity is defined as the total flow rate of the premixed gases per unit area of the burner surface. The separation distance between burner surface and stagnation plate, $H_p$, is an important parameter. Pictures of flames with different separation distances are shown in Figure 2.4. The six flames with the cold gas velocities of 6 cm/s has the same unburned composition of 20% (mol) ethylene and 30% (mol) oxygen in nitrogen. Obviously, with different separation distances, the flames are different. Note that the flames in these two figures are not the flames utilized in
Figure 2.3: Illustration of the coordinate system in the actual flame image

during this research. To acquire variation of the high-accuracy separation distance between burner surface and stagnation plate, the McKenna Burner was placed on a one-dimensional translation stage. Additionally, the whole burner system was supported by an automated two-dimensional translation stage controlled by a Labview program to acquire sufficiently precise burner position for laser extinction measurement.

In this work, two series of ethylene flames with the equivalence ratio ($\phi$) of 2.0 were tested at atmospheric pressure, and the cold gas velocities were varied to obtain different flame temperatures. The ethylene flame is popular in the research of soot formation, and the flame conditions used in this research can provide a proper range of soot production. The reference flame in this work was pure ethylene flame, and the unburned mixture contained 16% (mol) ethylene, 60% (mol) argon and 24% (mol) oxygen. The measurement was performed at different dimethyl ether (DME) mixing ratios ranging from 0% to 30% of the total carbon fed, where the total carbon fed meant the total carbon flowrate in unburned gases. The flowrate of the gases was controlled by thermal-based mass flow controllers (MFC, MKS Instruments), which were calibrated by the laboratory primary gas flow calibrator (Definer 220).
Figure 2.4: Pictures of typical Burner-Stabilized Stagnation (BSS) flames at a series of burner-to-stagnation separation distances

Detailed experimental conditions of premixed ethylene flames are listed in Table 2.1

Table 2.1: Experimental conditions for ethylene/DME flames at $\phi = 2.0$

<table>
<thead>
<tr>
<th>Flame</th>
<th>Cold gas velocity, $v_o (cm/s)$</th>
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<tr>
<td>A1</td>
<td>6</td>
<td>DME</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>A2</td>
<td>10</td>
<td>90</td>
</tr>
<tr>
<td>A3</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>A4</td>
<td>30</td>
<td>70</td>
</tr>
<tr>
<td>B1</td>
<td>8</td>
<td>0</td>
</tr>
<tr>
<td>B2</td>
<td>10</td>
<td>98</td>
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<td>10</td>
<td>90</td>
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<tr>
<td>B5</td>
<td>20</td>
<td>80</td>
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<tr>
<td>B6</td>
<td>30</td>
<td>70</td>
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</table>
2.3 Temperature Measurement

Thermocouples have been one of the most extensive and simplest experimental techniques to measure temperature in combustion research and high-temperature fluid investigations. However, the introduction of thermocouples into a flame raises the question of probe interference and detection accuracy, which may not neglect in some cases.

The temperature measurement in this work applied a rapid insertion technique similar to that described in [5, 22, 23, 24, 25]. Figure 2.5 and Figure 2.6 exhibit the schematic and real experimental setup in this thesis, respectively. A type-R thermocouple (Omega Engineer) was coated with silica to prevent surface catalysis [25, 26] and the fine wire diameter was 0.25mm with the bead diameter of 0.3mm. To realize the rapid insertion procedure, the thermocouple should be manually slid inwards and outwards the flame very smoothly. Then the temperature-versus-time trace was recorded by a data acquisition board (Compact DAQ, National Instruments) with the recording trigger at the desired position in the center of the flame. Despite the thermocouple was moved manually, the measured temperature profiles were found
Consider the deposition of large molecules or particles on the fine wire thermocouple and the radiation loss from the thermocouple in combustion regions, two procedures were employed to accurately derive the local flame temperature profiles from the output measured by this setup. The first step is to estimate the true junction temperature by means of extrapolating the temperature-versus-time curve to zero time (Figure 2.8) to eliminate soot deposition errors, Mcenally et al. [24] had verified the reasonability of this process in their work. The second step is to evaluate the impact of radiations. A comprehensively systematic radiation correction strategy for the temperature measurement was stated in [24, 25], the general energy balance on the thermocouple follows the equation below:

$$\dot{Q}_\text{catalytic reaction} + \dot{Q}_\text{conduction} + \dot{Q}_\text{convection} + \dot{Q}_\text{radiation} = C_p V \left( \frac{dT}{dt} \right)$$
In this work, several assumptions applied to simplify the computation of radiation corrections as listed below.

- Neglect catalytic effect as a result of the utilization of non-catalytic surface coating.

- Neglect conduction. Note that for long and thin thermocouple wires with length-to-diameter ratio > 200, conduction can be negligible \cite{27,28}. As for the thermocouple used here, the length was around 50cm and the wire diameter was 0.25mm.

- Radiation between flame and wire is neglected because it is considerably smaller than radiation between wire and surroundings \cite{27}.

- Wire emissivity for Type-R thermocouple was $0.22 \pm 0.02(\approx 1400K)$ \cite{29}. As the stay time of the thermocouple is rather short and flames are not very sooty in this work, the effect of soot coating on emissivity is neglected.

- Nusselt number correlation. For cylindrical geometry, when $0.02 < Re < 20$, 

Figure 2.7: Repeatability of temperature measurement
Figure 2.8: Typical time evolution of the junction temperature of the type-R thermocouple. The true junction temperature is estimated by extrapolating Temperature-versus-time curve to zero time.

Nusselt number took the following form \[30]\:

$$Nu = 0.34 + 0.65Re^{0.45}$$

where $Re$ is the Reynolds number.

- Local gas properties such as viscosity and thermal conductivity were calculated using TRANSPORT \[31\].

In the basis of these assumptions, the balance equation is \[24\]:

$$\epsilon_j \sigma T_j^4 = \left( \frac{k_{g_0} Nu_j}{2d_j} \right) (T_g^2 - T_j^2)$$

Where $T_g$ is the gas temperature and $T_j$ is the true junction temperature, $\epsilon_j$ is the overall emissivity of the thermocouple and $\epsilon_j = 0.22 \pm 0.02$ as suggested, $\sigma$ is the Stefan-Boltzmann constant so $\sigma = 5.67 \cdot 10^{-8}(Wm^{-2}K^{-4})$, $k_{g_0} = k_g/T_g$ and $k_g$ is
local gas thermal conductivity, $d_j$ is the diameter of the thermocouple wire, and $Nu_j$ is the Nusselt number.

In this thesis, temperature profiles in the centerline of various flames were measured as a function of distance above burner surface (H) for a series of separation distances ($H_p$) between burner surface and stagnation plate. Additionally, computational temperatures corresponding to the experimental flames were calculated by CHEMKIN PRO, which will be introduced later.

2.4 Probe Sampling and Scanning Mobility Particle Sizer

Now that the burner stabilized stagnation flame technique coupled with probe sampling and Scanning Mobility Particle Sizer (SMPS) have been developed to the study of soot size distribution functions in laminar premixed flames [32, 33, 34, 35], similar setup and procedures were applied in this thesis.

Figure 2.9 is the schematics of the experimental setup and Figure 2.10 is the photo of the setup in the lab, which are similar to the one in [36]. Soot particles were sampled through a horizontal stainless steel tube with an orifice sitting just above the center of the flame, the tube was embedded into the stagnation plate and the diameter of the orifice was 0.15mm. Nitrogen gas flowed through the tube at the rate of 28L/min (STP). To obtain the pressure at the orifice (marked as $P_{orifice}$), two highly precise pressure transmitters (Keller) were positioned upstream and downstream of the orifice at the same distance of 15cm and the measured pressure values were noted as $P_{up}$ and $P_{down}$, respectively. Hence, the pressure drop between the inner pressure and outer pressure of the orifice is:

$$\Delta P = \left( \frac{P_{up} + P_{down}}{2} \right) - P_0$$
where $P_0$ is the atmospheric pressure that was measured by another highly precise pressure transmitter. Naturally, a negative pressure drop of $\Delta P < 0$ impelled flame gases into the sampling tube and then the gas samples were carried by the nitrogen flow to the SMPS system.

In order to accurately control the pressure drop that deciding the quantity of sample gases and thus affected the dilution conditions of the sample gases, a needle valve coupled with a vacuum pump were connected to the flow downstream. In previous work, dilution ratio was determined as a function of $\delta P$, for instance in the works of [5, 36]. Because of the time limitation, the measurement of dilution ratios was not involved in this work. Instead, the normalized number density was employed to compare the PSDFs in different DME cases. Here the normalized number density was defined as:

$$\text{normalized number density} = \left( \frac{dn}{d\log D_p} \right) \frac{1}{N}$$
Where $D_p$ is the particle diameter, $N$ is the total number density directly measured from SMPS. Moreover, the normalized PSDFs for pure ethylene flame had a good agreement with the work in [36]. Given that [36] supplies an excellent model for researchers to testify SMPS setups, this good agreement adds reasonability and credibility of this thesis work.

The Scanning Mobility Particle Sizer (SMPS, TSI) contains several components: an impactor with the nozzle size of 0.071cm, an Electrostatic Classifier (model 3087), a nano-Differential Mobility Analyzer (DMA, model 3085) and a Condensation Particle Counter (CPC, model 3776). The flow rate of sample and sheath through the DME were 1.5 $L/min$ and 15 $L/min$. The scan time was 50 seconds up and 10 seconds down and after each scan, the orifice in the sampling pipe was cleaned using a fine wire under a microscope as the result that the accumulation of soot particles clogged the orifice. Figure 2.11 shows the photo of a clogged orifice taken under the microscope. Additionally, mobility measurement always over-predict the actual physical size of soot smaller than 10nm, which is ascribed to the limitation of the Cunningham slip
correction \[37\], hence a parameterized correlation is applied \[38\]:

\[
\frac{D_p}{D_{p,SMPS}} = \operatorname{tanh}(1.4566 + 0.010892D_{p,SMPS}) \times \left(1.0721 - \frac{0.4925}{D_{p,SMPS}}\right)
\]

Where \(D_{p,SMPS}\) (nm) is the mobility diameter directly measured from SMPS, \(D_p\) (nm) is the real particle diameter. All diameters in this thesis are corrected diameters.

2.5 Thermo-gravimetric Analysis

The oxidation property of soot particles depends on the structures, arrangement of polycyclic aromatic hydrocarbons and the surface functional groups. In other words, from oxidation analysis, we can get some information about physical structures and chemical compositions of soot particles. To study DME mixing effect on the reaction properties of soot to oxygen \(O_2\), four samples from Flame A1, A2, A3, A4 in terms of different fuel compositions were tested. A Thermos-Gravimetric Analyzer
(TGA, Model Q5000, TA Instruments) was used to burn the soot samples in high-temperature Platinum pans dynamically bathing in the nitrogen (N₂) environment from room temperature to 300°C at the heating rate of 2°C/min, and isothermally at 300°C for 10 minutes to desorb volatile compounds such as water vapor and volatile hydrocarbons. Then use air to oxidize soot samples with the heating rate of 1°C/min from 300°C to 700°C. The thermo-gravimetric data provided information about the variations in soot conservation (α) and conversation rates (dα/dt) which represented the oxidative properties of soot samples.

2.6 Elemental Analysis

The elemental composition of carbon (C), oxygen (O) and hydrogen (H) in soot samples was acquired using the FLASH 2000 CHNS/O Analyzer from Thermo Fisher Scientific Inc. The calibration curves of different elements were tested by standard chemicals such as sulfanilamide, BBOT and acetanilide. Because the samples collected are free of ash, the content of oxygen (O) was calculated through subtracting the contents of N, S, C, H from 100%.

2.7 Numerical Simulation

Numerical computations had been conducted to determine the thermodynamic properties and transport properties. The computed flame temperature profiles and concentrations of several major intermediate species were calculated using CHEMKIN PRO [39], and transport properties such as the viscosity, conductivity and diffusion coefficient in the gaseous phase were calculated using TRANSPORT [31]. The module used in CHEMKIN PRO is laminar premixed Burner-Stabilized Stagnation Flame. The governing equations and numerical schemes are described in [40] [41]. The temperature boundary conditions of the inlet gases was set the same as the lab
temperature, and the temperature boundary conditions of the stagnation plate was set as 445K. Highlight that the sensitivity analyses conducted in [42] demonstrates that the detailed structure of the BSS flame were insensitive to temperature boundary conditions, so it is acceptable to apply the above boundary temperatures in this work.

The reaction kinetic model employed here was KAUST-Aramco PAH Mech 2 Ver1.0 [43], which includes 202 species and 1352 reactions. This model is a newly developed chemical kinetic mechanism based on Aramco Mech 1.3 [44] to characterize the kinetic and thermochemical properties of C1-C4 based hydrocarbons and oxygenated fuels. Comparing with the previous mechanism, this model allows the computation of PAH molecular growth up to coronene ($C_{24}H_{12}$).
Chapter 3

Results and Discussion

3.1 Flame Temperature Profile

The temperature profile is an intrinsic character of flames and it is of crucial significance for the modeling of soot formation in combustion research. In this chapter, the effect of DME mixing on flame temperature profiles was elucidated with respect to DME mixing ratios and separation distances as a function of height above burner surface (H). As a consequence of the unavoidable touch between the ceramic tube of the thermocouple and the edge of burner and stagnation plate, the temperatures were not able to acquire at $H < 0.04\text{cm} \& (H_p - H) < 0.2\text{cm}$. All the data were corrected for thermocouple radiation. Moreover, the horizontal error bar on the measurement of $\pm 0.01\text{cm}$ indicates the uncertainty due to the finite thermocouple diameter and positional uncertainty of the thermocouple stage; the vertical error bar is based on the emissivity of the thermocouple, which ranges from 0.20 to 0.24.

Figure 3.1 and Figure 3.2 illustrate the measured flame temperatures for several separation distances between burner surface and stagnation plate $H_p$, ranging from $H_p = 0.55$ to $1.2\text{cm}$, in Flame B1 (pure ethylene flame) and Flame B6 (70% ethylene and 30% DME), respectively. For both flames, there is a similar tendency of the sharp temperature gradients when $H < 0.15\text{cm}$. Then after that region, flame temperatures become lower as the burner surface approaches to the stagnation plate,
Figure 3.1: Experimental flame temperature profiles with radiation correction as a function of distance above burner surface $H$ for six separation distances between burner surface and stagnation plate $H_p$ in Flame B1. The line is fitted to the data.

Figure 3.2: Experimental flame temperature profiles with radiation correction as a function of distance above burner surface $H$ for six separation distances between burner surface and stagnation plate $H_p$ in Flame B6. The line is fitted to the data.
Table 3.1: Maximum flame temperature of flames B1 & B6 for a series of separation distances $H_p$

<table>
<thead>
<tr>
<th>Separation Distance, $H_p$ (cm)</th>
<th>Maximum Temperature for Flame B1 (K)</th>
<th>Maximum Temperature for Flame B6 (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.55</td>
<td>1771.4</td>
<td>1801.9</td>
</tr>
<tr>
<td>0.7</td>
<td>1818.8</td>
<td>1846.2</td>
</tr>
<tr>
<td>0.8</td>
<td>1830.6</td>
<td>1856.8</td>
</tr>
<tr>
<td>0.9</td>
<td>1841.7</td>
<td>1864.1</td>
</tr>
<tr>
<td>1.0</td>
<td>1850.2</td>
<td>1869.8</td>
</tr>
<tr>
<td>1.2</td>
<td>1857.8</td>
<td>1876.4</td>
</tr>
</tbody>
</table>

which is attribute to the enhanced heat loss to the stagnation plate. The maximum temperatures of these flames are listed in Table 3.1. It is obvious that the peak temperature increases as separation distances increase. In the meanwhile, B6 has a higher peak flame temperature than B1 by 20 to 30K resulting from a higher mass flux and thus heat flux.

Comparison of experimental and computational flame temperatures (radiation corrected) at various separation distances $H_p$ for Flame B1 and B6 are shown in Figure 3.3 and Figure 3.4, respectively. Apparently, the measured temperature agrees well with the model prediction, especially in the pre-flame region where $H \leq 0.20 cm$. Nonetheless, a large discrepancy occurs after $H = 0.20 cm$, which can be attributed to the emissivity change because of the accumulation of soot particles on the thermocouple. This numerical simulation is expected to model the species and radicals distributions and mixture gas properties employed in this research.
Figure 3.3: Comparison of the radiation-corrected experimental and computational temperature profiles at assorted separation distances $H_p$ for Flame B1. Symbol: experimental flame temperature; dash line: computational flame temperature.
Figure 3.4: Comparison of the radiation-corrected experimental and computational temperature profiles at assorted separation distances $H_y$ for Flame B6. Symbol: experimental flame temperature; dash line: computational flame temperature.
Figure 3.5: Comparison of the radiation-corrected experimental and computational temperature profiles at separation distances $H_p = 1.2\,\text{cm}$ for various DME mixing ratios in Flame Series A. Symbol: experimental flame temperature; dash line: computational flame temperature.

In order to investigate the effect of DME mixing on flame temperature profiles, detailed comparisons between experimental and computational temperatures at separation distances $H_p = 1.2\,\text{cm}$ for various DME mixing ratios in Flame Series A & B were employed, which are described in Figure 3.5 and Figure 3.6. Similar to the trend of the comparisons between experiment and model prediction in Figure 3.3 and Figure 3.4, there is a large discrepancy after $H = 0.20\,\text{cm}$. An insight into the maximum flame temperatures of experimental and computational results at the separation distances of $H_p = 1.2\,\text{cm}$ for various DME mixing ratios in Flame Series A & B are illustrated in Figure 3.7. The simulated temperature is totally within the uncertainty of the experiment, and the range of the temperature difference between simulation
Figure 3.6: Comparison of the radiation-corrected experimental and computational temperature profiles at separation distances $H_p = 1.2\text{cm}$ for various DME mixing ratios in Flame Series B. Symbol: experimental flame temperature; dash line: computational flame temperature.

and the center value of the measurement is 3 to 16K. Obviously, peak flame temperatures are lifted as a consequence of DME addition, and the relationship between DME mixing ratios and peak flame temperature is nearly linear. Furthermore, the discrepancy between simulated temperature and the center value of measured temperature is proportional to DME mixing ratio. That is, as DME mixing ratio increases, this discrepancy increases, which indicates the simulated model becomes less accurate. It might because that the mechanism used here underestimates the role of DME.
Figure 3.7: Comparison of the maximum experimental (solid points) and computational (hollow points) temperature profiles at separation distances $H_p = 1.2\, \text{cm}$ for various DME mixing ratios in Flame Series A & B.

To figure out the reason for the temperature increase in the flames with DME addition, the adiabatic flame temperatures and flame temperature profiles of pure ethylene flame and pure DME flame were calculated. Table 3.2 illustrates that the adiabatic flame temperatures of ethylene is higher than that of dimethyl ether. However, the comparison of the peak flame temperatures shown in Figure 3.8 reveals the opposite result. From this figure, the peak flame temperature of pure ethylene flame is lower than that of DME. This phenomenon is related to the laminar flame speed and the heat loss to the burner. Because of the higher temperature gradient near burner surface in pure ethylene flame, the heat loss to the burner is larger compared with that in pure DME flame. So there is a higher peak flame temperature in pure DME flame. Accordingly, when DME is added into the ethylene flame, the peak temperature will increase as a sequence.
Table 3.2: Adiabatic flame temperatures of ethylene and DME flames

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Adiabatic flame temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>2521.7</td>
</tr>
<tr>
<td>Dimethyl ether</td>
<td>2264.3</td>
</tr>
</tbody>
</table>

Figure 3.8: The computational flame temperature profiles at separation distances $H_p = 1.2\text{cm}$ for pure ethylene flame and pure DME flame

### 3.2 Soot Size Distribution and Volume Fraction

Similar to the aforementioned discussion, the addition of DME has a compelling impact on flame structures. In this section, the effect of DME mixing on soot size distribution, number density and volume fraction will be expanded in details. Compared with the multi-university collaborative work on the technique of BSS probe/Scanning Mobility Particle Sizer in Camacho et al. [36], the setup involved in this study can reproduce the shape of the PSDFs for the same flame well except a spatial offset of separation distances.
Figure 3.9: Measured soot size distribution functions for Flame A1
Figure 3.10: Measured soot size distribution functions for Flame A2
Figure 3.11: Measured soot size distribution functions for Flame A3
Figure 3.12: Measured soot size distribution functions for Flame A4

Figure 3.9 demonstrates the measured evolution of normalized particle size distribution functions for Flame A1 at a series of separation distances between burner surface and stagnation plate. From this figure, soot particles start to nucleate at
$H_p = 0.55 \text{cm}$. Then the shoulder that results from soot mass growth and a distinct bimodal distribution is shown at $H_p = 0.8 \text{cm}$. It implies the competition between the generation of small particles and consumption by surface reaction and coagulation among particles. As separation distances continue to increase, soot nucleation is becoming less dominant and at last, the PSDF would transform into a unimodal distribution, which is out the range of this observation.

Figure 3.13: Measured soot size distribution functions for Flame Series A (A1, A2, A3, A4) in terms of DME mixing ratios at separation distances $H_p=0.55\text{cm}$, $0.7\text{cm}$, $0.8\text{cm}$, $0.9\text{cm}$

As for the flames with DME mixing, the measured evolution of normalized particle size distribution functions for Flame A2, A3, A4 at a series of separation distances are illustrated in Figure 3.10, Figure 3.11 and Figure 3.12 respectively. The development of PSDFs for Flame A2, A3, A4 are similar with Flame A1. However, there
Figure 3.14: Measured soot size distribution functions for Flame Series B in terms of DME mixing ratios at separation distances $H_p=0.7cm$

is a notable delay in soot formation process ascribed to DME adding. The separation distances where the apparent shoulder appears are in the order of Flame A1 ($H_p = 0.8cm$), Flame A2 ($H_p = 0.9cm$), Flame A3 ($H_p = 1.0cm$) and Flame A4 ($H_p = 1.2cm$). Moreover, the troughs move to the direction of smaller diameters as more DME mixed, which demonstrates that soot nucleation is inhibited due to DME addition. The extent of inhibition is proportional to the amount of DME mixing.

Adding further evidence to this argument, Figure 3.13 compares the evolution of normalized PSDFs for Flame Series A in terms of DME mixing ratios at separation distances $H_p=0.55cm$, 0.7cm, 0.8cm and 0.9cm. At $H_p = 0.55cm$, no soot is produced for DME adding flames. Then at $H_p = 0.7cm$, where soot nucleation dominants the PSDFs, the largest detected particle diameters decrease from Flame A1 to A3. After that, an apparent shoulder appears in Flame A1 at $H_p = 0.8cm$ while other flames
stay in the previous stage. Finally, at $H_p = 0.9\, \text{cm}$, excluding Flame A4, the PSDFs of the other three flames develop into different degrees of bimodal distributions which implies persistent nucleation combined with particle size growth. Meanwhile, a shift of the position of the troughs indicates the reduction effect of DME on soot nucleation and growth process. Nevertheless, Yoon et al. [21] found a synergistic effect of DME mixing in counterflow flames that DME enhanced the formation of PAHs and soot particles when ethylene doped with a small amount of DME (such as 5%, 14% or so).

To check the synergistic effect in our experimental flames, Flame B2 and B3 with low DME mixing ratios were considered. Figure 3.14 shows the PSDFs for flames with 2% and 5% DME mixing at $H_p = 0.7\, \text{cm}$, it is obvious that no synergistic effect in the operational flames in this thesis and soot nucleation rate is decreasing as the mixing amount of DME increases.

![Figure 3.14: Measured median diameter as a function of DME mixing ratios and separation distance in Flame Series B. The line is fitted to the data.](image)

Additionally, the median diameter and mean diameter can be regarded as the more visualized indicator of particulate mass and size growth. Figure 3.15 and Figure 3.16 depict the measured median and mean diameters as a function of DME mixing ratios and separation distance in Flame Series B (B1, B3, B4, B5, B6). For a fixed DME
mixing ratio, both median and mean diameters exhibit a linearly positive correlation with separation distances within the range of $0.55 \leq H_p \leq 1.2\text{cm}$. At the same separation distance, both median and mean diameters diminish as more DME mixed. Consequently, the increasing rate of mass and size growth of soot particles slows down for flames with fuels combined with DME, which is consistent with the above analysis.

Furthermore, the variation of the relative volume fraction of soot particles regarding DME mixing ratios is summarized in Figure 3.17. The relative volume fractions are defined as the ratios of the volume fractions between DME mixed flames and the pure ethylene flame. As expected, there is an exponential downtrend of the relative soot volume fractions for flames to DME mixing ratios at all the separation distances observed. Besides, the variation of relative number densities as a function of DME mixing ratios at a series of separation distances in Flame Series B is displayed in Figure 3.18. Here the relative number density is defined similar with relative volume fraction. In the nucleation-dominant stage, where $H_p = 0.55\text{cm}$ and $H_p = 0.7\text{cm}$, a sharp drop of soot number density in Flame At the DME mixing ratio of 10% and soot nucleation rate is much lower than pure ethylene flame. Then particle-to-particle
coagulation consumes more nascent soot and thus the rising speed of number densities starts to slow down, which contributes to the smaller inclination at $H_p = 0.8\text{cm}$. As particulate coagulation develops into a higher level, this reduction rate trend is growingly vigorous that the size of soot keeps expanding, which lead to the phenomena that soot number density remains constant or even decrease as a function of DME mixing ratio while soot volume fraction continues to increase at $H_p = 1.0\text{cm}$ and $H_p = 1.2\text{cm}$.

In conclusion, the nucleation and growth process of soot is significantly inhibited at the presence of DME. Undoubtedly, the augment of flame temperatures due to DME addition also contributes to the reduction of soot particulate size growth owning to the thermal decomposition of soot precursors. In order to explore more contributing factors to the effect of DME mixing, characterization such as oxidation behaviors of soot particles and chemical distributions in flames are investigated further.
Figure 3.17: Relative soot volume fraction as a function of DME mixing ratios at various separation distance in Flame Series B. Lines are linearly fitted to the data.
Figure 3.18: Relative number density as a function of DME mixing ratios at various separation distance in Flame Series B. Lines are fitted to the data.
3.3 Oxidation Behaviors and Elemental Analysis of Soot Particles

3.3.1 Oxidation Behaviors

Thermogravimetric analysis of soot in air flow reflected the oxidizability of soot particles. Figure 3.19 shows the conversion (α) and conversion rate profiles (dα/dt) of different soot samples with respect to temperatures. The conversion of soot is defined as

$$\alpha = \frac{M_0 - M_T}{M_0 - M_L}$$

where $M_0$ is the initial weight of dry soot (the weight at 300°C at the end of the isothermal process), $M_L$ is the weight of leftover (or ash, here $M_L = 0$), $M_T$ is the weight of partially oxidized soot at temperature T. Obviously, the addition of DME results in soot particulate being oxidized at lower temperatures and the oxidation process being faster, which indicates the increase of oxidizability of soot derived from DME doping flames. However, the difference of oxidation properties is small when the addition of DME is modest, and there is a striking variation as the mixing ratio increased to 30%. Similarly, the temperature index considered as an indicator of the soot oxidation reactivity shown in Figure 3.20 drew the same conclusion: as DME mixing ratios increasing, soot oxidation occurred and ended at the lower temperatures. This is found to be consistent with the elemental analysis results which will be illustrated later.

From aforementioned discussions, we know that DME mixing could reduce the total soot yielding in both number density and volume fraction. It is noteworthy that soot particles are oxidized while the nucleation, growth and coagulation processes are active. A better oxidizability can weaken soot formation to some extent. Take the temperatures of the maximum combustion rate in Figure 3.20 for example.
Figure 3.19: Profiles of the conversion and conversion rate of soot samples from Flame A1, A2, A3, A4 in terms of temperature. (a) Soot conservation versus temperature; (b) Soot conservation rate versus temperature.

As for higher DME mixing ratio, a decrease of temperature of maximum conversion rate represents the increase of soot oxidation reactivity with $O_2$, which means a decrease of soot resistance to oxidation during the soot formation or maturation processes. Subsequently, more soot particles are consumed during oxidation process, and the total amount of soot emitted is less. In the meanwhile, an increase of flame temperature favors the production of OH radicals and diminishes the production of benzene [45], in this case, leads to the reduction of soot formation and enhancement of the soot oxidation in some ways. Therefore, this oxidation behavior of DME adding flames strongly testifies the results of the variations in soot size distribution and soot volume.
Figure 3.20: Temperature index of soot samples at incremental DME mixing ratios. (a) Temperatures corresponding to 5% conversion; (b) Temperatures corresponding to 50% conversion; (c) Temperatures corresponding to 95% conversion; (d) Temperatures corresponding to maximum conversion rate.

3.3.2 Elemental Analysis

Figure 3.21 shows that the mass ratio between oxygen (O) and hydrogen (H) to carbon (C). Although there are two hollow points deviate from the growing tendency, it is apparent that the increasing DME mixing ratio gives rise to the augment of O/C and H/C mass ratios for both cold gas velocities cases. The O/C ratios suggest that soot with more DME adding should be easier to be oxidized as it has a higher number of oxygen atoms per C atom [46]. Song et al. [14] also mentioned that
the incorporation of greater surface oxygen led to faster oxidation and more drastic transformation of particle structures during the soot oxidation process. Furthermore, the role of surface oxygen groups was more crucial in structural transformation during the oxidation process than their initial structure and pore size distributions.

Figure 3.21: The O/C and H/C mass ratio of soot samples from different flames with respect to DME mixing ratio

The higher H/C can be associated to a higher number of active C−H sites available for oxidation [17], which also represents the oxidative reactivity of soot particles. A higher content of H promotes the possibility of H abstraction by O₂ or other radicals such as H, OH, CH₃, C₃H₃ from the reaction region of a flame. Therefore, it will facilitate the production of radical sites for O₂ attack, which results in the enhancement of soot oxidation rate [17, 46, 45].

Overall, the oxidation behavior of soot samples can be interpreted in light of the O/C and H/C mass ratios data, and it shows a positive correlation with the addition of DME.
3.4 Characteristics of Species and Radical Distributions

Numerical simulation was performed to clarify the effect of DME addition on the major species and radicals during soot formation. The model prediction of the mole fractions of methyl (CH₃), oxygen radical (O), acetylene (C₂H₂), propargyl (C₃H₃) and benzene (C₆H₆), which are essential in the process of PAHs and soot formation, was investigated as a function of H (height above burner surface) at \( H_p = 1.2 \text{cm} \) (separation distance is set as 1.2cm). Figure 3.22 and Figure 3.23 illustrate the concentration profiles of CH₃, O, C₂H₂, C₃H₃ in the flames with the cold gas velocity equals to 6cm/s and 8cm/s, respectively. Either of the figures shows a similar tendency of species and radical distributions related to DME mixing.

First, the computed concentrations of CH₃ for flame series A & B with different DME mixing ratios are shown in Figure 3.22 (a) and Figure 3.23 (a). In the high-temperature region of \( T > 1700 \text{K} \), where the distance above burner surface 0.05 < \( H < 0.2 \text{cm} \), DME addition gives rise to the augments of CH₃ concentrations and higher DME doping cases exhibit the higher CH₃ concentrations. This result is attributable to the pyrolysis reactions of DME under high temperature:

\[
C₂H₆O \rightarrow CH₃ + CH₃O
\]

\[
C₂H₅O \rightarrow CH₃ + CH₂O
\]

Note that methyl radicals will promote the production channels of aromatics species that spring from odd-carbon-numbered species [47, 48, 49], which means that when DME added, some reaction path including CH₃ initiated from DME will enhance benzene formation according to a similar route as for counterflow flames described in [50]:

\[
CH₃OCH₃ \rightarrow (CH₃OCH₂) \rightarrow CH₃ \rightarrow (\alpha - C₃H₅) \rightarrow C₃H₆ \rightarrow CH₃CCH₂ \rightarrow
\]
\[ p - C_3H_4 \rightarrow C_3H_3 \rightarrow (A_1-) \rightarrow A_1, \text{ where } A_1 \text{ represents benzene.} \]

Figure 3.22: Calculated axial profiles of the mole fractions of \( CH_3, O, C_2H_2, C_3H_3 \) relative to the height above burner surface in flames series A with the cold gas velocity equals to 6cm/s at \( H_p = 1.2cm \)

Nevertheless, the aforementioned magnitude of soot yielding implied a reversed situation that DME addition resulted in the drop of soot generation. This discrepancy can be identified in the exploration of the distributions of acetylene and propargyl radicals along the centerline of the flames.

Figure 3.22 (c) and Figure 3.23 (c) illustrate that the computed concentrations of \( C_2H_2 \) for flame series A & B with different DME mixing ratios. Highlight that the concentration of \( C_2H_2 \) is generally regarded as an indicator of the HACA (H-abstraction-
\( C_2H_2 \)-addition) reactions for PAHs formation and growth [6], it is manifest to infer
Figure 3.23: Calculated axial profiles of the mole fractions of $CH_3$, $O$, $C_2H_2$, $C_3H_3$ relative to the height above burner surface in flames series B with the cold gas velocity equals to 8cm/s at $H_p = 1.2cm$.

A positive relation between the $C_2H_2$ concentration and the HACA reaction rate. It can be observed from the figures that there is a notable decrease in the mole fractions of $C_2H_2$ for flames of DME addition. Given more detailed description in Figure 3.24, the proportion of the $C_2H_2$ mole fraction near the stagnation plate between Flame A4 and A1 is 72%. And this proportion shrinks to 67% between Flame B4 and B1, where the flame temperatures are higher. In this case, the effect of DME addition on the distributions of $C_2H_2$ is more vigorous when flame temperature is higher.

In addition, previous works indicate that the rates of odd carbon chemistry reactions for PAHs formation and growth were promoted by the elevation of $C_3H_3$.
Figure 3.24: The proportion of the \( C_2H_2 \) mole fraction near the stagnation plate of Flame A at various DME mixing ratios to the mole fraction of the pure ethylene flame for flames. Flame series A: cold gas velocity = 6cm/s; flame series B: cold gas velocity = 8cm/s.

concentrations \[51, 52\]. Figure 3.22 (d) and Figure 3.23 (d) demonstrate that flames with DME blending restrain the generation of \( C_3H_3 \) radicals. Hence, the reduction of both of the concentrations of \( C_2H_2 \) and \( C_3H_3 \) as DME addition is conducive to the reduction of soot particles.

Taken \( CH_3 \) into consideration, a comparison between the magnitude of the radicals concentration variations exemplifies that the reduction in the amount of \( C_2H_2 \) and \( C_3H_3 \) is relatively considerable than the increment of \( CH_3 \) as DME added. Accordingly, the impact of \( C_2H_2 \) and \( C_3H_3 \) is more significant, so the formation of PAHs and soot will decrease as DME increases.

Adding further credibility to the discussion is the increment of the concentrations of O radical in case of DME adding shown in Figure 3.22 (b) and Figure 3.23 (b). Notwithstanding that the quantity of O radicals from DME pyrolysis is relatively small compared with O radicals from oxygen gases supplied as the oxidizer,
the addition of DME promote the production of O radicals. Moreover, the analog drawn between the two figures elucidates that the mole fraction of O is higher when flame temperature is higher on account of the acceleration of DME pyrolysis in high-temperature region, which may be regarded as one factor for the drop of soot formation as flame temperatures increase.

Figure 3.25: Calculated axial profiles of benzene concentration relative to the height above burner surface in premixed flames at $H_p = 1.2cm$

Therefore, although the elevated concentrations of methyl radicals lead to a slight rise of aromatics in some extent as DME mixing ratios increase, the formation of PAHs and soot particles is suppressed because that the drop of the concentrations of acetylene and propargyl together with the incremental concentrations of oxygen atoms contribute more in soot formation and oxidation processes. Corresponding to this analysis, the effect of DME mixing on benzene production is implied in Figure 3.25, which shows the calculated axial profiles of the mole fractions of benzene for all the flames tested in this study. Generally speaking, benzene is regarded as one of
soot precursors. Accordingly, the apparent trend is consistent with the experimental observations that DME addition and cold gas velocity increment give rise to the decrease of benzene production.

For further understanding of the effect of DME addition on soot oxidation process, calculated concentrations of OH radicals at the separation distance of 1.2cm are shown in Figure 3.26. Flame Series B have higher flame temperature than Flame Series A, which indicates that the augment of temperature favors the production of OH. Moreover, the addition of DME also favors the production of OH. Note that soot oxidation is mainly caused by OH radical attacks. Therefore, the increase of OH concentration in DME mixed flames leads to the enhancement of soot oxidation.

![Figure 3.26: Calculated axial profiles of OH radical concentration relative to the height above burner surface in premixed flames at \( H_p = 1.2 \text{cm} \)](image_url)

Figure 3.26: Calculated axial profiles of OH radical concentration relative to the height above burner surface in premixed flames at \( H_p = 1.2 \text{cm} \)

Thus far, both of our experimental results and numerical simulations show that the ethylene flames mixed with DME exhibit monotonic decreasing tendency of aromatics production, which is proportional to DME mixing ratio. However, it is quite
different that there exists a synergistic effect of DME mixing in counterflow flames. Yoon et al. [21] found that the increase of $CH_3$ concentration exceeded the decrease of $C_2H_2$ concentration to a large extent in counterflow flames when ethylene doped with a small amount of DME (such as 14% or so). As the consequence, the synergistic effect enhanced the formation of PAHs and soot particles in mixture flames of ethylene and DME. This difference implies a different mechanism for soot formation between laminar premixed flames and diffusion flames.
Chapter 4

Concluding Remarks

In this research, experimental measurements coupled with numerical simulations in premixed ethylene flame were conducted to investigate the effect of dimethyl ether (DME) mixing on sooting behavior via evaluating the variation of particle size distribution functions (PSDFs). DME was mixed in premixed ethylene/oxygen/argon flames at the equivalence ratio of 2.0 and the mixing ratios of DME ranged from 0% to 30% of the total carbon fed. Two series of atmospheric pressure flames at different cold gas velocities were tested. Meanwhile, numerical results provided abundant information about flame temperatures and concentration distributions of crucial species. Based on the experimental observations and computational data, we draw the following conclusion:

1. The temperatures measured by thermocouple are consistent with the numerical results. Moreover, the maximum flame temperatures increase as DME mixing ratio increases. Meanwhile, the difference between simulated temperature and the center value of measured temperature is increasing as DME mixing ratio increases, which indicates that the mechanism applied here might underestimate the role of DME.

2. There is a notable delay in soot formation process ascribed to DME addition. It is ascribed to the fact that soot nucleation and mass/size growth are inhib-
ited because of DME addition and the extent of inhibition is increasing as the increasing amount of DME mixing.

3. Soot samples from flames with higher DME mixing ratio show a better oxidizability, which means more soot particles are consumed during oxidation process, so the total amount of emitted soot is less. Meanwhile, the augment of flame temperature favors the production of OH radicals and thus enhances soot oxidation process. Combined these two factors, DME addition can reduce soot yielding though the promotion of soot oxidation. Besides, as the oxidizability of soot particles becomes better, it will facilitate the catalytic or non-catalytic oxidation treatment during the post processing of particle emissions.

4. The oxidation behavior of soot samples can be interpreted in light of the O/C and H/C mass ratios, which show a positive correlation with the addition of DME. Hence, the increase of O/C and H/C mass ratios of soot from flames with higher DME mixing ratio, is responsible for the better soot oxidizability.

5. The concentration distributions from numerical simulations illustrate the reason for the suppressed soot formation. It is because the declined concentrations of acetylene, propargyl and benzene together with the incremental concentration of OH radicals lead to a lower soot nucleation rate and higher oxidation rate. Although more methyl radicals from DME pyrolysis may give rise to the production of benzene, it is relatively small compared with the above impact.

In summary, the addition of DME reduces soot emission in two main ways: on the one hand, it inhibits soot nucleation and mass/size growth, then the production of soot particles decreases; on the other hand, it promotes soot oxidation process by increasing the concentration of OH radicals and improving the oxidizability of the soot particles, then more particles are oxidized. Both of them are responsible for the reduction of soot emissions at the presence of DME.
REFERENCES


[18] S. Maji, S. Ahmed, W. A. Siddiqui, S. Aggarwal, and A. Kumar, “Impact of di-methyl ether (DME) as an additive fuel for compression ignition engine in re-


