DESIGN AND DEVELOPMENT OF A THERMOPHORETIC SOOT SAMPLING SYSTEM FOR HIGH-PRESSURE LAMINAR DIFFUSION FLAMES

by

Alex M. Vargas

A thesis submitted in conformity with the requirements for the degree of Masters of Applied Science
Graduate Department of Aerospace Engineering
University of Toronto

© Copyright 2016 by Alex M. Vargas
Abstract

Design and Development of a Thermophoretic Soot Sampling System for High-Pressure Laminar Diffusion Flames

Alex M. Vargas
Masters of Applied Science
Graduate Department of Aerospace Engineering
University of Toronto
2016

Pollutant formation processes associated with high-pressure combustion pose challenges to optical diagnostics and physical probing of the flames due to various technical problems in comparison to the atmospheric case. One preferred process of studying the size and morphology of soot in atmospheric flames is in situ thermophoretic sampling and transmission electron microscopy. In this work, a multi-probe high-pressure thermophoretic sampling system was developed and used successfully inside a high-pressure combustion chamber. All soot samples were measured at a constant height above the burner exit. Findings show that the mean primary soot particle size decreased about 36% from 2 to 10 atm. In addition, the corresponding soot volume fractions imply that the number of soot nuclei in the soot inception region of the laminar diffusion flames have a strong sensitivity to pressure. The higher amounts of soot are mainly determined by the increasing primary soot particle number densities as pressure increases.
Acknowledgements

I would like to thank my advisor, Professor Ömer L. Gülder, for the guidance he provided throughout my research. His critiques helped guide my journey at UTIAS.

I would also like to thank my family for their support and encouragement throughout the course of my degree. Their presence in my life helped me get through the more challenging stages. Muchas gracias.

To Dr. Emre Karataş: Thank you for helping me get started on my work. For introducing me to the laboratory equipment and for always making time when I had questions or needed help running the equipment.

To Dr. Frank Yuen: Thank you for all your help. The ideas and experience you shared with me truly enabled me complete my work here.

I want to thank all my colleagues at UTIAS, especially those who made my experience here one of kind. Thanks to those who joined me in the gym, played soccer and ultimate frisbee with me, boxed with me, challenged me at ping-pong, and most importantly, shared lunch over “chicken-plate” with me. Thank you for the time we spent together.

“The three most important decisions to make in life are: (i) choosing who you want to spend your time with from 9 am to 5 pm, (ii) choosing who you want to spend your time with from 5 pm to 9 am, and (iii) choosing who you want to spend eternity with.”

– Dr. C. Sallabarger.
Contents

List of Acronyms xi

Nomenclature xiii

1 Introduction 1
  1.1 Motivation ..................................................... 1
  1.2 Research Objectives ........................................... 4
  1.3 Outline of Thesis ............................................. 5

2 Literature Review 7
  2.1 Introduction ................................................... 7
  2.2 The Formation of Soot Particles ............................. 8
  2.3 Experimental Studies of Soot Morphology at High-Pressure . 11
    2.3.1 Studies of Soot Morphology with Laminar Diffusion Flames . 11
    2.3.2 Studies of Soot Morphology with Non-Intrusive Techniques 12
  2.4 Thermophoretic Sampling .................................... 13
  2.5 Transmission Electron Microscopy (TEM) ........................ 15
  2.6 Soot Geometrical Properties .................................. 17
    2.6.1 Soot Particle Size ........................................ 17
    2.6.2 Soot Fractal Dimension ................................... 18
    2.6.3 Soot Fractal Pre-factor .................................. 19
3 Experimental Apparatus

3.1 Introduction .................................................... 23
3.2 High Pressure Combustion Apparatus .......................... 23
   3.2.1 Design of the HPCC ........................................ 24
   3.2.2 HPCC Translational Stage ............................... 25
3.3 Design of the Thermophoretic Sampling System .............. 28
3.4 Thermophoretic Sampling System Operating Specifications ... 31
3.5 Burner Enclosure Design ....................................... 32
3.6 TEM-Grids for Sampling Soot .................................. 33

4 Experimental Apparatus Assembly and Installation ............ 37

4.1 Introduction .................................................... 37
4.2 Burner Enclosure Installation .................................. 37
4.3 TSS Assembly Procedure ....................................... 38
   4.3.1 TSD Assembly ............................................. 38
   4.3.2 MDS Assembly ............................................. 40
   4.3.3 HS Assembly .............................................. 41
   4.3.4 TSD, MDS, and HS Coupling ......................... 41
4.4 Installation of the TSS in the HPCC ......................... 42
   4.4.1 Opening the HPCC ...................................... 42
   4.4.2 Installation of the TSS Support Structure ............ 43
   4.4.3 Installing the MDS ...................................... 45
4.5 Installation of the Electrical Communication and Power Cables ... 46

5 Experimental Procedure ......................................... 48

5.1 Introduction .................................................... 48
5.2 Preliminary Tests .............................................. 48
5.2.1 Grid Exposure Time Tests ........................................ 49
5.2.2 Burner Enclosure Height Adjustment .......................... 49
5.2.3 Homing Sequence Procedure ................................... 50
5.2.4 TSD Sampling Probe Arm Alignment ......................... 50
5.3 HPCC and Burner Operating Procedures ......................... 52
  5.3.1 HPCC Closing Procedure ......................................... 53
  5.3.2 Flame Ignition ..................................................... 54
  5.3.3 Flame Stability .................................................... 55
  5.3.4 HPCC Pressurizing Procedure ................................. 56
  5.3.5 HPCC Depressurizing Procedure ............................... 58
5.4 Soot Sampling Experimental Procedure .......................... 58
5.5 Transmission Electron Microscopy (TEM) Data Analysis ........ 60
  5.5.1 TEM Image Analysis ............................................... 62
6 Results and Discussion .............................................. 66
  6.1 Introduction .......................................................... 66
  6.2 Flame Disturbance Caused by the Sampling Probe .......... 66
  6.3 Results of TEM Image Analysis ................................. 70
  6.4 Sources of Error .................................................... 76
7 Conclusion, Future Work ............................................. 80
  7.1 Conclusion ........................................................... 80
  7.2 Recommendations for Future Work ............................. 81
References ...................................................................... 83
Appendix A Thermophoretic Sampling System Construction Drawings 94
List of Tables

2.1 Soot pre-factor and fractal dimension of previous studies [52]. 20

3.1 Thermophoretic sampling system operating specifications 32

6.1 Breakdown of the number of size measurements by pressure and grid residence time 72

6.2 Primary particle size measurement statistics 78
# List of Figures

2.1 The different frameworks of PAH agglomeration [38]. ........................................ 9

2.2 General representation of an ordinary thermophoretic sampling mechanism [35]. .............................................................. 15

2.3 TEM image of aggregate soot particles sampled from an ethylene-air laminar diffusion flame at atmospheric pressure [68]. ......................... 16

2.4 Soot particle size relative to height above burner [30]. ......................... 18

3.1 Cross-section of the thermophoretic sampling system installed in the high-pressure combustion chamber. ........................................ 25

3.2 Schematic of the co-flow diffusion flame burner that was used in this work [83]. .............................................................. 26

3.3 High-pressure combustion chamber translation stage [81]. ......................... 27

3.4 Isometric view of the sampling system and the burner assembly. ......... 29

3.5 Schematic of the TSD. .............................................................. 29

3.6 Top view of the TSD and burner assemblies. One of the probe arms is shown to be concentric with fuel tube center axis. ......................... 30

3.7 Modified burner enclosure design. .............................................. 33

3.8 Top view of the sampling experiment apparatus and camera. .............. 34

3.9 Region with melted substrate material on the surface of a silicon nitride TEM-grid. .............................................................. 36
4.1 Installation of the burner enclosure on the co-flow annular burner.
4.2 Copper TEM-grid mounted on a sampling probe and secured by a strip of high-temperature resistant adhesive tape.
4.3 Motor drive system.
4.4 Schematic of the homing switch assembly.
4.5 Reference position of the high-pressure combustion chamber.
4.6 High-pressure combustion chamber stationed over the bottom flange support rods of the translational stage.
4.7 Isometric view of the TSS support structure installation.
4.8 (a) Isometric view of the main support plate and burner assembly. (b) Top view of the main support plate and burner assembly.
4.9 (a) Isometric view of the main support plate and burner assembly. (b) Top view of the main support plate, burner assembly, and MDS.
5.1 Flowchart of the homing sequence procedure.
5.2 View of the control panel of the touchscreen interface. The white dashed-line box outlines the home position record button.
5.3 Top view of a TEM-grid aligned co-axially with the fuel tube center axis.
5.4 An example of a custom made cap screw.
5.5 Isometric view of the high-pressure combustion chamber depicting the 32 custom made cap screws used to secure the top and bottom flanges.
5.6 Schematic of the gas delivery system [81].
5.7 Top view of the video camera and high-pressure combustion chamber experimental setup.
5.8 (a) The three velocity stages (1, 2, 3) that the sampling disk experiences when it is collecting soot samples. The sampling occurs during the small time window when the grid is exposed to the flame in velocity stage 2. (b) The three main stages (A, B, C) of probe motion during sampling.
5.9 Picture of a grid (TEMWindows, model: SN100-A50Q33) at 1000× magnification. The white regions are the TEM-grid substrate material and the black regions are the metallic grid structure. ............................. 63

5.10 Image of a soot aggregate sampled from a methane-air laminar diffusion flame at 4 atm. ................................................................. 64

5.11 Image of a soot aggregate particle with ten primary particle chosen and numbered. ................................................................. 65

5.12 Particle size measurement of a soot primary particle from the aggregate in Fig. 5.11. ................................................................. 65

6.1 Typical image series of the sampling process recorded at 10 atm. Starting from the left, a typical stable flame is shown at some time prior to sampling. Image A shows the flame when the probe makes first contact with the flame’s edge. Image B shows the flame when the TEM grid is concentric with the fuel nozzle tip. Finally, Image C shows the flame when the probe’s tail end leaves the flame envelope. ............................. 68

6.2 Image series taken during one sampling routine at 7.1 atm. Pictures were taken with a high frame-rate camera (Photron, model: SA5) and lens (Tamron, 180 mm F/3.5) at a rate of 5000 fps. ................................. 69

6.3 Images of typical flame shape distortion taken at the time when the TEM grid is concentric with the fuel nozzle. The pressure and grid exposure time are indicated at the bottom of each image. ............................. 70

6.4 Primary soot particle size measured by analysis of TEM images which were collected at a height of 3 mm above the burner exit. Each size distribution shows the total count of particle sizes measured at that pressure i.e $P = 2.3$ atm (320 samples), $P = 4.0$ atm (340 samples), $P = 5.4$ atm (300), $P = 7.1$ atm (340), $P = 10.0$ (380). ................................. 71
6.5 TEM image of soot aggregate particles at 2.3 atm (A), 4 atm (B), 5.4 atm (C), 7.1 atm (D), and 10 atm (E).  

6.6 Primary soot particle size measured by LII in a methane-air laminar diffusion flame on a burner in a high-pressure chamber identical to the burner and chamber used in this study. Measurements were taken at a flame height of 6 mm, whereas in the current work TEM images were collected at a height of 3 mm [25].  

6.7 Primary soot particle size measurements for different pressures and residence times. The error bars shown in the image correspond to two standard deviation for the size distributions.  

A.1 Enclosure clamp  
A.2 Burner main base  
A.3 Burner enclosure. Page 1  
A.4 Burner enclosure. Page 2  
A.5 Breadboard support tube  
A.6 TSM disk  
A.7 Probe cover  
A.8 TEM-grid probe  
A.9 Enclosure clamp rod  
A.10 Igniter holder  
A.11 Igniter holder cap  
A.12 Gearbox spacer for position 1 (3 mm above burner nozzle)  
A.13 Motor support bracket. Page 1  
A.14 Motor support bracket. Page 2
List of Acronyms

- AAOR - angular acceleration operating range
- AVOR - angular velocity operating range
- GETR - grid exposure time range
- HPCC - high-pressure combustion chamber
- HS - homing switch
- MDS - motor drive system
- PCS - programmable control system
- TEM - transmission electron microscopy
- TSD - thermophoretic sampling system
- TSS - thermophoretic sampling system
Nomenclature

\( D_f \) - fractal dimension [unitless].

\( d_p \) - soot particle size [nm]

\( k_f \) - fractal pre-factor [unitless]

\( m_T \) - total mass of one soot aggregate [mg]

\( m_i \) - mass of the \( i^{th} \) primary particle [mg]

\( N \) - number of primary soot particles in one aggregate soot particle [dimensionless]

\( n_{\text{pixel}} \) - number of pixels of an image containing an aggregate soot particle [dimensionless]

\( P \) - pressure [MPa]

\( R_g \) - radius of gyration [nm]

\( r_i \) - distance between the aggregate soot particle center of mass and the \( i^{th} \) primary particle [nm]

\( t_r \) - grid exposure time [ms]
Chapter 1

Introduction

1.1 Motivation

Soot production is a commonly observed phenomenon in open flames and in various combustion devices. A simple example is the presence of incandescent soot particles produced that make the candle flame visible with yellow/orange colour. Soot produced in some practical combustion systems, such as steam producing furnaces, increases the heat transfer rate from the combustion gases to the circulating fluids [1]. However, medical and environmental research indicate overwhelmingly that soot particles in the atmosphere are understood to be one of the main causes of lung-disease and one of the leading culprits of global warming [2–7]. The presence of soot in combustion systems could be both beneficial and problematic; therefore, there is a desire to improve our understanding of soot formation and oxidation processes so that combustion systems can be optimized for soot control.

The severity of the negative effects of soot is encouraging further research into understanding the mechanisms of its formation and emission into the atmosphere. Previous studies have focused on understanding the development of soot particles in laboratory flames and in practical combustion engine configurations. Extensive numerical and ex-
experimental studies on this subject have been reported in the combustion literature. A recent review paper on soot formation discusses many of these studies [8]. Numerical models that simulate soot formation have focused on studying the dominant chemical formation pathways that control the process in combustion. The results from experimental studies have been used in numerical models as empirical data for validation. In spite of these extensive studies, the fundamental physics and chemistry associated with soot formation remain incomplete and require further investigation.

Most of the fundamental soot experiments are done in idealized laboratory burners using both intrusive and non-intrusive diagnostic techniques. The results from these experiments have given insight into how soot particle architecture, also known as soot morphology, is affected by different fuel types, temperatures and pressures. However, not much is known about the effect that pressure has on soot morphology. As a consequence of this deficiency, most of the numerical models lack validation in this area. This is a severe problem because most practical combustion systems operate at elevated pressures, and the soot formation numerical models are needed for the design process of these systems.

The formation of soot is an artifact of partially-premixed and diffusive combustion. In both diesel engines as well as gas turbines for aircraft propulsion the mode of operation is mostly non-premixed (diffusion) and partially-premixed combustion. A reliable and consistent combustion process in these engines is possible with overall equivalence ratios much lower than the lean flammability limits. In addition, these engines operate at pressures exceeding 40 atm in gas turbines and 100 atm in diesel engines for thermal efficiency and compactness concerns [9–13].

Pressure has a significant degree of influence on soot concentrations in diffusion flames [8]. Turbulent diffusion flames are not easily characterized because of experimental limitations related to optical accessibility, complex flame geometries, and the vast range of time and length scales. Since the chemical reactions governing the various flame processes are intrinsically nonlinear, the responses of combustion events to pressure changes
are rarely monotonic [8]. Therefore, it is extremely difficult to scale measurements at atmospheric flames to high-pressure combustion. As a result, high pressure combustion has been one of the targeted research areas in industry and academia in recent years.

Currently, measurements of spatially and temporally resolved turbulent mixing rates in sooting turbulent diffusion flames are not feasible. Pressure compounds the problem further not only by affecting the soot formation and oxidation rates (mainly through changing the associated time scales), but by also altering the turbulence field and therefore modifying the mixing rates. Through the use of techniques such as the flamelet hypothesis, which proposes that turbulent flames are a collection of deformed laminar flames, the similarities between laminar and turbulent flames can be exploited [14]. Adopting the flamelet hypothesis may also enable the use of laminar diffusion flames in high-pressure experiments for tractable measurements. However, there are relatively few empirical studies on soot formation in laminar diffusion flames at elevated pressures due to experimental complications [8, 15].

Experimental research in laminar diffusion flames under elevated pressures is held back by the complications in designing an experimental apparatus and in operating instruments that require accessibility for intrusive and non-intrusive measurement techniques. In addition, the stability of laminar diffusion flames, especially originating from buoyancy effects, becomes an important issue at elevated pressures due to the increase in Grashoff number which scales with the square of pressure. These impediments have limited the number and the extent of experimental soot studies in laminar diffusion flames at elevated pressures [8, 15, 16].

A detailed account of soot formation in laminar diffusion flames under elevated pressures, and the intrusive and non-intrusive measurement methods, is given in a recent review paper [8]. Laser scattering and extinction techniques have been successfully used for investigating soot particle size, aggregate size, fractal dimension of the aggregate, and soot concentration in atmospheric flames [17–20]. Although, light extinction and
spectrally-resolved soot radiation have been used for soot concentration and temperature measurements at high-pressure laminar flames [21, 22], light scattering to determine the soot particle size in high-pressure diffusion flames has not yet been demonstrated. Another optical technique to measure soot particle size and concentration is laser-induced incandescence (LII) which has been successfully used at atmospheric conditions [23, 24]. However, the application of LII at high pressures faces several challenges that are not encountered at atmospheric pressure, in both experimental implementation and in the interpretation of the detected signals [25–27]. Recent refinements in the LII technique as well as in the LII heat transfer models have improved the technique to a certain extent, but it is still not clear whether LII is capable of measuring soot primary particle size at elevated pressures [28, 29]. This uncertainty necessitates the use of physical sampling approaches.

The thermophoretic sampling method for soot measurements was first reported by Dobbins and Megaridis to provide complementary information to optical techniques [30]. It has been used widely for atmospheric pressure flames where collected samples are analyzed by transmission electron microscopy (TEM), see for example, Köylü et al. [31], Hu et al. [32], as well as Hu and Köylü [33]. More recently, Leschowski et al. [34] reported a design for sampling soot particles from a high-pressure laminar premixed flame by adopting the pneumatically activated sampling systems of Dobbins and Megaridis and Lee et al. to high-pressures [30, 35].

1.2 Research Objectives

The objectives of the present study are: (i) to design and build a thermophoretic sampling system to integrate with the existing high-pressure combustion chamber at the University of Toronto Institute for Aerospace Studies (UTIAS), and (ii) to carry out proof-of-principle experiments on laminar diffusion flames to show the capabilities of the
designed system at elevated pressures.

Experimental setups capable of simulating high-pressure combustion conditions are limited. The combustion chamber at UTIAS was designed to conduct experiments up to 110 atm \[36\]. The thermophoretic sampling system integrated to the UTIAS chamber will allow for innovative research to be conducted to study the dependence of soot particle size on pressure. Currently, soot research at UTIAS is focusing on soot formation in diffusion flames at high pressures as influenced by fuel type, dilution and biofuel blending.

This thesis discusses the design and operation of a multi-probe thermophoretic soot sampling system. This sampling system provides an easy and precise mean of controlling the thermophoretic probe exposure time. It is capable of collecting ten consecutive samples in a single experimental run. In addition, it does not use pneumatic drivers which are associated with high levels of vibration \[35\]. Proof-of-principle experiments completed using this system in a high-pressure laminar methane-air diffusion flame are presented and discussed. The flame disturbance, as a result of physical sampling, is discussed qualitatively.

### 1.3 Outline of Thesis

This thesis has seven chapters, followed by a reference section, and an appendix. Chapter 2 outlines the importance and current status of soot particle research, reviews the current optical and invasive diagnostics that are used to measure soot geometric properties, and explains the electron microscopy technique for soot geometry analysis. Chapter 3 presents a technical description of the high-pressure combustion chamber that is the platform of the experiments in this study, discusses the design of the thermophoretic sampling system, summarizes the design of the burner enclosure used in the experiments, and discusses the type of grids used for sampling. Chapter 4 outlines the details of positioning the burner enclosure, assembling the thermophoretic sampling disk, installing
the thermophoretic sampling system inside the high-pressure combustion chamber and the positioning of the electrical communication and power cables for the thermophoretic sampling system. Chapter 5 explains the operational procedures of the high-pressure combustion chamber, the soot sampling system, and the transmission electron microscope. Chapter 6 summarizes the soot particle measurement results, and discusses the flame disturbance caused by the sampling process and the measurement uncertainties. Chapter 7 presents the conclusions of this work and recommendations for future research.
Chapter 2

Literature Review

2.1 Introduction

This chapter reviews the soot formation process and discusses previous non-intrusive and physical sampling experiments as well as soot morphology studies relevant to the current work. Section 2.2 discusses the chemical and physical steps that occur during soot formation. Section 2.3 presents the various experimental platforms and non-intrusive diagnostic techniques used for soot morphology studies at high-pressure; subsection 2.3.1 gives the rationale for the suitability of high-pressure laminar diffusion flames for soot morphology; subsection 2.3.2 discusses the advantages and disadvantages of the various non-intrusive techniques used in soot morphology research. Section 2.4 introduces the state-of-the-art, intrusive, diagnostic technique for sampling soot particles from a laminar diffusion flame. Section 2.5 presents the measurement capabilities of the transmission electron microscopy (TEM) imaging technique. Section 2.6 discusses four important soot geometric properties that can be obtained from TEM imaging: soot particle size (subsection 2.6.1), soot fractal dimension (subsection 2.6.2), soot fractal pre-factor (subsection 2.6.3), and the soot particle radius of gyration (subsection 2.6.4). The design and the development of the thermophoretic sampling system described in this thesis was guided
by the review and discussion summarized in this chapter.

## 2.2 The Formation of Soot Particles

Soot formation is a complex process involving chemical kinetics, heat transfer, mass transfer and fluid mixing [37]. As a result, it is sensitive to pressure, temperature, and fuel type. The soot formation process has several steps; the main steps are as follows: fuel pyrolysis, formation of soot nuclei, growth of primary soot particles, and formation of soot aggregates [8]. The following paragraphs review the soot formation steps in more detail.

The soot formation process begins when the fuel molecules are pyrolyzed, due to the intense heat during combustion, into molecular precursors [38]. These soot precursors are the molecular building blocks of soot. They chemically bond into cyclical aromatic rings known as benzene. Singular benzene molecules grow by chemically linking together to form polycyclic aromatic hydrocarbons (PAHs). The evolution of PAHs, such as their geometric configurations and chemical kinetics, is not well understood. At the moment, a consensus has not been reached with regard to which pathway leads to the formation of the first benzene molecule [39]. For example, Frenklach et al. developed a kinetic model and shock-tube experiments that showed benzene formation was controlled by the hydrogen-abstraction-carbon-addition (HACA) pathway [40–43]. However, one inconsistency with HACA is that it incorrectly models the rate of formation of PAHs that is necessary for soot formation [44, 45]. Miller and Melius proposed a different tract, the propargyl radical combination pathway, which correctly models PAH formation rates [44]. The latter pathway is supported with a more recent chemical kinetic model, which shows that benzene formation is controlled by the propargyl radical combination [45]. More empirical data relevant to benzene formation pathways to PAH molecular structures are needed to resolve this debate.
Eventually, PAH molecules grow large enough to become soot nuclei. This process is known as soot nucleation. Soot nuclei are believed to coalesce via three different frameworks. As shown in Fig. 2.1, framework A shows the coalescence of planar PAHs into curved structures, framework B shows the physical coalescence of planar PAHs into stacked structures, and framework C shows the chemical coalescence of PAHs into three-dimensional cross-linked structures [46–48]. The numerical models that simulate soot nucleation have been improved recently [46–48]. These numerical models are helping to identify the areas in the soot formation process that need to be investigated further with experiments. There are ample, but mostly indirect, experimental data that support the formation frameworks B and C. Nonetheless, the acquisition of direct empirical data on the molecular structure of PAH molecules could lead to breakthroughs in understanding the process of soot nucleation [38].

![Figure 2.1: The different frameworks of PAH agglomeration [38].](image)

High temperatures (and pressures in high pressure devices) involved in flames promote soot nuclei to grow through coagulation and agglomeration to form nano-scale structures known as soot primary particles. Images analyzed using TEM show that primary soot particles are solid and spherically shaped, measuring between 10 - 40 nm on average [49]. While these primary particles are forming, they also grow further through collisions and
adherence to one another. They form complex-shaped linked structures that are known as aggregate soot particles [48].

The final step in the soot formation process is the physical adherence of primary soot particles into soot aggregates. These aggregates have complex geometrical architectures that consist of spheroidal, ovoidal, planar, and curved structures [50, 51]. They may contain two to hundreds of primary particles that are physically connected. Primary particles connect through overlapping and/or carbon surface-growths [52]. The morphological properties of soot aggregates have been widely studied in different flame configurations at atmospheric pressure [49, 53–55]. The data from soot morphology studies, specifically soot primary particle sizes and soot fractal dimensions, are highly desirable for the numerical models that simulate soot formation in engines and furnaces. One of the limitations of these simulations is their inaccuracy in modeling soot particle sizes at high-pressures.

Availability of the empirical data is crucial in validating the numerical models that simulate soot formation. Experimental studies on soot morphology have provided some of this data [17–20, 33, 55, 56]. While most of these studies have focused on the effects that fuel type has on soot morphology; one aspect that requires further investigation is the effect that pressure has on soot morphology. It is important to investigate this aspect because the combustion systems that produce soot typically operate at pressures above atmospheric. However, the high-pressure aspect adds another level of complexity to soot morphology experiments. Regardless of their experimental complexity, studies that investigated the effects of pressure on soot have been successfully completed [22, 36, 57, 58]. Mainly non-intrusive methods have been used for these studies at high pressures, but some recent advancements in the design of intrusive techniques have allowed for complementary measurements to be taken [34].
2.3 Experimental Studies of Soot Morphology at High-Pressure

Experimental studies of soot formation at high-pressures is a relatively new field in combustion research. There is a limited number of experimental platforms and diagnostic techniques that have been used successfully. Experiments that investigate soot formation are primarily conducted on three different platforms: co-flow diffusion flames, premixed flames and shock-tubes. All of these platforms have been used for soot formation research to some extent, but only one of these platforms is commonly used for soot morphology research.

Due to oxidation, premixed flames cannot simulate the rich pyrolysis regions required to form soot particles. Therefore, these flames are not typically used for soot morphology research. Moreover, shock-tubes are not used in soot morphology research due to experimental complications in collecting samples of soot from these systems. Further, it is difficult to take tractable measurements of soot particle size in shock-tubes due to their short residence time [8]. The most common platform for soot morphology research is a diffusion flame. One of the frequently used configurations is the co-flow laminar diffusion flame which is annular in shape.

2.3.1 Studies of Soot Morphology with Laminar Diffusion Flames

In practical combustion devices, combustion is turbulent and takes place at high pressures; however, the majority of experiments reported in the literature that investigate soot morphology have been conducted with laminar flame configurations at atmospheric pressure. One of the complexities of turbulent combustion experiments is that the high-levels of intermittency and short residence times make it difficult to track the time-resolved measurements that are conducted for soot morphology studies [8, 20]. Despite their more simplistic configuration, laminar flame experiments that were used to study
soot morphology have produced results that approximate soot surface growth rates in turbulent flames by adopting the flamelet hypothesis [14]. This concept assumes that turbulent flames are collections of deformed laminar flames.

2.3.2 Studies of Soot Morphology with Non-Intrusive Techniques

The most common non-intrusive techniques used for soot morphology studies use light scattering and extinction methods. These methods have successfully measured soot particle size, aggregate size, soot aggregate fractal dimension, and soot concentration in atmospheric flames [17–20]. Furthermore, extinction methods have been used for soot concentration and temperature measurements with high-pressure laminar flames [21, 22, 36, 57–63]. The results from these high-pressure experiments have shown that maximum soot volume concentration increased and co-flow flame diameter decreased as pressure increased, but flame height remained constant. However, the use of light scattering for soot morphology studies in high-pressure diffusion flames has not yet been demonstrated. Another optical technique to measure soot particle size and concentration is laser-induced incandescence (LII) which has been successfully used at atmospheric conditions [23, 24]. The application of LII at high pressures introduces several challenges, in both experimental implementation and in the interpretation of the detected signals, that are not encountered at atmospheric pressure [25–27]. Recent refinements of the LII technique, as well as in the LII heat transfer models, have improved this method to a certain extent. However, it remains unclear whether LII is capable of measuring soot primary particle size at elevated pressures [28, 29]. This uncertainty necessitates the use of physical sampling approaches.
2.4 Thermophoretic Sampling

Experimental studies of soot morphology using intrusive techniques are typically conducted at atmospheric pressure. The advantage of using intrusive techniques is that soot morphology can be analyzed directly. Thermophoretic sampling is the most common intrusive technique. Using this technique, samples of soot particles from a flame are taken and their morphology is analyzed \textit{ex situ} using a transmission electron microscope. One main disadvantage of this intrusive technique is that the flow and chemical reactions within the flame are disturbed at the location where the probe is inserted, creating experimental errors that are difficult to estimate [35]. However, the thermophoretic sampling technique has the potential for further development to be an effective tool in investigating the effect of pressure on soot morphology [14, 34].

Thermophoretic sampling has been used as an intrusive technique for other nano-scale particle morphology research [38, 64, 65]. After the adaptation of this technique to soot research about 30 years ago, further improvements have been reported in the literature. The following discussion presents the thermophoretic particle deposition mechanism known as thermophoresis and reviews some of the previous thermophoretic sampling systems developed.

Megaridis provides a clear description of the thermophoretic particle deposition process [66]: “Nano-scale particles inside a non-isothermal environment are driven from the high to low temperature regions. This particle transport down the temperature gradient is known as thermophoresis”. Thermophoretic sampling of soot particles is based on this mechanism. Soot particles are captured by thermophoretic deposition which is driven by the temperature gradient in the vicinity of a cold transmission electron microscopy (TEM) grid inside the flow field of a sooting flame. This temperature gradient is established by briefly exposing a TEM-grid surface, initially at room-temperature, into the hot flame. The cold surface serves a second important role; it freezes heterogeneous reactions of the particles that are already captured [66]. This chemical freezing action inhibits changes
in the soot morphology after the particles have adhered to the probe surface.

The thermophoretic sampling method for soot measurements was first reported by Dobbins and Megaridis [30] to provide complementary information to optical techniques. It has been used widely for atmospheric pressure flames where collected samples are analyzed by TEM, see for example, Samson et al. [67], Köylü et al. [31], Hu et al. [32], Hu and Köylü [33]. More recently, Leschowski et al. [34] reported a design for sampling soot particles from a high-pressure laminar premixed flame by adopting the pneumatically activated sampling systems of Dobbins and Megaridis [30] and Lee et al. [35] to high pressures.

In general, there are two types of thermophoretic sampling techniques: (i) ordinary thermophoretic sampling, which collects particles along the sampling path, and (ii) localized thermophoretic sampling, which collects particles at a position of interest inside or in the smoke region of the flame [35]. In typical ordinary and localized thermophoretic sampling systems, the probe is exposed to the flame for 2 - 30 ms [33, 35]. The soot samples are collected on the surface of TEM-grids and are further analyzed using TEM. More discussion on TEM analysis is given in section 2.5.

In a localized thermophoretic sampling system, an additional shield protects the probe from collecting particles outside of the desired position. One of the first thermophoretic soot sampling schemes implemented ordinary thermophoretic sampling in laminar diffusion flames at atmospheric pressure conditions [66]. Other researchers added a retractable shield to protect the grid and used a pneumatic cylinder to push the probe to take silica particle samples at various heights along the center axis of a premixed laminar flame at atmospheric pressure [65]. To improve the sampling accuracy of soot particles, TEM-grids were attached to the tips of probes used in laminar and turbulent flame experiments [53]. A general representation of this design can be seen in Fig. 2.2.

After soot particles are collected, typically they are taken to another facility to be examined with a transmission electron microscope. During the transportation of the
particles, it is assumed that their morphology does not change because the TEM-grid has essentially frozen any heterogeneous reactions in the particles. TE-microscopes are capable of identifying particles that measure about 2 nm in diameter. The next section discusses TEM and its application in soot morphology research.

2.5 Transmission Electron Microscopy (TEM)

Megaridis and Dobbins were the first to introduce TEM for soot particle size measurements [30]. This technique is tedious, but it remains the main method of measuring soot particles due to its simplicity. Soot morphology analysis using TEM consists of taking high-magnification pictures of the TEM-grids, then, using an image processing software, soot particle sizes are measured manually and soot fractal dimensions are calculated. These quantities are used to characterize the mass properties of soot [38, 49, 55].

Soot particle size is determined by measuring the longest length of the semi-circular projection of a primary soot particle on an image. The soot fractal dimension is measured from TEM pictures of aggregate soot particles. The software used in this analysis
calculates soot fractal dimension based on the soot agglomerate projected area, perimeter, and resolution of the image. In order to identify clearly the primary particles from an aggregate on a TEM-grid surface, it is crucial that aggregates are imaged singularly. If multiple aggregates are stacked or entangled, the images will depict these aggregates out of focus due to the aggregates vibrating during imaging. It has been shown that the soot deposit area on a TEM-grid should be smaller than 15% of the total surface area of the TEM-grid to avoid aggregates from stacking [35]. An example of a TEM image of a collection of aggregate soot particles is seen in Fig. 2.3.

One drawback to using TEM for soot particle research is that this method has been shown to damage the surfaces of the primary particles [38]. In the process of imaging the agglomerates, the high-power electron beam used in transmission electron microscopes burns holes in the surface of the carbon soot particles. Even with this drawback, TEM can be effectively used to measure soot particle sizes by limiting the time that the samples are exposed to the electron beam.

![TEM image of aggregate soot particles](image)

**Figure 2.3:** TEM image of aggregate soot particles sampled from an ethylene-air laminar diffusion flame at atmospheric pressure [68].
2.6 Soot Geometrical Properties

Previous studies have identified the main geometrical properties of soot particles to be the soot particle size, soot aggregate fractal dimension, fractal pre-factor, and soot radius of gyration [30, 31, 35, 49, 52–55, 67, 69, 70]. The following subsections discuss in more detail the definition and importance of each of the soot geometrical properties.

2.6.1 Soot Particle Size

The soot particle size is defined as the longest length of a single primary soot particle. Previous studies refer to the soot particle size as the primary particle diameter. However, it is not completely correct to define the soot particle size as a diameter. Typical soot primary particles, as observed from TEM images, have structures that are a combination between an ovoid and a sphere with a rough surface [38, 52]. Average soot particle sizes range between 10 – 40 nm depending on fuel type, location of sampling, and pressure. Megaridis and Dobbins [67], as well as Samson et al. [67] showed that soot particle sizes, collected at atmospheric pressure, increased slightly as the sampling height increased along the center axis of the flame. The results from the studies conducted by Megaridis and Dobbins are depicted in Fig. 2.4. Megaridis and Dobbins performed their experiments using ethene and methane fuels, and in both cases, the average soot particle size was between 10 – 40 nm at various heights. They concluded that fuel type effects are minimal on soot particle size. Samson et al. adopted the thermophoretic sampling system developed by Megaridis and Dobbins and measured soot particle sizes about 20 – 30 nm in the smoke region of an acetylene flame produced by a co-annular laminar diffusion flame burner.
2.6.2 Soot Fractal Dimension

The soot fractal dimension, $D_f$, is one of the parameters used in soot morphology studies to characterize the complex structures of soot agglomerates. The fractal dimension is a characteristic number specific to an object whose structure is invariant with scale (magnification). It characterizes the self-similarity of the structure at different magnifications. Apart from the inherent interest of knowing the fractal dimension of soot agglomerates, this parameter is also used to calculate the number of primary particles, $N$, that compose an agglomerate. This calculation is expressed through the power law relationship for soot aggregates given as [67]:

$$N = k_f \left( \frac{2R_g}{d_p} \right)^{D_f},$$

(2.1)

where $k_f$ is the fractal pre-factor, $R_g$ is the radius of gyration, and $d_p$ is the soot particle size. Applying least-square fittings to the power law relationship shown in Eqn. 2.1 has been used as a method to determine the mean value of the fractal dimension for
large collections of agglomerates [49]. The value of the fractal dimension for individual agglomerates is usually measured directly from their projected images [52, 71].

In the literature, values for $D_f$ differ greatly; Table 2.1 presents the values for $D_f$ extracted from several studies. Lapuerta et al. recently investigated the vast differences in values for $D_f$ of soot aggregates and concludes that this vast range in values is primarily due to the complexity of determining an accurate value for $N$ from two-dimensional TEM images [52, 72, 73]. Imaging three-dimensional aggregates exceed the capabilities of the current electron microscopes used in TEM. These microscopes cannot capture the depth of the aggregate structure, making it difficult to account for primary particles that are stacked over one another. The areas in the image where stacking of particles might be present is seen as a darker shade of gray. It is difficult to accurately deduce the number of primary particles that could be stacked in that gray region. This inaccuracy is a source of a systematic error in the measurements using TEM. However, recent developments in TEM have shown that three-dimensional reconstruction of agglomerate structures is possible with computerized tomography (3D-TEM); however, more studies need to be conducted to establish this imaging technique [74–76].

2.6.3 Soot Fractal Pre-factor

The soot fractal pre-factor is the second parameter used in soot morphology studies to characterize the complex geometrical structures of soot aggregates. Agglomerates with similar size and fractal dimensions could exhibit different shapes. The soot fractal pre-factor is a dimensionless parameter that accounts for these differences by expressing how the space is being filled by the agglomerate mass and how the primary particles are packed [33, 49, 52, 55]. There is a lack of agreement in the values for the pre-factor as noted in Table 2.1. This spread in the values is associated with the corresponding dispersion in agglomerate shapes and the use of different experimental techniques to determine the soot fractal pre-factor values. The incongruence in pre-factor values indicate the need to
Table 2.1: Soot pre-factor and fractal dimension of previous studies [52].

<table>
<thead>
<tr>
<th>References</th>
<th>Application</th>
<th>Fractal Pre-factor</th>
<th>Fractal Dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>Meakin</td>
<td>Simulations with agglomerates in general.</td>
<td>1.05</td>
<td>1.74</td>
</tr>
<tr>
<td>Samson</td>
<td>Experiments with soot from combustion of acetylene.</td>
<td>3.49</td>
<td>1.40</td>
</tr>
<tr>
<td>Mountain and Mulholland</td>
<td>Soot simulations.</td>
<td>5.80</td>
<td>1.90</td>
</tr>
<tr>
<td>Megaridis and Dobbins</td>
<td>Experiments with soot from combustion ethene and methane.</td>
<td>2.18 (1.80)</td>
<td>1.62 (1.74)</td>
</tr>
<tr>
<td>Wu and Friedlander</td>
<td>Simulations with agglomerates in general.</td>
<td>1.30</td>
<td>1.84</td>
</tr>
<tr>
<td>Puri et al.</td>
<td>Experiments with soot from combustion of ethene.</td>
<td>9.00</td>
<td>1.74</td>
</tr>
<tr>
<td>Cai et al.</td>
<td>Experiments with soot from combustion of methane.</td>
<td>1.23</td>
<td>1.74</td>
</tr>
<tr>
<td>Köylü et al.</td>
<td>Experiments with soot from combustion of acetylene, propylene, ethylene, and propane.</td>
<td>8.50</td>
<td>1.82</td>
</tr>
<tr>
<td>Sorensen and Roberts</td>
<td>Soot simulations.</td>
<td>1.57 - 1.81</td>
<td>1.3</td>
</tr>
<tr>
<td>Brasil et al.</td>
<td>Soot simulations.</td>
<td>1.27</td>
<td>1.82</td>
</tr>
<tr>
<td>Lee et al.</td>
<td>Experiments with diesel soot.</td>
<td>4.95</td>
<td>1.83</td>
</tr>
<tr>
<td>Gmachowski et al.</td>
<td>Simulations with agglomerates in general.</td>
<td>0 - 215</td>
<td>1 - 3</td>
</tr>
<tr>
<td>Park et al.</td>
<td>Experiments with diesel soot.</td>
<td>1.90</td>
<td>1.82</td>
</tr>
<tr>
<td>Hu and Köylü</td>
<td>Experiments with soot from combustion of acetylene.</td>
<td>1.90</td>
<td>1.77</td>
</tr>
<tr>
<td>Neer and Köylü</td>
<td>Experiments with diesel soot.</td>
<td>1.90</td>
<td>1.77</td>
</tr>
<tr>
<td>Ouf et al.</td>
<td>Experiments with soot combustion of acetylene, toluene, and polymethyl metacrylate.</td>
<td>2.44</td>
<td>1.78</td>
</tr>
</tbody>
</table>

consider it as a variable to be further modeled [52].

2.6.4 Soot Particle Radius of Gyration

The soot particle radius of gyration can be described mathematically as the linear distance from the center of mass to a theoretical point in space where the entire mass of the aggregate would be located and gives an equivalent inertia to the original aggregate. Theoretically, this parameter is calculated using the following equation [55]:

\[
R_g = \left( \frac{\sum_{i=1}^{N} m_i r_i^2}{m_T} \right)^{1/2}
\]

where \( m_T \) is the total mass of the soot aggregate, \( m_i \) is the mass of the \( i \)th primary particle whose center is at a distance \( r_i \) from the center of mass of the soot agglomerate. The theoretical approach to determine the soot radius of gyration is more commonly adopted by numerical models that simulate soot agglomerations. These models are able to calculate \( m_i \) and \( r_i \) values for each of the primary particles that compose the agglomerates.
Chapter 2. Literature Review

However, determining $m_i$ and $r_i$ values from the projected images of soot agglomerates is more complex due to overlapping of primary particles.

Other properties of the projected image have been used to estimate the radius of gyration. One of these approximations estimates the radius of gyration with less than 1% error if the size of the pixel of the projected image of the soot agglomerates remains below 1.3 nm [72]. This digital analysis counts the number of pixels ($n_{\text{pixel}}$) of the projected image that are occupied with soot primary particles. The radius of gyration of an agglomerate using the pixel-counting technique is determined by using the following expression:

$$R_g = \left( \frac{\sum_{i=1}^{n_{\text{pixel}}} r_i^2}{n_{\text{pixel}}} \right)^{1/2}. \quad (2.3)$$

Another digital technique that estimates the radius of gyration uses the square root of the area of the smallest box with length $L$ and width $W$ that surrounds the projection of a soot agglomerate [67], so that:

$$N \propto \left( 2\sqrt{LW} \right)^{D_t}. \quad (2.4)$$

This technique has the advantage of being very simple to compute and allowing batches of TEM soot images to be analyzed more efficiently. However, studies that used this approximation have concluded that it underestimates soot fractal dimensions [49, 55, 67, 77]. Various correction factors have been proposed so that the approximation in [67] can be used in soot morphology studies, but further investigation of soot particle sizes is required to verify this approximation [49].

In summary, soot morphology studies involve the investigation of the geometrical properties of soot particles. A large number of experiments using non-intrusive and intrusive techniques have shown how these properties are affected by fuel type [17–20, 33, 55, 56]. On the other hand, the effects of pressure on soot morphology have only been recently reported in the literature [25, 34]. There are a number of complica-
tions associated with soot morphology studies at high-pressure, such as probe vibrations induced by the pneumatic drivers in thermophoretic sampling [34]. The next chapter describes the design of a new thermophoretic sampling system that is motor driven and can be applied in studies of soot morphology at high-pressures.
Chapter 3

Experimental Apparatus

3.1 Introduction

This chapter describes the experimental set-up that was used in this work. Section 3.2 gives the details of the existing high-pressure combustion chamber (HPCC) (subsection 3.2.1) and the translational stage (subsection 3.2.2). Section 3.3 describes the thermophoretic sampling system (TSS) that was designed and built as part of this thesis work. Section 3.5 describes the modification of the existing burner enclosure to permit the operation of the TSS. Finally, section 3.6 discusses the types of TEM-grids available for nano-particle sampling and highlights the important characteristics of the specific TEM-grid that was used in the experiments for this work.

3.2 High Pressure Combustion Apparatus

The platform for experiments in this work is the high pressure combustion apparatus at UTIAS. The full experimental capabilities of this apparatus are described in various publications [57, 58, 60–63, 78–80]. This system consists of two main components: (i) the HPCC, and (ii) the three-axis translational stage. These are discussed in turn in the following subsections.
3.2.1 Design of the HPCC

Similar to other high-pressure combustion vessels, the HPCC at UTIAS was designed to be cylindrical in shape. The three main parts of the HPCC are: (i) the cylindrical chamber, (ii) the top flange, and (iii) the bottom flange. The HPCC weighs 680 kg, and was manufactured from A36 stainless steel to protect it from corrosion [81]. The cylindrical chamber is made from a 25.4 cm (10 inch) diameter pipe that has a wall thickness of 18.24 mm (0.718 inch). The height of the chamber measured between the top and bottom flanges is 60.0 cm. As seen in Fig. 3.1, the chamber is attached to the top and bottom flanges with 32 bolts. Each flange requires 16 bolts to maintain the chamber sealed when high-pressure experiments are being conducted. These bolts have a nominal diameter of 3.8 cm and a length of 25.4 mm. Physical access into the chamber, which is required for mounting the thermophoretic sampling system, is achieved by detaching the bottom flange from the cylindrical chamber. The processes of detaching the bottom flange from the chamber is discussed in the next chapter.

The HPCC was designed to sustain a laminar diffusion flame at pressures up to 110 atm [36]. Optical access into the chamber is achieved through three view ports mounted at 0°, 90°, and 180° at the mid-height of the chamber, as shown in Fig. 3.1. This view port configuration allows for line-of-sight measurements as well as 90° scattering and imaging experiments. In the center of the HPCC is the co-flow laminar diffusion flame burner. The design of this burner is based on the one developed by Miller and Maahs [82]. The exit diameter of the fuel tube is 3.0 mm, while the exit diameter of the co-flow air tube is 25.4 mm, as shown in Fig. 3.2. The fuel tube nozzle protrudes 2.5 mm above the co-flow air tube nozzle tip. The burner design has several features that help improve the stability of the resulting flame. The first feature is that fuel tube exit tip is tapered on both the inner and outer diameters. This taper was designed to prevent any recirculation zones from forming. The second feature involves metal porous inserts to straighten the flow of the gases as they leave the burner exit. This was accomplished
in the co-flow air tube section by two pieces of porous sintered metal foam. One piece of sintered metal foam was inserted in the fuel tube just below the fuel tube exit. The third feature is a flame enclosure which fits over the co-flow air tube, as shown in Fig. 3.1. The enclosure helps to stabilize the laminar diffusion flame from aerodynamic forces during experiments. Further discussion on the burner enclosure design is presented in section 3.5.

![Figure 3.1: Cross-section of the thermophoretic sampling system installed in the high-pressure combustion chamber.](image)

### 3.2.2 HPCC Translational Stage

The entire HPCC is mounted on a 3-axis translational stage. A schematic of this stage system is shown in Fig. 3.3. The stage uses motor powered worm gears and linear bearings to translate the chamber. The entire stage is controlled via computer with the appropriate
software. The stage is equipped with linear encoders to monitor the spatial location of the chamber with a precision of 5 \( \mu \text{m} \). The encoders also eliminate the error introduced by backlash in the gears. The HPCC is secured to the translational stage using a mounting plate welded on to the outer wall of the chamber. Six steel hex-head bolts (1 - 64 UNC

Figure 3.2: Schematic of the co-flow diffusion flame burner that was used in this work [83].
Chapter 3. Experimental Apparatus

2B) connect the chamber to the translation stage. The robust and versatile design of this stage allows for detailed spatial measurements of the flame as well as convenient access to open the chamber for service and experimental apparatus installation.

Access to the combustion chamber is needed for various tasks. After the installation and operation of the TSS, the chamber should be opened to remove soot samples collected for analysis, and to place new sample grids. The HPCC provides access by separation of its bottom flange. To remove the bottom flange, the HPCC is lowered until the bottom flange rests over the four support rods located at the base of the translation stage. Then, the 16 bolts that secure it are removed. Finally, the HPCC is elevated, leaving the bottom flange resting on the flange supports and exposing the burner assembly.

Figure 3.3: High-pressure combustion chamber translation stage [81].
3.3 Design of the Thermophoretic Sampling System

The TSS consists of a sampling disk, a motor drive system (MDS), and a programmable control system (PCS). The entire system and burner assembly is displayed in Fig. 3.4. The central part of the TSS is the sampling disk. As shown in Figs. 3.5 and 3.6, the sampling disk houses ten sampling probe arms. The probe arms extend radially outwards to a maximum diameter of 109.5 mm. The radial extension of each probe arm can be adjusted by ±1.25 mm so that flame localized thermophoretic sampling could also be conducted. Each sampling probe arm holds a 3 mm diameter TEM-grid (SPI, model: 3520C) in a pocket that is located at the end of the probe arm. This pocket has a depth of 0.5 mm. In the center of the pocket is a 2.5 mm diameter hole that, during sampling, exposes the surface of a TEM-grid to the flame. The TEM-grids are secured using high-temperature resistant adhesive tape strips that measure 3 mm and 8 mm in width and length, respectively. These strips are centered and placed over the rim of the TEM-grid and the probe. Then the edges of the strips are wrapped around the probe.

The circular sampling disk is driven by the MDS, which consists of a stepper motor (Parker, model: OS22B), a 10:1 ratio gearbox (Parker, model: 10:1-PX23), a rotational encoder (Parker, model: 755A-23A), and a homing limit switch (Crousset Switches, model: 831860CFD0). The stepper motor is mounted to the gearbox using a flexible coupler. This method dampens the vibrations that arise from the shaft misalignment between the stepper motor and the gearbox. The gearbox has a custom made output shaft with a flat-top design to secure the thermophoretic sampling disk (TSD). The rotational encoder is mounted to the bottom of the stepper motor, and its purpose is to track the stepper motor displacement with a precision of ±0.0014°. The homing switch, used by the PCS, determines the home position of the TSD and allows tracking of angular displacement during experiments.
Figure 3.4: Isometric view of the sampling system and the burner assembly.

Figure 3.5: Schematic of the TSD.
The PCS is mainly used to allow the user to control the grid exposure time and velocity profile of the grid through the flame. The time period during which the grid is exposed to the flame is a critical parameter of the soot sampling process. If the sampling time is too long, soot aggregates could stack on top of each other, compromising the clarity of the TEM images. Furthermore, a long exposure time could cause the flame to burn the grid surface. On the other hand, if the exposure time is too short, there is a possibility that soot particles would not be collected [20, 35]. The safe range of exposure times should be determined by trial and error, and an experimental procedure for this is discussed in subsection 5.2.1. The tried and tested exposure times along with other TSS operating specifications are discussed in the following section.
3.4 Thermophoretic Sampling System Operating Specifications

The specifications of the thermophoretic sampling system are presented in Table 3.1. The motor driver and stepper motor performance specifications were directly retrieved from the Parker Motion ZETA6104 installation guide [84]. The thermophoretic sampling system specifications presented in the table refer to the system’s tested operating specifications. That is, the values presented for the disk angular velocity and corresponding grid exposure time were determined in the experiments. For example, the grid exposure time was validated by counting the number of frames from a high frame-rate image series that recorded the sample taking process. More discussion on the high frame-rate image series is presented in chapter 6.

To clarify, the specifications presented in the table below do not represent the overall operating capabilities of the thermophoretic system. They simply present the operating conditions that were used to take the proof-of-principle experiments for this work. This sampling system was designed to give users the capacity to alter the sampling time. To do this, users can change the angular dynamic parameters of the stepper motor by using the PCS to set the angular velocity operating range (AVOR) from 1 – 50 rev/s, and the angular acceleration operating range (AAOR) from 1 – 9999 rev/s². Extrapolating from the values of the AVOR, the respective grid exposure time range (GETR) is 52.9 – 2.65 ms. The AVOR, AAOR, and GETR represent the full range of the TSS angular dynamic capabilities.
Table 3.1: Thermophoretic sampling system operating specifications

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Motor Driver (Parker, model: ZETA6104) Performance</strong></td>
<td></td>
</tr>
<tr>
<td>Position Range</td>
<td>$\pm 2,147,483,648$ steps</td>
</tr>
<tr>
<td>Stepping Accuracy</td>
<td>$\pm 0$ steps</td>
</tr>
<tr>
<td>Velocity Range</td>
<td>$1 - 2,000,000 \frac{\text{steps}}{s}$</td>
</tr>
<tr>
<td>Velocity Accuracy</td>
<td>$\pm 0.02%$ of maximum rate</td>
</tr>
<tr>
<td>Velocity Repeatability</td>
<td>$\pm 0.02%$ of set rate</td>
</tr>
<tr>
<td>Acceleration Range</td>
<td>$1 - 24,999,975 \frac{\text{steps}}{s^2}$</td>
</tr>
<tr>
<td>Motion Algorithm Update Rate</td>
<td>2 ms</td>
</tr>
<tr>
<td><strong>Stepper Motor (Parker, model: OS22B)</strong></td>
<td></td>
</tr>
<tr>
<td>Static Torque, Nm (oz-in)</td>
<td>1.09 (155)</td>
</tr>
<tr>
<td>Rotor Inertia, $\text{kgm}^2$ (oz-in$^2$)</td>
<td>0.253 (1.390)</td>
</tr>
<tr>
<td><strong>Thermophoretic Sampling System</strong></td>
<td></td>
</tr>
<tr>
<td>Number of steps per revolution</td>
<td>$250,000 \frac{\text{steps}}{\text{rev}}$</td>
</tr>
<tr>
<td>Angular position accuracy of sampling disk</td>
<td>0.00144 $\frac{\text{deg}}{\text{step}}$</td>
</tr>
<tr>
<td><strong>Grid exposure time and its corresponding sampling disk angular velocity</strong></td>
<td></td>
</tr>
<tr>
<td>Exposure time: 7.56 ms</td>
<td>$1.0 \frac{\text{rev}}{s}$</td>
</tr>
<tr>
<td>Exposure time: 5.4 ms</td>
<td>$1.4 \frac{\text{rev}}{s}$</td>
</tr>
<tr>
<td>Exposure time: 4.2 ms</td>
<td>$1.8 \frac{\text{rev}}{s}$</td>
</tr>
</tbody>
</table>

3.5 Burner Enclosure Design

The purpose of the original design of the burner enclosure was to protect the laminar flame from any gas movements within the chamber that may induce flame oscillations. It has an overall diameter of 44.5 mm and in the modified design (Fig. 3.7) a provision is
made for a horizontal slot that allows the sampling disk probe arms to physically access the flame and to take samples. In order to sample at different heights along the flame’s vertical axis, the enclosure is adjusted manually to the desired height. This procedure is described in detail in subsection 5.2.2. Another function of the enclosure is to secure a flame igniter 25 mm above the fuel nozzle tip. Visual alignment of the probe to the burner nozzle is facilitated though a vertical slot which contains a quartz window. As seen in Fig. 3.8, a camera was aligned with one of these view ports to record video and take photographs of the flames.

![Diagram of modified burner enclosure design](image)

Figure 3.7: Modified burner enclosure design.

### 3.6 TEM-Grids for Sampling Soot

The most common TEM-grids used in soot sampling are copper grids coated with a carbon substrate. Due to their popularity in other nano-scale sampling research, a larger variety of grid materials and substrate materials is available. Some of these grids were tested using the TSS in order to determine which one would produce the best sampling
results. The main parameters that were investigated qualitatively were the grid temperature resistance and the grid architecture. These grid parameters were observed to have the most effect on the quality of the soot aggregate images analyzed using TEM.

Grid temperature resistance was observed to be the critical parameter in these experiments. It is limited by the temperature resistance of the substrate material. Typically, TEM-grids are comprised of a 20 µm thick copper or nickel grid with a 20 nm thick non-metallic substrate. In other high-temperature application research, silicon nitride and molybdenum substrate materials have successfully been used [85, 86]. The results from these studies have shown that using these substrate materials significantly increases the clarity of the images processed with TEM. In an effort to adopt these materials for soot sampling, silicon nitride grids were tested. However, these grids did not remain intact during the sampling process. As seen in Fig. 3.9, silicon nitride substrate was observed to
melt near the soot particle deposits. In this work, grids with a carbon substrate yielded the best results for the temperature and pressure conditions tested.

The grid architecture has a significant influence on TEM imaging results. A typical grid is manufactured from a metallic thin sheet, typically copper or nickel, and has a nano-manufactured rectangular mesh cut into it. The mesh is necessary for proper TEM imaging because it provides the structural support for the substrate material as well as provide access for particles to collect on the surface of the substrate material. Grids can be manufactured with a wide range of mesh sizes. Mesh sizes are typically measured as the distance between two adjacent mesh pockets. This distance is also known as the pitch and is measured in $\mu$m. Grids with a large pitch, such as 30 – 600 $\mu$m, exhibit more structural robustness than grids with a low pitch, such as 5 – 15 $\mu$m. However, grids with a large pitch have two disadvantages: (i) less mesh surface area is exposed for sampling and (ii) more heat is absorbed by the metallic grid during sampling which can cause the substrate material to condense and/or break. The main drawback of using meshes with a low pitch is a decreased structural integrity. This limits their applicability in soot thermophoretic sampling due to the high dynamic nature of this method. The experiments in this study showed good sampling results using grids with 15 $\mu$m.

The TEM-grids used in the present study were comprised of a copper grid material, coated with a carbon substrate, and had 200 meshes. These grids were able to withstand the flame temperatures and high-pressure environment during the experiments. From TEM analysis, the soot aggregate image contrast was comparable to published results in the literature [30, 33, 70, 87].

Soot samples were collected and retrieved using the experimental apparatus described in this chapter. The TSS was installed next to the burner assembly of the HPCC for these experiments. The installation procedure for this experimental apparatus is discussed in the next chapter.
Figure 3.9: Region with melted substrate material on the surface of a silicon nitride TEM-grid.
Chapter 4

Experimental Apparatus Assembly and Installation

4.1 Introduction

This chapter discusses the assembly and installation of the components that are a part of the thermophoretic sampling system (TSS) and co-flow burner. Section 4.2 describes the installation and alignment of the burner enclosure. Section 4.3 gives the details of the step-by-step process required to construct the TSS. Section 4.4 describes the step-by-step process of installing the TSS in the HPCC. Finally, Section 4.5 discusses the installation procedure of the electrical communication and power cables.

4.2 Burner Enclosure Installation

The burner enclosure is installed to protect and stabilize the flame from re-circulating air inside the HPCC. It has a glass window which allows for the visualization of the flame during experiments. For proper visualization, the glass window is aligned parallel to the 90° view-port of the HPCC. The burner enclosure is manually fitted onto the burner co-flow tube, as shown in Fig. 4.1. The burner enclosure height can be adjusted manually.
by changing the distance that the enclosure overlaps with the rim of the co-flow annular burner. The minimum burner enclosure overlap was determined to be 4.5 mm in order to visualize the entire flame height from outside the HPCC.

Figure 4.1: Installation of the burner enclosure on the co-flow annular burner.

### 4.3 TSS Assembly Procedure

The process of constructing the TSS requires four main steps: (i) assembly of the TSD, (ii) assembly of the MDS, (iii) assembly of the HS, and (iv) coupling of the TSD, MDS, and HS assemblies together. These steps are discussed in detail in the following subsections.

#### 4.3.1 TSD Assembly

The TSD is comprised of ten sampling probes arms mounted to a disk with a diameter of 86 mm. The sampling probes are housed in slots that are cut into the bottom surface of
the disk. Each probe is secured to the disk using one button-head bolt (M2-3 mm). Once the sampling probes are properly secured to the disk, the TEM grids can be mounted to the TSD probe arms. This was accomplished by using strips of high-temperature resistant adhesive tape that measured 3 mm in width and 8 mm in length. These strips were placed over the rim of the grid and the probe arm, as shown in Fig. 4.2. To correctly place the grids on the probe arms, first, the grid was placed in the grid pocket located at the tip of the sampling probe arm. Then, a strip of the high-temperature resistant adhesive tape was placed over both the rim of the grid and the probe arm. The tape was secured in place by overlapping the ends of the strip of tape.

Figure 4.2: Copper TEM-grid mounted on a sampling probe and secured by a strip of high-temperature resistant adhesive tape.
4.3.2 MDS Assembly

The MDS controls the motion of the TSD during experiments by controlling the rotation of a stepper motor which is physically connected to the TSD via a gearbox. The MDS has three main components: (i) a gearbox, (ii) a mounting bracket, and (iii) a stepper motor. These components are shown in Fig. 4.3. Four socket-head bolts (M5-45 mm) are used to assemble the stepper motor, mounting bracket, and gearbox together.

Figure 4.3: Motor drive system.
4.3.3 HS Assembly

The homing switch is used to establish a home position for the TSD. In order to home the TSD before experiments, the homing switch is triggered by a plastic lobe which is located on the bottom surface of the TSD. The lobe is set in place by aligning it between two sampling probe arms and securing it using the probe arm button-head bolts (M2-3 mm), as shown in Fig. 4.4. The HS can be adjusted manually up to ±3 mm in both the horizontal and vertical directions to ensure proper triggering of the switch.

Figure 4.4: Schematic of the homing switch assembly.

4.3.4 TSD, MDS, and HS Coupling

The final step in constructing the TSS requires the TSD, MDS, and HS assemblies to be physically connected. The HS is installed on the top surface of the MDS gearbox with
a mounting bracket and two socket-head cap screws (M5-15 mm), as shown in Fig. 4.4. Then, the TSD is connected to the gearbox of the MDS using six socket-head cap screws (M5-20 mm). The bolts are inserted from the top side of the TSD and placed into the threaded holes of the gearbox’s flat-top output shaft, as shown in Fig. 4.3. Once the TSS is assembled following the steps that were discussed in the previous subsections, the TSS is now able to be installed in the HPCC.

4.4 Installation of the TSS in the HPCC

This section discusses the step-by-step procedure that is required to properly install the TSS in the HPCC. To begin the discussion of the step-by-step procedure, a physical and representative reference position for the HPCC is established. This reference position is selected to be 100 cm above the translational stage base, as shown in Fig. 4.5. At this reference position the HPCC is assumed to be closed and only containing the co-flow laminar diffusion flame burner.

4.4.1 Opening the HPCC

The first step in the process of opening the HPCC is to loosen the bolts that attach the bottom flange to the HPCC. The bolts will be fully removed in a later step. Second, the HPCC is lowered, using the translational stage, until the bottom flange rests over the support rods of the stage, as shown Fig. 4.6. Third, the bolts that secure the bottom flange of the HPCC are removed. Fourth, the HPCC is raised, using the translational stage, a distance of 120.0 cm above the translational stage base. Finally, the HPCC is secured at this height by connecting the support bolts of the translational stage to the top flange of the HPCC. Once the HPCC is secured at the top of the translational stage, the installation of the TSS can proceed.
4.4.2 Installation of the TSS Support Structure

The installation of the TSS support structure must be completed prior to installing the TSD, MDS, and HS coupled assembly. The TSS support structure is secured to mounting studs located on the bottom flange of the HPCC. Four mounting studs with M6 threads and measuring 10 mm in height, 15 mm in length, and 15 mm in width are welded to the top surface of the bottom flange. The purpose of these studs is to serve as anchors for mounting experimental equipment; such as the TSS support structure. These studs are depicted in Fig. 4.7. Only three of the four studs are used to secure support structure to
the bottom flange. The next step in the installation process is to secure the main support plate of the TSS. Three socket-head cap screws (M6-145 mm) are passed through the corner holes of the main support plate. Then, three 135 mm long steel tubes with an inner diameter of 10.92 mm and an outer diameter of 12.70 mm are fitted over the entire length of the socket-head cap screws to function as sleeves and provide the necessary height offset of the main support plate. Next, the main support plate with the socket-head cap screws and steel sleeves is then aligned so that the front of the main support plate faces the front of the flange as depicted in Fig. 4.8(b). Finally, the three socket-head cap screws are threaded into the mounting studs.
4.4.3 Installing the MDS

The MDS is installed by securing it to the main support base of the TSS. First, four steel offset spacers measuring 19 mm in height, 6.4 mm in inner diameter, and 12.7 mm in outer diameter are placed coaxially with four mounting holes of the main base plate, as depicted in Fig. 4.8. Second, four socket-head cap screws (1/4-20 UNC) are passed though the four slots of the MDS mounting bracket. Third, the sampling disk is aligned to slide into the slot of the burner enclosure. Fourth, the four socket-head cap screws are passed through the spacers and threaded into holes on the main support plate. The slots allow $\pm 3.3$ mm of adjustment along the $45^\circ$ axis that is shown in Fig. 4.9. This adjustment is necessary to appropriately position the sampling arms of the TSD assembly. The TEM-grid on the sampling arm must align coaxially with the fuel nozzle tip. This alignment process is discussed in more detail in subsection 5.2.4.
4.5 Installation of the Electrical Communication and Power Cables

In order to control remotely the TSS from outside the HPCC, the power cables and communication cables are passed through access port holes located on the cylindrical wall of the HPCC. This procedure completed by means of a high pressure resistant multi-hole gland (Conax, model: M4MH). This gland provides a tight vacuum seal up to 680 atm. Two glands were required to install all the cables necessary for operating the TSS. In total, three cables are passed through the glands: one communication cable with an outer diameter of 6.35 mm (1/4 in), and two direct current power cables (one +5 volts, one ground) each with a diameter of 1.6 mm (1/16 in). The communication line connects the stepper motor to the motor driver that is located outside the HPCC, and the DC power cables are used to connect the homing switch to a programmable
Chapter 4. Experimental Apparatus Assembly and Installation

Figure 4.9: (a) Isometric view of the main support plate and burner assembly. (b) Top view of the main support plate, burner assembly, and MDS.

controller.
Chapter 5

Experimental Procedure

5.1 Introduction

This chapter describes in detail the preliminary tests and experimental procedures that were carried out in chronological order. Section 5.2 describes the preliminary tests that were conducted to operate, align, and position the TSS. Section 5.3 describes the HPCC and burner operating procedures. Section 5.4 describes the soot sampling procedure. Finally, Section 5.5 discusses the TEM imaging procedure.

5.2 Preliminary Tests

The preliminary tests were conducted with the HPCC fully open so that the components of the TSS were accessible. These tests include: determining grid exposure times, adjusting the burner enclosure height, homing the TSD, and aligning the TSD sampling probe arms with the burner fuel nozzle tip. Each of these tests is discussed in more detail in the following subsections.
5.2.1 Grid Exposure Time Tests

As discussed previously in chapter 2, the grid exposure time is a critical parameter in thermophoretic soot sampling. It directly affects the quantity of soot that deposits on a TEM-grid. With the current TSS design, the grid exposure time is determined by the angular velocity of the sampling disk. The user inputs an angular velocity value via a touchscreen and the PCS proceeds to calculate the corresponding sampling disk velocity profile. The velocity profile describes the different angular dynamic stages achieved by the sampling disk during sampling. As seen in Fig. 5.8(a), the velocity profile exhibits three dynamic stages: rapid angular acceleration from 0 – 25 rev/s from 0 – 0.06 s, constant angular velocity of 25 rev/s from 0.06 – 0.34 s, and rapid angular deceleration from 25 – 0 rev/s from 0.34 – 0.4 s. In the grid exposure time tests, the sampling disk angular velocity was varied to determine an appropriate range of exposure times.

Typically, a grid exposure time is deemed appropriate if the ratio of soot covered area over the total grid surface area is less than 15% [35, 73]. Most thermophoretic soot sampling systems are able to appropriately collect soot within an exposure time range of 2 – 70 ms [35]. However, these typical systems collect samples from flames at atmospheric pressure and have not investigated the effect that pressure has on grid exposure time. At high pressures, the soot volume fraction of methane-air laminar diffusion flames increases [8, 36, 60]. With a larger amount of soot forming in these flames, it was expected that the range of appropriate exposure times would be on the lower end of a typical exposure time range. In this work, multiple exposure times were tested for pressures up to 10 atm. From the tests performed, an appropriate range of exposure times was determined to be 4.0 – 8.0 ms.

5.2.2 Burner Enclosure Height Adjustment

The height of the burner enclosure is adjusted to maintain sampling height consistency in the experiments and to ensure that the TSD rotates without interfering with the
burner enclosure slot during sampling. Any physical interference between these two components is undesirable due to the high angular velocities associated with the sampling experiments. The total clearance distance between the TSD and the burner slot is 1.0 mm. To ensure there is a proper clearance, the TSD is set to rotate continuously at $1 \text{ rev/s}$ until a 0.5 mm metal shim is able to be inserted between the components.

### 5.2.3 Homing Sequence Procedure

In order to control and track the rotation of the TSD, a home position was established. This home position is determined when the homing switch of the HS assembly (refer to subsection 4.3.3) is triggered by the plastic lobe located on the bottom surface of the TSD. Once the switch is triggered, the TSD rotation is stopped and the disk’s angular position is saved to the memory of the PCS as the home position. To accomplish this procedure, a homing sequence that is programmed into PCS is used, as seen in Fig. 5.1. This sequence starts by setting the TSD angular velocity and acceleration parameters to the constant values of $1 \text{ rev/s}$ and $1 \text{ rev/s}^2$, respectively. Then, the TSD is rotated at this low speed until the lobe of the TSD triggers the homing switch. Once the switch is triggered, the PCS stops the TSD rotation. The user can then save the current TSD position by pressing the home position record button on the touchscreen interface, as shown in Fig. 5.2.

### 5.2.4 TSD Sampling Probe Arm Alignment

In order to properly take the samples, the TEM grids must sweep directly above the center axis of the fuel tube. This requires that the TEM grids are coaxially aligned with the fuel tube during the grid exposure time. To ensure that the grid and fuel tube are properly aligned, a sampling probe arm alignment procedure is carried out. This alignment procedure starts by centering a TEM-grid with the center axis of the MDS assembly, as shown in Fig. 4.9. The MDS center axis is denoted as the 45° axis. The
TEM-grid centering is accomplished by continuously adjusting the stepper motor angular displacement using the PCS until the grid is aligned with the 45° axis. The stepper motor angular displacement is adjusted by inputing different displacement values into the travel distance input on the top left hand corner of the touchscreen interface shown in Fig. 5.2. Throughout the alignment process, the angular velocity and acceleration of the TSD were kept constant at 1 rev/s and 10 rev/s², respectively. To initialize the TSD rotation, the direction of rotation toggle button is set to clockwise and the GO button is triggered. The direction of rotation toggle and the GO buttons are shown in Fig. 5.2. Once a TEM-grid is aligned with the 45° axis, the MDS is manually maneuvered over until the grid is directly above the fuel tube nozzle, as shown in Fig. 5.3.

Once the preliminary tests were completed, the TSD was homed (following the pro-
Chapter 5. Experimental Procedure

5.3 HPCC and Burner Operating Procedures

Before starting any experiment, all electronic systems are turned on and allowed to reach operating conditions for 30 minutes. Then, the internal pressures of the air and fuel tanks were checked to be at least 136 atm (2000 psi) [81]. This was done to ensure there would be sufficient back-pressure to supply the proper flow of air and fuel into the HPCC for the high pressure experiments. Next, the HPCC was closed. Then, the flame was ignited and monitored until it reached a stable state. Next, the HPCC was pressurized to the desired pressure. Then, soot samples were collected using the TSS. Finally, the HPCC was depressurized and the samples were removed. The following subsection outlines the
Chapter 5. Experimental Procedure

5.3.1 HPCC Closing Procedure

Before the HPCC was closed, a thin layer of high-vacuum grease was spread over the top surface of the bottom flange. Then, the translational stage was used to lower the HPCC until it rested over the bottom flange. Next, 16 flat washers, with a 38.1 mm inner diameter, were placed concentric with the 16 through-holes on the bottom of the HPCC. Then, 16 custom made cap screws were placed through the washers and into the through-holes. One of these custom made cap screws is depicted in Fig. 5.4. Each custom cap screw comprised of a bolt (1.5-6 UNC, SA354) and a hex nut (1.5 UNC).
As seen in Fig. 5.5, these cap screws were placed in a circular configuration around the center axis of the HPCC. Once installed, the bottom ends of these cap screws protrude approximately 40 mm below the bottom flange. Next, 16 hex nuts and flat washers were screwed to the protruding end of custom cap screws. The cap screws were tightened 4.3 Nm using a torque wrench [81]. Once the HPCC was closed and the cap screws were tightened, the translational stage was activated to raise the HPCC 10.0 cm so that the fuel line could be connected to the burner.

![Figure 5.4: An example of a custom made cap screw.](image)

5.3.2 Flame Ignition

To ignite the flame, first, the fuel flexible tube, located below the translational stage, was connected to the fuel line input located on the bottom flange of the HPCC. Then, the air and fuel mass flow controllers (Brooks, model: SLA5850) are set to the desired flow rates. A schematic of the fuel and air delivery system is depicted in Fig. 5.6. Next,
5.3.3 Flame Stability

As described in a previous study [81], the stability of a laminar diffusion flame similar to the one used in this work was characterized by two different motions, flame sway and flame tip flicker. Flame sway is defined as the laminar diffusion flame exhibiting a left to right movement. This movement can be oscillatory and/or random. To decrease the magnitude of the flame sway, an increase in the co-flow air to the burner rectified this phenomenon. This provided a stronger flow stream of air around the diffusion flame to keep the flame centered in the burner. The second type of flame instability, the flame
flicker, is observed to be minimized by changing the fuel mass flow rate. It is observed that as the rate increased, the flame had a greater tendency to flicker. This effect occurred due to the pressure gradient in the fuel mass flow controller (MFC). To increase the stability, the pressure gradient across the MFC should be between 0.14 and 0.20 MPa. The fuel mass flow rate used in the experiment is kept constant at $55 \text{ mg s}^{-1}$ to match the condition of the previous experiments in this laboratory.

### 5.3.4 HPCC Pressurizing Procedure

To increase the pressure in the chamber, the back-pressure by-pass valve was closed, and the pressure was allowed to gradually build up with air and combustion products (flames are over ventilated). Reference Fig. 5.6 to view the schematic of the fuel and air delivery system.
delivery system. The combustion chamber pressure was monitored by a pressure trans-
ducer, and the spring-loaded back-pressure regulator was adjusted manually until the
desired pressure was maintained steadily. This method allowed the system to pressurize
while maintaining an ignited flame. During pressurization, the flame height shortened,
increasing the possibility of flame extinction. To prevent flame extinction, the air mass-
flow controller was constantly adjusted so that the air flow into the co-flow tube did not
extinguish the flame. The internal pressure of the HPCC was increased by periodically
adjusting the back pressure regulator. Adjusting this device decreased the amount of
air that was being vented, therefore increasing the internal pressure of the HPCC. For
reasons of establishing a stable flame and ensuring the internal pressure remained at the
desired level, the system was monitored for at least 20 minutes prior to taking samples
[36, 81].

Figure 5.7: Top view of the video camera and high-pressure combustion chamber exper-
imental setup.
5.3.5 HPCC Depressurizing Procedure

To depressurize the HPCC, first, the flame was extinguished by closing the fuel mass flow controller. Once the flame was extinguished, the air mass flow controller was closed and the bypass exhaust valve was opened to depressurize the HPCC [36, 81]. The location of the bypass exhaust valve in the air delivery system is depicted in Fig. 5.6. Venting the compressed air continued until the internal pressure of the HPCC reached the desired level.

5.4 Soot Sampling Experimental Procedure

Once the subject flame was established at the desired pressure and fuel flow rate, the sampling procedure was started. First, the flame is monitored by a video camera (Sony, model: DSC-F505V) which was positioned in front of the 90° view port, as depicted in Fig. 5.7. The camera was used to record flame heights before and after each sample was taken to ensure that the fuel mass flow remained constant. The flame heights were extracted by using the width of the fuel nozzle tip as a constant reference scale. Therefore, a scale of millimeter/pixel on the screen was used to compute flame height. Next, the user set the desired TSD angular velocity with which the disk would rotate in order to sample the flame. Then, the user presses the Go button on the touchscreen interface (a screen-shot of the touchscreen interface was given in Fig. 5.2) to actuate a probe to sweep across the flame. The TSD is only allowed to travel 36° during one probe sweep.

In order to take high frame-rate pictures of the sampling process, the camera (Photron, model: SA5) was placed in the same location as the video camera and the process of sampling was performed as explained previously. Once the samples were collected, the next step was to remove the sampling disk so that the soot samples could be taken to an electron microscope for TEM analysis.

To remove the sampling disk, first, the HPCC is de-pressurized to atmospheric pres-
sure following the procedure in subsection 5.3.5. Second, the fuel line is disconnected from the bottom flange. Third, the HPCC is opened following the procedure in subsection 4.4.1. Fourth, the MDS is removed from the TSS. Finally, the sampling disk is extracted from the MDS. Then, the TEM-grids are removed from the TSD sampling probes.

TEM-grid removal is a delicate process. First, the adhesive tape is removed from the sampling probe with fine-toothed tweezers (TEM grids are attached to the tape). Second, the TEM grids are removed from the tape by carefully detaching the rim of the grid while avoiding breaking or damaging the substrate material of the grid. Finally, the removed grids are placed in TEM-grid cases to be transported to the electron microscopy for TEM analysis.

Although the sampling disk rotation can be programmed to have any desired velocity profile (as a function of time) when the probe arm sweeps through the flame, a constant angular velocity through the flame was adopted for the proof-of-principle experiments reported in this work. Consequently, the angular velocity parameter is the only variable that determines the grid exposure time. The grid exposure time, $t_r$, is defined as the time it takes the probe to traverse the diameter of the flame at the sampling height. The graphical representation of when the grid is exposed to the flame during one probe sweep is depicted in Fig. 5.8(a) and Fig. 5.8(b) shows the three main stages of the probe sweep motion relative to the flame. The time between sweeps of the sampling probes was determined to be no less than 0.5 s. This resting time allows the laminar flame to reach a stable state. During sampling, only one probe is exposed to the flame. Soot particles are collected when the probe is swept through the slot in the flame enclosure, and the TEM-grid is exposed to flame. To sample the flame at different heights, the flame enclosure and MDS can be adjusted vertically by $\pm7.5$ mm. This vertical adjustment allows for soot samples to be taken from the tip of the fuel tube to 5 mm above the laminar flame using the current flame enclosure.
In high-pressure laminar diffusion flames, the typical flame diameter is on the order of 3 mm and decreases with increasing pressure [60]. Thus, the sampling of the soot at a given height with a small TEM grid at a constant angular speed yields the average soot size at that flame height (averaged over the flame diameter).

Figure 5.8: (a) The three velocity stages (1, 2, 3) that the sampling disk experiences when it is collecting soot samples. The sampling occurs during the small time window when the grid is exposed to the flame in velocity stage 2. (b) The three main stages (A, B, C) of probe motion during sampling.

5.5 Transmission Electron Microscopy (TEM) Data Analysis

In this work, TEM was used to take photographs of soot aggregate particles and calculate the soot particle sizes. In the process of taking photographs, only one TEM-grid is
analyzed at a time. The grid is inserted into the microscope using a 20 cm long probe. The TEM images were taken with a high-voltage electron microscope that is capable of imaging particles down to 2 nm (Hitachi, model: H-7000). The microscope has three major components: the beam column, the image graphic adjuster, and the camera. The central component of the microscope is the beam column which is under vacuum. To produce the electron beam required for particle imaging, electrons are extracted from an electrode, located at the top of the beam column, with an electro-magnet. The electrons are then accelerated towards the specimens of the TEM-grid by electro-magnets located on the walls of the beam column. Once the electrons collide with the grid, they scatter and adhere on phosphorous panels which glow green when an electron adheres to them. This green glow is magnified though lenses and forms the two-dimensional projection of the specimen on the TEM-grid. The camera of the microscope is then used to take pictures of that projected image.

The camera is controlled through software. The camera is connected to a monitor for live-feed imaging. The camera field of view is controlled manually by the user. The process of taking an image using the electron microscope is as follows: the images are manually focused using the camera software’s image graphic adjuster, then a picture is taken. The image graphic adjuster allows the operator to control the magnification, beam concentration, and focus of the displayed image [88, 89]. The magnification of the image is adjusted by turning the magnification knob which adjusts the system’s magnification lenses. The lenses can magnify specimens up to 400,000× their original size. However, it is not always easy to depict highly-magnified particles because the beam light intensity decreases in strength at high magnification levels. This is also known as low beam concentration. Beam concentration is the amount of light reflection caused by the scattering of the electron beam. Proper control of the the electron beam is necessary to reduce light noise in the background of the resulting images. If the beam concentration is too low, the electron beam is not aligned with the particle of interest which decreases
the clarity of the image. The resolution of the images is dependent on the magnification capabilities of the microscope. For particles in the nano-scale range, it is crucial to align the beam concentration and magnification to allow for focus on the soot specimens. Some grids are made of materials that make it difficult to contrast with the particle of interest. The grid material chosen in the experiments, which is copper with a carbon substrate, proved to give the highest quality images.

5.5.1 TEM Image Analysis

Lapuerta et al. devised a recipe for TEM image analysis of soot particles and this was used as the basis for the present TEM analysis [52]. Lapuerta et al. proposed to take TEM images of a single soot aggregate, then choose 10 primary particles at random from that aggregate. These primary particles are numbered from 1 – 10 and a box is drawn around each particle for clear identification. Ten particles are chosen so that the soot particle size measurements yield an average value for soot particle size associated with that aggregate.

The TEM image analysis consisted of four major steps. First, a TEM image is taken of an aggregate particle with the electron microscope. Second, the picture data area (i.e. magnification, scale, file name, date and resolution) of the picture is recorded on a data list and then cropped. Third, 10 primary particles of the aggregate are chosen randomly, then outlined with black boxes and numbered 1 – 10. Fourth, the longest length of the particle is measured using the Fiji image-processing software [90]. The steps explained above are discussed in more detail below.

In the first step, the electron microscope is used to take an image of a soot aggregate. To accomplish this, a grid containing soot samples is initially inserted into the TEM and the default magnification is set at 1000×. At this magnification level, the aggregate particles cannot be depicted as shown in Fig. 5.9. To locate the aggregate particles, the magnification is set to 20,000× so that a larger area of the grid could be visualized.
When a soot aggregate is located, the magnification is set from $80,000\times$ - $100,000\times$ to display a detailed view of the soot aggregate. Once the magnification is set, the focus and beam concentration are adjusted until a $1024 \times 1024$ bit image is clearly depicted. It is important that the perimeters of the primary particles in the aggregate are clearly depicted so that particle size measurements can be performed. Nonetheless, not all the primary particles will be clearly visualized since these are three-dimensional structures and the depth component of these particles is not taken into account with this TEM. Once the image of the aggregate was clear and detailed, the image was captured using the camera software.

Figure 5.9: Picture of a grid (TEMWindows, model: SN100-A50Q33) at $1000\times$ magnification. The white regions are the TEM-grid substrate material and the black regions are the metallic grid structure.
In the second step, the image is cropped so that only the aggregate and the substrate layer of the grid are seen, as shown in Fig. 5.10. Another reason for cropping the images is to allow software to calculate the soot fractal properties. Typically, this type of software requires images that only contain the aggregate particles. Then, image segmentation techniques are used to calculate the fractal dimension. In the third step, ten primary particles on the image are chosen at random and enumerated with a box. An example of this step is given in Fig. 5.11. In the fourth step, the longest length of the soot particles is measured using Fiji. With this software, a soot length was measured by establishing the length/pixel scale of the soot aggregate image. The length/pixel (nm/pix) scale was recorded on the image when it was taken using the electron microscope. Once the scale of the image is known, a measuring line was drawn between two points on the perimeter of a primary soot particle as seen in Fig. 5.12.

![Figure 5.10: Image of a soot aggregate sampled from a methane-air laminar diffusion flame at 4 atm.](image)
Figure 5.11: Image of a soot aggregate particle with ten primary particle chosen and numbered.

Figure 5.12: Particle size measurement of a soot primary particle from the aggregate in Fig. 5.11.
Chapter 6

Results and Discussion

6.1 Introduction

This chapter describes and discusses the results obtained from the TEM image analysis of soot particles collected from laminar diffusion flames of methane at various pressures. Section 6.2 discusses the disturbance of the flame caused by the sampling probe intrusion into the flame. Section 6.3 discusses the effect of pressure on the soot particle size, presents the log-normal particle size distributions, and presents TEM images of soot particles collected at various pressures. Section 6.4 discusses the estimated error in soot primary particle size measurements.

6.2 Flame Disturbance Caused by the Sampling Probe

One of the major disadvantages of thermophoretic intrusive sampling is the interference caused by the physical probe which induces disturbances to the flame height and shape. In this work, the flame disturbance was analyzed by capturing high frame-rate image series of the sampling process in a similar manner to the work presented in [34]. From these image series, changes in flame shape and flame height were observed to be primarily hydrodynamic since the flow field of the flame is altered by the insertion of the probe.
Three examples of the image series captured during the proof-of-principle experiments are presented below in order to qualitatively describe the flame disturbance.

The image series were recorded using a high frame-rate camera (Photron, model: SA5) and a lens (Tamron, 180 mm F/3.5) to observe the disturbance of the flame by the sampling probe. These images were recorded for flames at 2.3, 4, 5.4, 7.1 and 10 atm pressures without using image filters so that the background luminosity seen in the image is limited by the sensitivity of the camera and the lens only.

The image series displayed in Figs. 6.1 and 6.2 show the extent of the flame disturbance caused by sampling probe arms. As shown in Fig. 6.1, raw images of a stable flame (un-sampled) and unstable flames (sampled: pictures A, B, and C) show the distortion in the gas flow that is caused by the sweeping action of the sampling probe arms across the flame. From the raw images in Fig. 6.2, it is seen that the flame height decreases and increases until a height stability is reached at 109.2 ms after the sampling process started. Starting from the left, a stable flame is shown at time 0 ms. Next, the following three flame snapshots show the distortion in the flame shape caused by the sampling probe as it is swept through the cross-section of the flame. Then, a collection of five flame snapshots, denoted as the 1\textsuperscript{st} oscillation, show the change in height of the flame. Next, a collection of five other flame snapshots, this collection of snapshots is denoted as the 2\textsuperscript{nd} oscillation, show the next following decrease in flame height. Finally, the last set of three flame snapshots, denoted as the 3\textsuperscript{rd}, 4\textsuperscript{th}, 5\textsuperscript{th} and so on, show the some of the snapshots that capture the final changes in flame height until the flame reaches the stable height of 10 mm. Similar flame height decrease and increase was observed for the other flames sampled in the experiments.

To maintain consistency of the flames being sampled, soot particles were collected from flames that had an initial (un-sampled) stable height of 10 mm. In order to ensure that the flames reached a stable height of 10 mm, the time between sweeps of the sampling probe arms ranged from 30 seconds to 20 minutes depending on the grid residence time.
and the pressure condition tested. Higher pressure testing conditions required a longer wait time between sweeps to ensure the system reached that desired pressure. The fuel used in the proof-of-principle experiments was chosen to be methane. For all the experiments, the methane mass flow rate was set to be $0.55 \frac{mg}{s}$, which corresponds to a carbon flow rate of $0.41 \frac{mg}{s}$. This fuel flow rate was chosen to match that of previous experiments [36, 60, 79]. The co-flow air flow rate was set to about $0.34 \frac{g}{s}$.

The typical effects that pressure and grid exposure time have on the flame cross-section when the TEM grid is concentric with the fuel nozzle tip is depicted in Fig. 6.3. The pressure and grid exposure time conditions associated with flames A1, A2, B1, and B2 are indicated below each image. Increasing pressure is observed to decrease the cross-section size of the flames. This change in flame cross-section size was expected since similar results were observed previously by Charest et al. [57]. Another interesting observation made from Fig. 6.3 is that a decrease in grid exposure time is observed to cause a larger breakdown of the flame shape in the region near the probe. This is most likely due to the increased velocity and momentum associated with the probe when it sweeps though the flame in lower grid exposure time conditions.

![Figure 6.1: Typical image series of the sampling process recorded at 10 atm. Starting from the left, a typical stable flame is shown at some time prior to sampling. Image A shows the flame when the probe makes first contact with the flame’s edge. Image B shows the flame when the TEM grid is concentric with the fuel nozzle tip. Finally, Image C shows the flame when the probe’s tail end leaves the flame envelope.](image-url)
Figure 6.2: Image series taken during one sampling routine at 7.1 atm. Pictures were taken with a high frame-rate camera (Photron, model: SA5) and lens (Tamron, 180 mm F/3.5) at a rate of 5000 fps.
Figure 6.3: Images of typical flame shape distortion taken at the time when the TEM grid is concentric with the fuel nozzle. The pressure and grid exposure time are indicated at the bottom of each image.

6.3 Results of TEM Image Analysis

Primary soot particle size distributions shown in Fig. 6.4 were measured manually from images obtained using a Hitachi (model: H-7000) transmission electron microscope. The images contained 1 – 3 soot aggregates from samples collected at pressures of 2.3, 4, 5.4, 7.1 and 10 atm. The measurement process started with choosing ten primary particles per aggregate on the TEM image. Each primary particle was chosen manually and its perimeter was clearly identified with a numbered box on the TEM picture following the procedure in another study [73]. In total, 1680 soot particle size measurements were taken. The breakdown of the size measurement at each pressure and grid residence time is given in Table 6.1. As shown in the table, at least 100 particle size measurements were analyzed for each pressure and grid residence time. Due to the electron microscope
limited availability, the TEM analysis on the samples was performed, on average, 48 hours after the experiments were completed and the samples removed. Sample removal was performed immediately after the depressurization procedure of the HPCC. TEM analysis of each grid took about 6 hours.

![Graph](image)

Figure 6.4: Primary soot particle size measured by analysis of TEM images which were collected at a height of 3 mm above the burner exit. Each size distribution shows the total count of particle sizes measured at that pressure i.e. $P = 2.3$ atm (320 samples), $P = 4.0$ atm (340 samples), $P = 5.4$ atm (300), $P = 7.1$ atm (340), $P = 10.0$ (380).
Table 6.1: Breakdown of the number of size measurements by pressure and grid residence time

<table>
<thead>
<tr>
<th>Pressure</th>
<th>Grid residence time</th>
<th>Row Sum</th>
</tr>
</thead>
<tbody>
<tr>
<td>atm</td>
<td>4.2 ms 5.4 ms 7.56 ms</td>
<td>– 320</td>
</tr>
<tr>
<td>2.3</td>
<td>110 100 110</td>
<td>340</td>
</tr>
<tr>
<td>4.0</td>
<td>100 140 100</td>
<td>300</td>
</tr>
<tr>
<td>5.4</td>
<td>100 100 100</td>
<td>340</td>
</tr>
<tr>
<td>7.1</td>
<td>100 100 140</td>
<td>340</td>
</tr>
<tr>
<td>10.0</td>
<td>100 130 150</td>
<td>380</td>
</tr>
<tr>
<td><strong>Column Sum</strong></td>
<td><strong>510 570 600</strong></td>
<td><strong>1680</strong></td>
</tr>
</tbody>
</table>

Although a limited number of TEM images were taken for each grid sample, it was possible to construct primary particle size histograms at all the pressures tested. From the particle size distributions shown in Fig. 6.4, the mean primary soot particle sizes were measured to greatly decrease with increasing pressure. For example, the mean particle sizes at 2.3 atm and 10 atm were measured to be 27.6 nm and 17.5 nm, respectively. This decrease in mean primary particle diameters suggests that higher pressures significantly decreases soot particle sizes. Assuming that soot nuclei form via coalescence of smaller PAH clusters and consequent surface growths, then pressure is relatively slowing down this process in order to arrive to smaller soot primary particle sizes at elevated pressures.

In order to explain why the process of soot particle coalescence is relatively slowed down, it is important to understand the gas dynamics of these particles. At pressures between atmospheric and 2.3 atm, the size of the primary soot particles is comparable to the mean free path of the combustion gases in a laminar diffusion flame. Assuming that the combustion gases in this flame are around 1500 K [22], the Knudsen number, Kn, for this soot-gas system is about 20, which is in the free molecular regime close to the transition regime. At 5.4 atm, the Kn number is about 10 (in the transition regime), and at 10 atm, the Kn number is about 5 which is still in the transition regime but
approaching the near-continuum regime. Park et al. modeled the coalescence of particles in the transition regime by implementing the harmonic mean coagulation kernel [91]. In their analysis, coagulation rates significantly decrease for particles in the transition to near-continuum regime from large Kn numbers to smaller ones.

Moreover, results from experiments using optical techniques have shown that soot volume fraction is significantly increased at pressures above atmospheric [25]. Thomson et al. measured increasing soot volume fraction at different flame heights in a methane-air laminar diffusion flame at pressures between 0.5 – 4.0 MPa. This increase in soot volume fraction also increases radiative heat loss and leads to overall lower flame temperatures [22]. Lower flame temperatures could also lower the coagulation rates. Increased soot volume fraction is due to the increased soot number density regardless of the soot particle size.

For the experiments conducted in this work, the elevated pressures were also observed to affect the overall soot agglomerate structure. Soot aggregates at pressures in which they were sampled are presented in Fig. 6.5. The agglomerates formed at the higher pressures were observed to be comprised of smaller linked structures between their associated primary particles. This observation could be an indication that at elevated pressures the distance that a primary particle overlaps over another primary particle is increased and must be taken into consideration in the models that simulate soot agglomeration.

Overall, these results indicate that thermophoretic sampling of soot at high-pressures is an effective method to measure soot primary particles sizes at different pressures. This can be applicable to fundamental research that investigates the soot volume concentrations at elevated pressures without the need to have particle bulk density or refractive index data [31]. Since, particle geometry can be directly analyzed using an electron microscope, the local soot concentrations and morphology can be measured manually.
Thomson et al. measured radially resolved primary particle sizes in a methane-air laminar diffusion flame using LII at various pressures as shown in Fig. 6.6 [25]. Thomson et al. concluded that the primary soot particle size increases as the pressure is increased. At a given pressure, soot size profiles, in general, exhibit a symmetric, annular shape, similar to the annular shape of the soot volume fraction profiles. The particle diameter not only increases steeply with increasing pressure, but also displays a larger variation.
from the flame centerline to the annular locations. However, as stated by Thomson et al., what is measured with LII is the effective soot primary particle size. The effective primary particle size measured with LII at elevated pressures does not represent the soot primary particle diameter because the shielding effect on heat conduction between aggregated particles and the surrounding gas is neglected [23]. For this reason, the effective primary particle diameter is a function of the primary particle diameter and the aggregate morphology. As a result it is not possible to determine whether a change in measured effective particle diameter is caused by a variation of the primary soot particle size, aggregate characteristics, or both without complementary experiments such as thermophoretic sampling. The results from the sampling experiments conducted in this work showed a 36.5% decrease in mean primary particle size from 2.3 to 10 atm which suggest that the effective soot primary particle size that Thomson et al. measured is mainly due to aggregate characteristics.

Figure 6.6: Primary soot particle size measured by LII in a methane-air laminar diffusion flame on a burner in a high-pressure chamber identical to the burner and chamber used in this study. Measurements were taken at a flame height of 6 mm, whereas in the current work TEM images were collected at a height of 3 mm [25].
6.4 Sources of Error

There are many possible sources of error in an experimental set-up as complicated as a thermophoretic sampling system in a high-pressure combustion chamber. The errors can be classified as those arising from the diagnostic system and analysis, and those due to the combustion chamber and gas delivery system.

The sources of error pertaining to the thermophoretic sampling system and TEM analysis arise from the distortion of the flame induced by the probe, the accuracy of the angular positioning of the sampling disk, and the uncertainty in the manual measurements of the soot primary particle sizes. In order to minimize the error due to the probes of the thermophoretic sampling system, the sampling probe arms were designed according to criteria set in the recent investigation by Lee et al. [35]. Lee et al. concluded that measurement uncertainty in thermophoretic sampling is mainly due to probe vibrations during sampling. These vibrations cause disturbances in the gas flow of the flame and produce a variation in the measurement of soot particle sizes that are observed during the TEM analysis. Lee et al. also concluded that using a probe with an aspect ratio (thickness/width) larger than 0.2 is optimal because it reduces probe vibration and the inherent irreversible errors caused by it. The probe used in the presented design had an aspect ratio of 0.25. Probe vibrations were not observed during the high-frame rate analysis conducted in this work. Therefore, the error arising from probe vibrations was considered to be negligible. The sampling disk angular positioning accuracy stems from the accuracy of the motor driver. The motor driver that was used in the sampling experiments (Parker, model: Zeta6104) has an angular position, velocity, and acceleration accuracy of ±0.02%. One of the reasons why this motor driver was specifically chosen to be installed in the thermophoretic sampling system was due to its high accuracy, thus, decreasing the angular positioning error of the thermophoretic sampling system.

The error from manually measuring the soot primary particle diameters arises from the pixel resolution of the TEM image. The pictures of the particles that were analyzed
had different pixel resolutions which was a result of imaging the soot particles using different magnifications. The magnifications used ranged from 80,000× to 150,000×. Discussion on the TEM picture analysis process was presented in section 5.5, but broadly speaking, the TEM image magnification was chosen based on the ability to take the clearest picture of the agglomerate at the highest magnification. The particle size measurement uncertainty was calculated to be ±1 pixel length. The image resolutions ranged from 0.45 to 0.98 nm/pix, which translates to a 1% – 5% error in the primary particle size measurements.

A larger error was determined from the primary particle size histograms that are shown in Fig. 6.4. At each pressure, the size of 300 – 380 primary particles was averaged to obtain the mean soot particle size within an experimental uncertainty (95% confidence interval) of less than 5%. The particle size distributions shown in Fig. 6.4 depict a slight asymmetry (all the distributions exhibit a skew to the left) which is characteristic of soot particle size measurements [34, 92]. The lower and upper limits of the 95% confidence interval were chosen to be the 2.5 and 97.5 percentile of the calculated soot particle size [93]. The lower and upper limit values for the distributions are presented in Table 6.2. Due to the asymmetry in these distributions, these limits are not equidistant from the mean soot primary particle size. The spread of the particle size distributions, represented by errors bars in Fig. 6.7, correspond to two standard deviations of the particle size distributions. Another interesting statistic that was observed from the measured distributions was that the variance also decreased as pressure increased. Lapuerta et al. observed a similar trend with soot particle size distributions that were generated numerically. The decrease in the variance of the distributions was associated with an increase in compactness in soot aggregate morphology [52, 72, 73].
Table 6.2: Primary particle size measurement statistics

<table>
<thead>
<tr>
<th>Pressure (atm)</th>
<th>Mean (nm)</th>
<th>Measurement distribution lower limit - 2.5(^\text{th})%</th>
<th>Measurement distribution upper limit - 97.5(^\text{th})%</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.3</td>
<td>27.6</td>
<td>12.9</td>
<td>51.9</td>
</tr>
<tr>
<td>4.0</td>
<td>24.6</td>
<td>12.1</td>
<td>44.5</td>
</tr>
<tr>
<td>5.4</td>
<td>23.0</td>
<td>12.2</td>
<td>39.8</td>
</tr>
<tr>
<td>7.1</td>
<td>18.0</td>
<td>9.00</td>
<td>32.5</td>
</tr>
<tr>
<td>10.0</td>
<td>17.5</td>
<td>7.91</td>
<td>33.5</td>
</tr>
</tbody>
</table>

Figure 6.7: Primary soot particle size measurements for different pressures and residence times. The error bars shown in the image correspond to two standard deviation for the size distributions.
Experimental error sources associated with the high pressure combustion chamber and gas delivery system mainly came from the fuel and air flow controllers and the pressure regulator that monitors the internal pressure of the combustion chamber. The flow controllers were calibrated before each experiment. The uncertainty was less than 1%. The internal pressure of the combustion chamber was regulated manually, and the observed drift in pressure was ±2 psi.

The discussion in this section indicates the total uncertainty in soot particle sizes measured from samples taken with a thermophoretic sampling system and analyzed using TEM imaging. The total experimental uncertainty was estimated to be within 15% (95% confidence), which is similar to other work of this type [32]. Errors arising from the diagnostic apparatus or the high pressure combustion chamber and gas delivery system did not have a large impact on the overall uncertainty in this work.
Chapter 7

Conclusion, Future Work

7.1 Conclusion

A thermophoretic sampling system that uses a rotating sampling disk with multiple probes was designed and built. This sampling system displays a more efficient method of taking samples of particles at high-pressures by allowing up to 10 samples to be taken in one experimental run. The rotating disk design allows for easy and precise control of the grid residence time down to 2.65 ms. It was installed in a high-pressure combustion chamber with a co-flow laminar diffusion flame burner and samples of soot particles were taken in pressure conditions up to 10 atm at a height above the burner of 3 mm. The mean primary particle size was observed to decrease significantly by about 36% as the pressure increased from 2.3 to 10 atm. It was argued that lower coagulation rates as a result of decreasing Knudsen number from about 20 at 2.3 atm to about 5 at 10 atm is the leading cause for the mean soot particle size decrement with increasing pressure.

The effect of the sampling system on the flame was analyzed using image series taken with a high frame-rate camera. Soot particle sizes were measured from TEM images taken from a flame sampled at pressures of 2.3, 4, 5.4, 7.1, and 10 atm. From the image series, flame disturbances in the form of wrinkles were observed to be the largest at the
height where the probe was inserted and decreased along the center axis of the flame to the flame tip. Observing the background of the image series it was clear that the flame luminosity increased as the grid residence time decreased.

### 7.2 Recommendations for Future Work

With further analysis of the samples, pressure dependence of other soot morphology properties such as fractal dimension, fractal pre-factor, and radius of gyration are possible. Experimental data that shows how pressure affects soot morphology could help resolve long standing problems about the refractive indices of soot, and motivate combustion research to understanding the complex process of soot formation in engines and furnaces. Understanding this process is believed to be one of the major steps necessary to control soot production in practical combustion systems, such as engines and furnaces. Soot concentration in the combustion stage of these systems could be optimized in order to take advantage of the high heat transfer properties that soot exhibits, and decrease the amount of soot emitted with the exhaust gases. By optimizing soot concentrations in practical combustion systems, it could be possible to revert the negative effects that it has on humans and the environment.

The following points list a number of recommendations for future work that could be carried out by further developing the TSS designed and further analyzing the data from this research.

1. The current TSS designed shows potential to increase the sampling capabilities of thermophoretic sampling as a diagnostic to collect soot particle sizes measurements at different pressures. The TSS allows multiple samples to be taken, up to 10 samples during an experimental run. However, there are two major design recommendations that would improve the performance of the TSS: (i) improve the method for attaching TEM grids to the sampling probe arms, and (ii) invest in a
stepper motor and gearbox that are designed to function in pressures above 10 atm since the current stepper motor and gearbox of the MDS are not able to function at pressures above 10 atm.

A better method of securing the TEM grids to the sampling probe arms is necessary. The current method uses strips of adhesive tape to attach the grids to the sampling arms. With this method, attaching the grids is straightforward and does not present difficulties. However, the problem with the current method is during the removal process of the grids from the probe arms to take to the TEM for further analysis. In the process of removing the grids, the adhesive tape caused some grids to break. This problem could be avoided by adapting a probe cover to pinch the rim of the grid and secure it in place. This method of securing grids is used in TEM microscope probe arms [74–76].

The probe cover system requires a mechanical hinge mechanism and a cover design that exposes as much of the grid substrate surface as possible. To further analyze the effects that pressure has on particle size, it is desirable to collect soot particle sizes at pressures above 10 atm [8, 34, 37].

2. The analysis conducted in this work focused on determining the effect of pressure on soot particle size. With further analysis, the data collected during these experiments could provide insightful data about the effects of pressure on soot fractal properties. This analysis requires further TEM image processing analysis. The results from this analysis could aid researchers to determine the refractive indices of soot [49].

3. Another area of research that could be further investigated with the TSS is in the area of biofuels. Investigating soot particle sizes for various biofuels at high-pressures could be carried out at UTIAS.
References


laminar co-annular non-premixed methane/air flame at pressures between 0.5-4.0 MPa. *Applied Physics B: Lasers and Optics*, 83:469–475, 2006.


REFERENCES


[61] Gülder Ö. L., Intasopa G., Joo H. I., Mandatori P. M., Bento D. S., and Vaillancourt M. E. Unified behaviour of maximum soot yields of methane, ethane and


[title = References]
Appendix A

Thermophoretic Sampling System

Construction Drawings

Figure A.1: Enclosure clamp
Figure A.2: Burner main base

Figure A.3: Burner enclosure. Page 1
Figure A.4: Burner enclosure. Page 2

Figure A.5: Breadboard support tube
Figure A.6: TSM disk

Figure A.7: Probe cover
Appendix A. Thermophoretic Sampling System Construction Drawings

Figure A.8: TEM-grid probe

Figure A.9: Enclosure clamp rod
Figure A.10: Igniter holder

Figure A.11: Igniter holder cap
Figure A.12: Gearbox spacer for position 1 (3 mm above burner nozzle)

Figure A.13: Motor support bracket. Page 1
Appendix A. Thermophoretic Sampling System Construction Drawings

THE 2D PROFILE OF THIS PART IS SHOWN. THIS FILE IS INTENDED TO BE SAVED AS A DXF FILE FOR CNC MACHINING UNLESS OTHERWISE SPECIFIED:

dimensions are in inches

QUANTITY: 1

MOTOR SUPPORT

ANGLES

TOLERANCES:

= 0.1

= 0.01

= 0.005

= 0

30'

Figure A.14: Motor support bracket. Page 2