SOOT MEASUREMENTS USING LASER INDUCED INCANDESCENCE FOR ETHENE COMBUSTION UNDER ENGINE-RELEVANT CONDITIONS

by

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ABSTRACT

With growing concerns over the detrimental effects of soot emission, it has become important to study possible emission reduction strategies and explore new measurement techniques to advance soot diagnostic capabilities. In this study, the potential of using nitrogen as a fuel diluent to reduce soot is measured in a series of combustion experiments under engine-relevant conditions using Laser Induced Incandescence (LII).

In the first part of this research, a calibration was conducted to allow conversion of LII signals into soot mass concentration values. This calibration was performed by measuring samples of different, but known, soot concentration with LII under different configurations.

Secondly, a test plan was designed for this study using a statistical design-of-experiment technique, response surface methodology (RSM). The concept of RSM is to conduct a small number of experiments strategically and use the results to create an empirical model. Using this approach, a test matrix of 135 experiments was developed.

Finally, combustion experiments were carried out in a shock tube. In these experiments, soot concentration within a combusting ethene jet was measured with LII. The LII results were then processed and used as inputs for building the empirical models, from which the following trends were observed:

- Addition of nitrogen was observed to lower the levels of soot within the fuel jet.
- Increases in pre-combustion temperature reduced the level of soot detected.
- Changes in fuel injection pressure and pre-combustion pressure were observed to cause competing effects on the level of soot detected. This might be caused by underlying changes in air fuel ratio associated with changes in the two pressures.

The results of this work indicate fuel dilution with nitrogen can be a potential soot reduction strategy for non-premixed gaseous-fuelled combustion systems. This study also shows that the ability to instantaneously generate a map of soot distribution within a combusting fuel jet makes LII more powerful than traditional soot diagnostic techniques.
TABLE OF CONTENTS

ABSTRACT ................................................................. ii
TABLE OF CONTENTS .................................................. iii
LIST OF TABLES .......................................................... v
LIST OF FIGURES ........................................................ vi
LIST OF ABBREVIATIONS ................................................. viii
ACKNOWLEDGEMENTS .................................................... ix
1.0 INTRODUCTION ...................................................... 1
  1.1 Research Objectives .................................................. 3
  1.2 Organization of the Thesis ........................................... 4
2.0 BACKGROUND INFORMATION ........................................ 6
  2.1 Introduction .......................................................... 6
  2.2 Non- Premixed Combustion of a Gaseous Jet ......................... 6
  2.3 Soot Formation Mechanisms and Soot Reduction Strategies .......... 7
    2.3.1 Soot Chemical Kinetics ........................................... 8
    2.3.2 Influence of Fuel Composition on Soot Emission ................. 12
    2.3.3 Practical Combustion Modifications to Reduce Soot Emission .... 14
  2.4 Soot Diagnostic Techniques ......................................... 16
    2.4.1 Intrusive Techniques ........................................... 17
    2.4.2 Non-intrusive Techniques ..................................... 17
    2.4.3 Laser Induced Incandescence: Principle of Operation .......... 19
    2.4.4 Laser Induced Incandescence: Fundamental Theory ............. 20
  2.5 Summary ........................................................... 23
3.0 LASER INDUCED INCANDESCENCE (LII) CALIBRATION ................. 24
  3.1 Introduction ....................................................... 24
  3.2 LII System and Various Calibration Instruments ..................... 24
    3.2.1 LII System: Laser Source .................................... 24
    3.2.2 LII System: Laser Optics .................................... 25
    3.2.3 LII System: Intensified Charge-Coupled Device (ICCD) Camera .... 26
    3.2.4 LII System: System Control Unit ................................ 26
    3.2.5 LII System: LII Test Section .................................. 26
    3.2.6 Soot Concentration Measurement: Aethalometer .................. 27
    3.2.7 Soot Source: Propane Diffusion Flame .......................... 29
    3.2.8 Soot Source: Graphite Aerosol Generator ...................... 30
  3.3 Calibration Set-up ................................................ 31
  3.4 Results and Discussion ........................................... 35
  3.5 Conclusions ..................................................... 36
4.0 STATISTICAL EXPERIMENTAL DESIGN ................................ 37
  4.1 Introduction ...................................................... 37
  4.2 Central Composite Designs ........................................ 37
  4.3 Experimental Design Procedures ................................... 40
  4.4 Statistical Analysis for RSM Experiments .......................... 44
    4.4.1 Multiple Regression Analysis .................................. 44
    4.4.2 Model Checking: Residuals and Coefficient of Determination .... 45
    4.4.3 Error Analysis: Standard Error of Predicted Response ........ 46
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.4.4</td>
<td>Model Analysis: Significance of Parameters</td>
<td>47</td>
</tr>
<tr>
<td>4.5</td>
<td>Summary</td>
<td>47</td>
</tr>
<tr>
<td>5.0</td>
<td>SHOCK TUBE COMBUSTION EXPERIMENTS</td>
<td>48</td>
</tr>
<tr>
<td>5.1</td>
<td>Introduction</td>
<td>48</td>
</tr>
<tr>
<td>5.2</td>
<td>Experimental Apparatus</td>
<td>48</td>
</tr>
<tr>
<td>5.3</td>
<td>Experimental Procedure</td>
<td>52</td>
</tr>
<tr>
<td>5.4</td>
<td>Experimental Results</td>
<td>53</td>
</tr>
<tr>
<td>5.5</td>
<td>Response Surface Model</td>
<td>59</td>
</tr>
<tr>
<td>5.5.1</td>
<td>Digital Image Processing</td>
<td>59</td>
</tr>
<tr>
<td>5.5.2</td>
<td>Construction of the Response Functions</td>
<td>60</td>
</tr>
<tr>
<td>5.5.3</td>
<td>Discussion of the Most-Soot Response Surfaces</td>
<td>65</td>
</tr>
<tr>
<td>5.5.4</td>
<td>Residual Analysis</td>
<td>81</td>
</tr>
<tr>
<td>5.5.5</td>
<td>Significance of Parameters</td>
<td>84</td>
</tr>
<tr>
<td>5.5.6</td>
<td>Comparison of the Most-Soot Model to Other Models</td>
<td>85</td>
</tr>
<tr>
<td>5.6</td>
<td>Conclusions</td>
<td>94</td>
</tr>
<tr>
<td>5.7</td>
<td>Recommendations</td>
<td>96</td>
</tr>
<tr>
<td>6.0</td>
<td>SUMMARY AND RECOMMENDATIONS</td>
<td>97</td>
</tr>
<tr>
<td>REFERENCES</td>
<td></td>
<td>100</td>
</tr>
<tr>
<td>APPENDIX A</td>
<td>AETHALOMETER CORRECTION</td>
<td>110</td>
</tr>
<tr>
<td>A.1</td>
<td>Determination of M_{BC,MEASURED}</td>
<td>110</td>
</tr>
<tr>
<td>A.2</td>
<td>Determination of C and R(ATN)</td>
<td>111</td>
</tr>
<tr>
<td>A.3</td>
<td>Results</td>
<td>112</td>
</tr>
<tr>
<td>A.4</td>
<td>References</td>
<td>114</td>
</tr>
<tr>
<td>APPENDIX B</td>
<td>ATTENUATION CORRECTION</td>
<td>115</td>
</tr>
<tr>
<td>B.1</td>
<td>Methods and Results</td>
<td>115</td>
</tr>
<tr>
<td>B.2</td>
<td>References</td>
<td>117</td>
</tr>
<tr>
<td>APPENDIX C</td>
<td>MATLAB CODES FOR DATA ANALYSIS</td>
<td>118</td>
</tr>
<tr>
<td>APPENDIX D</td>
<td>MATLAB CODES FOR IMAGE PROCESSING</td>
<td>130</td>
</tr>
<tr>
<td>APPENDIX E</td>
<td>SHOCK TUBE OPERATING PROCEDURE</td>
<td>134</td>
</tr>
<tr>
<td>APPENDIX F</td>
<td>OVERALL AIR/FUEL RATIO CALCULATIONS</td>
<td>137</td>
</tr>
<tr>
<td>F.1</td>
<td>Calculations and Results</td>
<td>137</td>
</tr>
<tr>
<td>F.2</td>
<td>References</td>
<td>142</td>
</tr>
<tr>
<td>APPENDIX G</td>
<td>IGNITION DELAY DATA</td>
<td>143</td>
</tr>
<tr>
<td>G.1</td>
<td>Introduction</td>
<td>143</td>
</tr>
<tr>
<td>G.2</td>
<td>Effect of Nitrogen Addition, P_i, T_0, and P_0 on Ignition Delay</td>
<td>143</td>
</tr>
<tr>
<td>G.3</td>
<td>Conclusions</td>
<td>148</td>
</tr>
<tr>
<td>G.4</td>
<td>References</td>
<td>149</td>
</tr>
<tr>
<td>APPENDIX H</td>
<td>ESTIMATING THE EFFECT OF SIGNAL TRAPPING</td>
<td>150</td>
</tr>
<tr>
<td>H.2</td>
<td>References</td>
<td>150</td>
</tr>
</tbody>
</table>
LIST OF TABLES

Table 3.1 Laser Specifications .................................................. 25
Table 3.2 Camera Settings ......................................................... 26
Table 3.3 AE21 Aethalometer: Description of Parts ....................... 27
Table 3.4 Settings for the Propane Diffusion Flame ......................... 30
Table 3.5 Settings for the Graphite Aerosol Generator ...................... 30
Table 3.6 Expected and Actual GAG Output Soot Concentration ........... 31
Table 3.7 Calibration Set-up ..................................................... 31

Table 4.1 CCF Design (Coded) Matrix ......................................... 41
Table 4.2 Definition of the Coded Values ..................................... 42
Table 4.3 Test Matrix (Rearranged to the Actual Order Tested) .......... 42
Table 4.4 ICCD Camera Timing with Referenced to the Fuel Injector Trigger Signal... 43

Table 5.1 T-statistics for the Most-Soot, Average-Soot, and Random-Model ............ 94

Table A.1 Expected and Actual GAG Output Soot Concentration ........... 114

Table B.1 Correction for the Calibration Results .......................... 117

Table F.1 Original Injector Calibration Data ................................ 137
Table F.2 Injector Mass Flow Rate ........................................... 137
Table F.3 Mass of Air inside the Shock Tube Driven Section .............. 138
Table F.4 Overall Air/Fuel Ratio .............................................. 139
Table F.5 Ignition Delay Data .................................................. 141
Table F.6 Mean Centerline AFR at Start of Ignition ......................... 142

Table G.1 Detected Ignition Delay Data ...................................... 144
LIST OF FIGURES

Figure 2.1 Lift-off of a Gaseous Methane Jet ........................................... 7
Figure 2.2 Graphical Representation of the Stages in Soot Formation ................. 8
Figure 2.3 Particles from the Exhaust of a Predominantly Natural Gas-Fuelled Engine 11
Figure 2.4 Energy Exchange Mechanisms during an LII Process .......................... 20

Figure 3.1 LII Component Placement .............................................................. 25
Figure 3.2 Dilution Loop .................................................................................. 28
Figure 3.3 Soot Extraction System .................................................................. 29
Figure 3.4 Set-up 1: Propane Diffusion Flame and Borosilicate Tube ................. 32
Figure 3.5 Set-up 2: Graphite Aerosol Generator and Borosilicate Tube ............. 33
Figure 3.6 Set-up 3: Graphite Aerosol Generator and the Shock Tube Optical Section 34
Figure 3.7 Calibration Curves .......................................................................... 35

Figure 4.1 Hypothetical "One Variable at a Time" Experiment ............................. 38
Figure 4.2 Illustration of a Three-variable CCRD ............................................. 40
Figure 4.3 Various Central Composite Designs ............................................... 40
Figure 4.4 Timing Sequence ............................................................................ 44
Figure 4.5 Typical Standardized Residual Plot ............................................... 45
Figure 4.6 Typical Residual Plot: Effect of Ignition Delay on Residuals ............... 46

Figure 5.1 Shock Tube Facility ........................................................................ 49
Figure 5.2 Typical Image Sequence Captured to Identify the Start of Ignition .......... 51
Figure 5.3 Typical Temporal Sequence of LII Images ..................................... 54
Figure 5.4 Typical Temporal Sequence of Luminosity Images .......................... 55
Figure 5.5 Data Collected at 2.0 ms ASOI ...................................................... 55
Figure 5.6 Actual Camera Timing .................................................................... 57
Figure 5.7 Effect of Acquisition Timing and Ignition Delay on Detected Soot Levels 58
Figure 5.8 Average-Soot Model vs. Most-Soot Model ..................................... 62
Figure 5.9 Model Validation Results ................................................................. 63
Figure 5.10 Contour Plot: Nitrogen Addition and Injection Pressure ................. 66
Figure 5.11 Contour Plot: Nitrogen Addition and Pre-combustion Temperature ..... 67
Figure 5.12 Contour Plot: Nitrogen Addition and Pre-combustion Pressure ........ 68
Figure 5.13 Contour Plot: Injection Pressure and Pre-combustion Temperature 69
Figure 5.14 Contour Plot: Injection Pressure and Pre-combustion Pressure 70
Figure 5.15 Contour Plot: Pre-combustion Temperature and Pre-combustion Pressure 71
Figure 5.16 Effect of Nitrogen Addition to Ethene over Time (Response Prediction) 73
Figure 5.17 Effect of Injection and Pre-combustion pressure on Overall AFR .......... 78
Figure 5.18 Mean Centerline AFR ................................................................ 79
Figure 5.19 Standardized Residuals for Equation (5.2) to (5.5) ......................... 81
Figure 5.20 Effect of Fuel Dilution, P, T0, and P0 on Residuals ....................... 83
Figure 5.21 Effect of Variations in Ignition Delay on Residuals ........................... 83
Figure 5.22 T-statistic for Model Parameters ................................................... 84
Figure 5.23 Response Surface Comparison Based on Nitrogen Addition and P1 .... 86
Figure 5.24 Response Surface Comparison Based on Nitrogen Addition and T0 .... 87
LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>%N₂</td>
<td>Volume percent nitrogen in fuel</td>
</tr>
<tr>
<td>AFR</td>
<td>Air/fuel ratio</td>
</tr>
<tr>
<td>ASOI</td>
<td>After start of ignition</td>
</tr>
<tr>
<td>BC</td>
<td>Black carbon</td>
</tr>
<tr>
<td>BT</td>
<td>Borosilicate tube</td>
</tr>
<tr>
<td>C</td>
<td>Corrected for attenuation</td>
</tr>
<tr>
<td>CCC</td>
<td>Central composite circumscribed</td>
</tr>
<tr>
<td>CCD</td>
<td>Central composite design</td>
</tr>
<tr>
<td>CCF</td>
<td>Central composite faced</td>
</tr>
<tr>
<td>CCI</td>
<td>Central composite inscribed</td>
</tr>
<tr>
<td>CCRD</td>
<td>Central composite rotatable design</td>
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<tr>
<td>CFD</td>
<td>Computational fluid dynamics</td>
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<tr>
<td>EGR</td>
<td>Exhaust gas recirculation</td>
</tr>
<tr>
<td>EPA</td>
<td>Environmental protection agency</td>
</tr>
<tr>
<td>Euro IV</td>
<td>European emission standards IV</td>
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<tr>
<td>Euro V</td>
<td>European emission standards V</td>
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<tr>
<td>GAG</td>
<td>Graphite aerosol generator</td>
</tr>
<tr>
<td>HACA</td>
<td>Hydrogen abstraction acetylene addition</td>
</tr>
<tr>
<td>ICCD</td>
<td>Intensified charge-coupled device</td>
</tr>
<tr>
<td>ICE(s)</td>
<td>Internal combustion engine(s)</td>
</tr>
<tr>
<td>LII</td>
<td>Laser induced Incandescence</td>
</tr>
<tr>
<td>NC</td>
<td>Not corrected for attenuation</td>
</tr>
<tr>
<td>NOx</td>
<td>Oxides of nitrogen (include NO, NO₂)</td>
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<tr>
<td>PAH</td>
<td>Polycyclic aromatic hydrocarbons</td>
</tr>
<tr>
<td>PDF</td>
<td>Propane diffusion flame</td>
</tr>
<tr>
<td>Pᵢ</td>
<td>Injection pressure</td>
</tr>
<tr>
<td>PLII</td>
<td>Planar laser induced Incandescence</td>
</tr>
<tr>
<td>PM</td>
<td>Particulate matters</td>
</tr>
<tr>
<td>P₀</td>
<td>Ambient (pre-combustion) pressure</td>
</tr>
<tr>
<td>RSM</td>
<td>Response surface methodology</td>
</tr>
<tr>
<td>STOS</td>
<td>Shock tube optical section</td>
</tr>
<tr>
<td>SVF</td>
<td>Soot volume fraction</td>
</tr>
<tr>
<td>TIRE-LII</td>
<td>Time resolved laser induced incandescence</td>
</tr>
<tr>
<td>T₀</td>
<td>Ambient (pre-combustion) temperature</td>
</tr>
<tr>
<td>UBC</td>
<td>University of British Columbia</td>
</tr>
</tbody>
</table>
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1.0 INTRODUCTION

The internal combustion engine (ICE) has revolutionized the way humans and goods are transported. Today, ICEs are the most dominant power source for on-road transportation applications. They are relatively cheap to manufacture and the infrastructure for fuel distribution is well developed. Regrettably, ICEs emit significant amounts of particulates, oxides of nitrogen (NOx), and carbon dioxide (CO2) into the atmosphere. They are also responsible for the rapid consumption of oil. Among the various issues, the problem of particulate emission has received increasing attention due to its adverse health, environmental, and engineering implications.

Particulates, especially those smaller than 2.5 \( \mu \text{m} \) in diameter, have a significant impact on human health because of their ability to penetrate to the depths of the respiratory system. Exposure to fine particulates can cause asthma attacks, pneumonia, bronchitis, and even premature death in people with pre-existing cardiac or respiratory disease [1][2]. Also, engine-emitted particulates are often coated with carcinogenic or mutagenic compounds such as polycyclic aromatic hydrocarbons (PAHs) [3][4].

Engine-emitted particulates also contribute to various other environmental problems. Solar scattering from fine particles suspended in the lower atmosphere reduces visibility [5]. Also, as most of the particulates emitted from ICEs are composed of carbon, they are black in color. It is believed the presence of these particles, either in the atmosphere or on the ground, can reduce the albedo of the Earth and aid in amplifying the effects of global warming [6].

Soot particles inside the cylinders of an ICE can create various engine performance issues as well. This is because the presence of soot particles within a flame can enhance radiative heat transfer to the engine. Not only will this reduce the amount of energy available to do work, it can also overheat and damage the engine.
As the adverse effects of particulate emission become more apparent, emission standards have become more stringent. In the United States, the Environmental Protection Agency (EPA) 2007/2010 on-highway heavy-duty diesel engine emissions standards demand a 98% reduction in particulate emission from the current standards (down to 0.1g/bhphr) [7]. In Europe, the current European Emission Standards (Euro V) for heavy-goods vehicles, when compared to its predecessor (Euro IV), also demand a particulate emission reduction from 0.1g/kWh to 0.02g/kWh [8]. A similar reduction is demanded in Australia as well, since its standards are derived from those enforced in the European Union and the United States [9].

To meet these strict standards, various methods for reducing particulate emissions are under development. Generally, most of the emission reduction research can be classified into the following categories:

- **Alternative fuel and fuel additives**: Fuel composition has been identified as a factor that affects soot formation [10]. As an example, it has been shown that by increasing the nitrogen content in gaseous fuels (such as ethene [11], methane [12], and natural gas [12]), soot emissions from the combustion of these fuels can be reduced.

- **Improved engine design and engine operation**: Engine design and operating strategies can also affect the amount of soot formed. For instance, it has been shown that soot emission from diesel engines can be reduced by operating an engine at higher fuel injection pressures [13].

- **Improved use of after-treatment devices**: Another approach for reducing soot emission is to increase the efficiency in removing particulates from exhaust gas, rather than controlling the amount formed in combustion.

The development of emission reduction technologies is faced with numerous challenges. For instance, the transition to a cleaner burning fuel, such as natural gas or hydrogen, requires extensive modifications to existing distribution networks. Research in this field is further complicated by the need for new emissions diagnostic techniques. As the level
of particulate emission is increasingly reduced, new strategies must be developed to improve diagnostic capabilities.

A soot diagnostic technique that has received much attention in recent years is Laser Induced Incandescence (LII). With LII, soot particles present in the measurement zone are heated to high temperature by a laser pulse. The resultant incandescence from these particles is measured. By studying the intensity of this incandescence, soot concentration in the measurement zone can be deduced. Studies have indicated that LII can offer high sensitivity and excellent temporal and spatial response [14] [15]. Also, LII can be used to generate an instantaneous map of spatial distribution of soot within the measurement zone; this new ability gives LII an advantage over traditional diagnostic techniques.

1.1 Research Objectives

The overall goal of this work is to better understand soot emission and identify possible emission reduction strategies by applying LII to measure soot concentration in non-premixed, gaseous fuel combustion under engine-relevant conditions. The specific objectives of this study are divided into two categories.

First, this study attempts to advance soot emission research at the University of British Columbia (UBC) by:

- **Calibrating and implementing an LII system**: A system calibration is performed to establish a quantitative relationship between soot mass concentration and the incandescence observed. This calibration is necessary because LII techniques have never been applied at UBC prior to this study.

- **Designing a test plan using the concept of response surface methodology (RSM)**: RSM is a design-of-experiment technique that can be used to improve experimental efficiency. As the first combustion research at UBC to formally adopt this technique, this study aims to present the steps involved in using RSM in detail to set an example for future UBC research.
Secondly, by quantifying the effect of fuel dilution with nitrogen on soot formation under engine-relevant conditions, the potential of using an inert gas as a fuel diluent to achieve cleaner combustion is determined. To reach this objective, combustion experiments are performed to measure the effect of fuel (i.e. ethene) dilution with nitrogen on soot formation using LII. (Ethene is selected as the baseline fuel because its high tendency to generate soot makes it a suitable fuel for testing a new LII system, although ethene may not be considered as a typical automotive fuel.) These experiments are conducted in a shock tube, a combustion device capable of creating engine-relevant test environments (i.e. injection pressure, pre-combustion pressure, and pre-combustion temperature) and providing optical access for LII. Also, taking advantage of the improved temporal resolution offered by LII (compared to gravimetric techniques, for example), an attempt is made to quantify soot formation by measuring soot concentration at various times during a combustion event. This should provide information on the effect of various combustion conditions on the entire soot formation process, instead of focusing only on the soot concentration in the combustion products.

1.2 Organization of the Thesis

This thesis is organized into five further chapters.

Chapter 2 presents an introduction to soot generated from non-premixed combustion. It also discusses the process of soot formation in general and how it can be affected by changes to the four parameters considered: fuel dilution, injection pressure, pre-combustion temperature, and pre-combustion pressure. This is followed by an introduction to LII, which includes a comparison between LII and other soot diagnostic techniques and a summary of the theory behind LII.

Chapter 3 provides an overview of the LII system. It also presents the procedure and results of a LII system calibration. From this calibration, a relationship is found to allow conversion of LII signals measured in this study to absolute soot concentration values.
Chapter 4 presents a test matrix that has been designed for this research. An introduction to the concept of statistical experimental design is provided. Chapter 4 also discusses the principles of the statistical data analysis performed in this study.

Chapter 5 describes the experiments and the data post-processing procedures that have been performed to quantify the effect of nitrogen addition to ethene on soot emission from shock tube combustion. It also discusses the results obtained from this research.

Finally, Chapter 6 summarizes the main findings of this research.
2.0 BACKGROUND INFORMATION

2.1 Introduction

This literature review contains three components: it begins with a brief introduction to non-premixed gaseous combustion. Then, an overview of soot formation and a summary of various strategies for soot reduction are presented. Finally, this review provides a comparison between laser-induced incandescence (LII) and other soot diagnostic techniques, followed by an introduction to the concept behind LII.

2.2 Non-Premixed Combustion of a Gaseous Jet

The process of a non-premixed gaseous combustion can be described in three stages.

First is the jet development stage. This is when gaseous fuel is injected into the oxidizer. Once injected, the gas jet is then carried away from the fuel injector by its own momentum. From this moment, oxidizer will begin mixing into the fuel jet, creating a distribution with nearly pure fuel at the core of the jet that gradually changes to a leaner mixture at the jet periphery. It should be noted that due to turbulent mixing, the exact mixture fraction around the jet will typically be spatially and temporally non-uniform.

The second stage involves the combustion of fuel. It begins with ignition of the gaseous fuel, which may be initiated by auto-ignition or by an ignition source such as a pilot flame, spark plug, or hot surface. Immediately following ignition, the premixed fuel at the jet periphery is consumed in the form of an edge flame [16]. Afterwards, the combustion process settles into the form of a diffusion flame. Fuel from the core of this combusting fuel jet diffuses to the periphery and oxidizer from the surroundings diffuses into the core; thus, the combustion process will occur in a reaction zone surrounding the jet, where the local air-fuel ratio is near-stoichiometric [17]. Note that near the nozzle exit, a high local strain rate is induced by the high relative velocity between the oxidizer
and injected fuel, preventing fuel from igniting and combusting in this region. Because of this, the flame may be observed to recede from the injector nozzle [18] and appear "lifted", as shown in Figure 2.1. It should be noted that immediately downstream of this lifted region, combustion occurs in the form of a triple flame (rather than a diffusion flame). A triple flame is a rich pre-mixed flame (due to air entrainment in the lifted section) in the center of the jet that is immediately surrounded by a diffusion flame and further surrounded by a lean pre-mixed flame on the outside [19], as indicated in Figure 2.1. It is noted that downstream of this triple flame region is where the main diffusion combustion occurs.

![Figure 2.1 Lift-off of a Gaseous Methane Jet](Adapted from [20])

The third combustion stage occurs after the closing of the injector needle. At this stage, the remaining gas will continue to mix and burn until there is insufficient fuel remaining to support further combustion.

### 2.3 Soot Formation Mechanisms and Soot Reduction Strategies

According to Prakash [21], soot represents the largest portion (40%-80% by mass) of diesel engine (a non-premixed combustion) emitted particulate matter (PM); other PM constituents include materials such as volatile organics, fuel derived sulfate particulates, and wear metals [22]. Although the exact composition of diesel generated soot is variable, it can be considered as a solid carbonaceous substance that contains at least 1%
hydrogen by weight, which corresponds to an empirical composition of approximately eight parts carbon to one part hydrogen, C₈H [23]. The following review will consider the formation mechanism of soot and strategies for its reduction.

2.3.1 Soot Chemical Kinetics

Soot particles are formed in a process that involves several physical and chemical reactions, as shown in Figure 2.2. In this review, the formation process of soot is discussed in three separate stages: the inception of molecular precursors, nucleation, and surface growth/coagulation. It should be noted that at each stage in the formation process, soot oxidation can occur where soot or soot precursors are burned in the presence of oxidizing species to form gaseous products such as carbon monoxide (CO) and CO₂ [24].

![Figure 2.2 Graphical Representation of the Stages in Soot Formation (Adapted from Svensson [25])](image)

Inception of Molecular Precursors

Macroscopically, soot is formed in a fuel-rich combustion environment, where the lack of available oxygen prevents complete combustion of fuel in the region. Microscopically, soot formation begins with a gaseous phase precursor. Several models have been proposed to identify the precursor responsible for soot formation. The majority of the literature indicates that PAHs are the dominant molecular species for soot formation [10] [26] [27] [28]; however, it should be noted that other possible soot precursors – such as polyynes [29], polyacetylenes [30], and ionic species [31] – have been proposed as well.

Under the PAH model, several mechanisms have been proposed to describe the formation process of the first aromatic ring in the combustion products. One of these is that proposed by Moriarty et al., which suggests that acetylene (C₂H₂) reacts with propargyl
(C₃H₃) to form a cyclopentadienyl (C₅H₅) radical. This radical then reacts to form benzene (C₆H₆), which is the base ring structure of PAHs [29] [32] (note that the methyl (CH₃) radical in the following reaction can be produced from the fragmentation of larger hydrocarbon radicals):

\[
\begin{align*}
C_2H_2 + CH & \rightarrow C_3H_3 \\
C_2H_2 + C_3H_3 & \rightarrow C_5H_5 \\
CH_3 + C_5H_5 & \rightarrow CH_3C_5H_5 \\
CH_3C_5H_5 & \rightarrow CH_2C_5H_4 + H \\
CH_3C_5H_4 & \rightarrow CH_2C_5H_4 + H \\
CH_2C_5H_4 & \rightarrow C_6H_6
\end{align*}
\]

Precursor Growth and Particle Nucleation

Once a precursor is formed, it will grow to form a larger molecular ring. This growth can be described using the hydrogen abstraction C₂H₂ addition (HACA) process proposed by Frenklach [29]. HACA is a repetitive process of the steps outlined in Equation (2.2). First is the abstraction of a hydrogen atom from an aromatic ring (A₁), resulting in the formation of an aromatic radical (A₁*). This is followed by the addition of an acetylene molecule to the radical, which results in the formation of a larger aromatic ring (A₁⁺₁).

\[
\begin{align*}
A_1 + H & \rightarrow A_1^* + H_2 \\
A_1^* + C_2H_2 & \rightarrow A_1^*C_2H_2 \\
A_1^*C_2H_2 + H & \rightarrow A_1^*C_2H + H_2 \\
A_1^*C_2H + C_2H_2 & \rightarrow A_1^*C_4H
\end{align*}
\]

When a precursor grows to a certain mass, soot nucleation occurs. Various mechanisms for soot nucleation have been proposed. One suggestion is that soot nucleation is a continuous PAH growth and coagulation process which produces nuclei that are in the form of large condensed PAH particles [33]. Another proposal is that soot nuclei are created from a fast and irreversible polymerization process of polyynes that are in the form of polymeric globules [34]. It has also been suggested that soot nucleation is a condensation reaction of gas phase PAH species [24]. On top of these debates in soot
nucleation mechanisms, the exact mass at which soot nucleation occurs is another topic of discussion, as indicated by Seinfeld and Pandis [10].

**Particle Growth and Agglomeration**

During the stage of particle growth, collisions and adhesions between soot nuclei and the process of surface growth by HACA combine to produce primary particles that are typically 10 nm in diameter [24]. In addition, organic materials can attach onto the surface of these primary particles as adsorption and condensation of the organic fractions occurs. This surface growth process fills the void volume surrounding the collided nuclei, which maintains a spherical shape in the primary particles formed. Subsequent growth will turn primary particles into spherules that are approximately 15 nm to 30 nm in diameter [24].

As the growth process continues, the probability of collision and adhesion between larger particles increases. When particles larger than 10 nm collide, the effect of surface growth becomes relatively minor as it is no longer fast enough to fill the larger volume surrounding these particles [24]. This results in a loss of overall spherical geometry in the product of large-particle collisions [35] and explains why individual spherules in a soot particle are spherical while the aggregate as a whole exhibits a chain-like structure.

In the agglomeration process, up to 4000 spherules can combine together to form a cluster similar to the one shown in Figure 2.3. These clusters are typically the type of soot particles found in combustion exhaust [36]. Note that during this agglomeration stage, the process of surface growth continues to merge together spherules within the cluster. This mechanism is referred to as obliteration [37] and it serves to increase the diameter of spherules, reduce the number of spherules in the cluster, and restore spherical shape in spherules. Thus, the final number of spherules present in a soot particle depends on the extent of the agglomeration and obliteration processes.
Particle Oxidation

Soot oxidation is a heterogeneous (gas-solid) reaction. During and immediately after combustion, oxidation and destruction of soot particles may occur as some of these particles diffuse to areas of high temperature and high soot oxidant concentration. The rate of soot oxidation is dependent on the rate of diffusion as well as on the kinetics of the reaction [24]. Possible oxidants include oxygen (O₂), atomic oxygen (O), hydroxide radicals (OH), CO₂, and water (H₂O). Among these possibilities, O₂ is a dominant oxidizer; the global mechanism for soot oxidation by O₂ can be described by the following reaction [38], in which carbon particles are converted to CO₂ and CO. In Equation (2.3), α is a measure of the completeness of the reaction:

$$C + \alpha O_2 \rightarrow 2(\alpha - 0.5)CO_2 + 2(1 - \alpha)CO$$  \hspace{1cm} (2.3)

It should be noted that often more than 90% of soot formed is oxidized before combustion ends [21] [24] and it is only the non-oxidized fraction of soot particles at the end of combustion that may be emitted as exhaust.

This concludes the review on soot formation mechanisms. A summary on various methods to reduce soot emission now follows.
2.3.2 Influence of Fuel Composition on Soot Emission

Fuel composition can affect soot formation [39]. It is therefore possible to control soot formation by modifying fuel composition through the use of fuel additives. Possible additives include inert gas diluents, hydrogen, oxygenated additives, and metallic additives. The following discussion primarily focuses on understanding the effect of inert gas diluents on soot formation because of its relevancy to this study. Generally, the use of fuel diluents can influence soot formation in four ways:

1. Thermal effect: Flame temperature usually decreases as a fuel is diluted with an inert gas such as nitrogen; this can be approximately observed in a calculation of the adiabatic flame temperature for fuels such as methane and a mixture of 80% methane/20% nitrogen (by volume) under stoichiometric conditions.

   This reduction in flame temperature has various implications on the amount of soot generated in a combustion process. Schug et al. have suggested that by adding inert gas such as nitrogen and argon to the fuel, the reduced flame temperature could assist in reducing the amount of soot formed by hindering the soot nucleation and growth process [40]. However, it should also be noted that soot oxidation rates can be reduced at lower temperatures. Thus, the net effect is expected to be a balance between the reduced soot formation and oxidation rate.

2. Dilution effect: Various studies have been performed to show the effects of fuel dilution on soot reduction [11] [41] [42]. Fuel dilution can reduce the amount of carbon available in the combustion process and modify the overall fuel/oxidizer ratio. Axelbaum et al. [11] found a 64% reduction of soot when nitrogen was added to ethene and concluded that 86% of the observed reduction was due to dilution effect and the remaining 14% was due to thermal effect. Gulder and Snelling [41] also studied an ethene/nitrogen diffusion flame and found a 93% reduction of soot when the fuel was diluted from 100% ethene to a 22% ethene/78% nitrogen mixture. While they related this reduction to a change in fuel composition, Stipe [42] suggested that these observations were the result of a
slower coagulation rate of particle formation during the combustion of diluted fuels.

3. Chemical effect: Fuel additives can reduce soot emission by directly participating in the soot formation and oxidation process. Cotton et al [43] studied a non-premixed (propane) flame and observed that metallic additives such as calcium, strontium, and barium could catalyze decomposition of water vapor in the combustion exhaust to produce OH radicals (as well as the decomposition of hydrogen molecules to hydrogen atoms, which react with water to produce OH radicals), which in turn oxidized soot particles and its precursors. McTaggart-Cowan [44] observed a reduction in engine-emitted PM when the fuel used in that study was changed from methane to a methane/hydrogen mixture; it was speculated that the addition of hydrogen had led to an increased presence of OH radicals in the combustion products, which promoted soot oxidation.

4. Turbulence effect: Fuel dilution with an inert gas can indirectly reduce soot emission by enhancing fuel-air mixing as well. As an example, consider a case with two fuels: pure methane and a methane/nitrogen mixture. If both fuels are injected by the same fuel injector for the same injection duration, the injected mass will be higher for the mixture because of its higher density. Thus, the mixture can transfer more kinetic energy to the ambient air than the pure methane [12]. McTaggart-Cowan suggested [12] that an increase in turbulence due to the injection of a higher density mixture might improve late-stage combustion and particle burn up, resulting in lower engine-out particulate emissions. Results have shown that fuel dilution has resulted in up to 80% reductions in both the number and the mobility volume (a measure of particle size) of the particles in the exhaust. Note that for some of the high nitrogen dilution cases considered, black carbon (soot) emissions were no longer detectable by the gravimetric measurement device employed in that study as the concentration was reduced to a very low level.
2.3.3 Practical Combustion Modifications to Reduce Soot Emission

The condition under which non-premixed combustion occurs can affect the amount of soot produced. Some of the parameters that define combustion conditions are as follows:

1. Injection pressure ($P_i$): Studies have shown that increasing $P_i$ can reduce the amount of soot formed in both liquid [13] [45] and gaseous fuel engines [46].

For non-premixed diesel combustion, at higher $P_i$, the increased momentum in a liquid fuel jet can lead to an increase in lift-off length, allowing for better air entrainment and fuel-air premixing [13]. Thus, the number of localized fuel rich (soot formation) zones typically reduces as $P_i$ increases. Also, at high $P_i$, injection velocity increases, which reduces the time a particle takes to move through the soot-forming region of the flame. Thus, there is less time for a soot particle to form before it is moved to the oxidation-dominant region at the flame tip [45].

In a previous study on a predominantly gaseous-fuelled system (a direct-injected, pilot-ignited, heavy-duty natural gas engine) [46], the effect of $P_i$ on PM emission was tested over a range of exhaust gas recirculation (EGR) fractions. (EGR is an engine operating parameter implemented to reduce nitrogen oxide formation). PM emission was observed to reduce by a factor of four when $P_i$ was increased from 17MPa to 25MPa at 50% EGR fraction. The authors attributed the reduction to an improved fuel/oxidizer mixing and shortened combustion duration associated with increased $P_i$, which respectively inhibited soot formation and allowed more time for soot oxidation.

2. Ambient temperature ($T_o$): It has been shown that an increase in $T_o$ can reduce the amount of soot produced from non-premixed combustion by inhibiting its formation [47] and enhancing its oxidation [45] process. In a modeling study conducted by Wu [47], it has been found that an increase in $T_o$ would lead to a higher consumption of the C$_6$H$_5$ radical. The reduced availability of C$_6$H$_5$ would lead to reduced production of pentalene (C$_8$H$_6$) through the following reaction:
\[ C_6H_5 + C_2H_2 \rightarrow C_8H_6 + H. \] The author suggested that C₈H₆ is an important component in PAH growth and that its reduction can lead to a lower the production of naphthalene (C₁₀H₈), phenanthrene (A₃), and pyrene (C₁₆H₁₀) in subsequent reactions [47]. As discussed in Section 2.3.1, PAH is an important component in soot formation. Thus, this reduction in PAH growth can ultimately reduce the amount of soot formed. In addition, soot oxidation is also improved at high T₀. As mentioned in Section 2.3.1, a high temperature environment is needed for soot oxidation to occur. It has been previously shown [45] that soot oxidation rate would increase with increasing T₀.

Another approach to inhibit soot formation is to cool the flame to below 1000 K [48]. This leads to a reduced soot formation rate and a lack of radicals like the C₃H₃ described in Equation (2.1) available to form soot precursors at sufficiently low temperatures.

3. Ambient pressure (P₀): An increase in P₀ typically increases the amount of soot detected in non-premixed gaseous fuel combustion. As an example, McCrain [49] has found that peak soot concentration in a laminar diffusion flame would scale with ambient pressure as P₀^{1.7} for ethene and P₀^{1.2} for methane, for pressures up to 25 atm.

It has been observed in a numerical study that the formation of acetylene and the reaction rate for PAH production is promoted at elevated P₀ [50]. Since acetylene and PAHs are important components of the soot precursor formation and the HACA process, it is believed that soot formation is enhanced as P₀ increases. At the same time, the higher soot concentration present in high-P₀ combustion could increase radiative heat transfer away from the flame and thus inhibit soot oxidation [51] [52] (since soot oxidation is favored at higher temperatures). Combined, these effects are believed to promote soot production at elevated P₀.
4. Air fuel ratio: A change in either \( P_i \) or \( P_0 \) can indirectly vary both the overall and local air fuel ratio (AFR). For fixed injection duration, fuel density (and thus injected mass) decreases with decreasing \( P_i \). Thus, in experiments where \( P_0 \) is also fixed (where the mass of air within the combustion zone remains constant), a decrease in \( P_i \) can result in a leaner overall and (possibly) a leaner local AFR.

An inverse relationship between the amount of soot produced and AFR has been shown experimentally [53] and numerically [54]. As the overall AFR becomes leaner, combustion temperature, the number of localized fuel rich zones, and the amount of unburned fuel were observed to reduced, leading to a reduced soot formation. Also, soot oxidation is typically enhanced as a lean AFR implies more oxygen is available in the combustion zone. Thus, considering the effect of AFR, a decrease in \( P_i \) has two opposing effects on soot formation. Directly, a lower \( P_i \) may result in a relatively poorer air and fuel mixing, which may enhance soot formation. Indirectly, however, a decrease in \( P_i \) may cause both the overall and local AFR to become leaner, which may inhibit soot formation and promote soot oxidation.

2.4 Soot Diagnostic Techniques

Soot concentration is a parameter commonly measured to quantify the amount of soot generated or emitted. Depending on the diagnostic technique employed, soot concentration is presented either on a mass basis (e.g. mg/m\(^3\)) or a volumetric basis (e.g. soot volume fraction (SVF)). Besides concentration, soot particle size is also commonly measured – as fine particles pose a more serious health hazard than coarse ones. Thus, to fully study the impact of soot emission from a certain source, both soot concentration and particle size are often quantified.

Several diagnostic techniques are available for measuring soot concentration and particle size. Generally, these techniques can be classified as either intrusive or non-intrusive.
2.4.1 Intrusive Techniques

Intrusive techniques typically require diverting a portion of the flow of interest to an external measuring device. Some commonly used intrusive soot diagnostic devices include: an Aethalometer (for measuring black carbon (BC) concentration in a gas stream [55] [56] [57]), a Particle Mobility Analyzer (for measuring particle size distributions [58] [59] [60]), and other particle collection systems (where soot particles can be collected and subsequently viewed with an electron microscope to study their structures [12] [56], for example).

Although experiments based on intrusive techniques are relatively simple to set up, they have two weaknesses:

- The flow of interest is disturbed.
- These techniques have poor temporal and spatial resolution [61].

Therefore, intrusive techniques are typically applied to sample an exhaust gas stream, as opposed to directly sampling combustion products in the reaction zone to minimize disturbance. Also, these techniques are only suitable for experiments in which temporal and spatial resolution is not a concern.

2.4.2 Non-intrusive Techniques

Several non-intrusive soot diagnostic techniques are available. Most of these techniques require a laser-based light source and a method for light detection. Non-intrusive techniques are often preferred to intrusive techniques because:

- They offer better temporal and spatial resolution [61] [62].
- Since they are non-intrusive, they can be applied to measure soot concentration present within the combustion zone and not just in the exhaust gas [15] [63] [64]. Thus, the process of soot formation can be studied in greater detail.
Light scattering is a non-intrusive soot diagnostic technique that can be used to measure soot concentration. Despite its successful application in previous studies [14] [65], there are several disadvantages in using light scattering for soot concentration measurements:

- It is vulnerable to interference caused by air or dust particles in the measurement region because these contaminations can also scatter light [61].
- Since the strength of the scattered signal is related to both the sixth power of particle diameter and the number density of soot particles in the flow, this method is very sensitive to particle size and may possibly lead to a strong bias in the results [64] [66]. For example, when larger particles are present in the flow of interest, the measured concentration tends to over predict the actual value [61].

Another non-intrusive method for measuring soot concentration is light extinction [67] [68] [69] [70]. It is based on the concept that light is absorbed and scattered by particles within the flame. By measuring the optical attenuation across a known distance, SVF in the probed region can be determined. Although light extinction is a relatively simple method to setup, it has the following weaknesses:

- The relationship between optical attenuation and SVF is developed based on the assumption that soot particles are spherical [71] [72]. This assumption is invalid as soot particles typically exhibit a chain-like structure, as shown in Figure 2.3.
- In order to relate optical attenuation to SVF, the refractive index of soot ($m$) must be known. However, the exact value of $m$ is unknown because it is a function of soot composition, a property that changes throughout the combustion process [73]. Thus, SVF obtained from extinction experiments is subjected to the uncertainty in the assumed value of $m$.

Laser Induced Incandescence (LII) is a method that does not suffer from any of the deficiencies described. In fact, as LII receives increasing attention in soot reduction researches, more of its potentials and benefits have been identified:

- The signal observed from LII is first-order proportional to soot concentration in the measurement region [74]. This is perhaps the characteristic that makes LII more preferable than other laser-based soot diagnostic techniques.
• Snelling et al. [75] have applied LII to quantify particulate concentration in the exhaust of a diesel research engine. The study has demonstrated that the wide dynamic range and lower detection limit of LII make it suitable for measuring soot emission from the cleaner engines that are currently being developed.

• Besides making exhaust measurements, LII can also be configured for measuring soot concentration in the combustion zone. Dec and Kelly-Zion [76] and Pickett and Siebers [45] [77] have applied planar laser induced incandescence (PLII) to produce a qualitative 2D image of soot distribution inside the cylinder of a direct-injected diesel engine and a constant volume combustion vessel, respectively. Advancing this technique, Morgan et al [78] have implemented PLII to quantify the soot concentration detected within a cross section of a combusting diesel fuel spray.

• Using a point-wise measurement approach instead of PLII, Snelling et al. have experimentally shown that LII can provide a fine spatial resolution of ~0.5 mm [79].

• Besides measuring soot concentration, studies have also shown that LII is capable of measuring soot primary particle size [14] [61] [80] [81].

2.4.3 Laser Induced Incandescence: Principle of Operation

With LII, a pulsed laser (either in the form of a beam or a sheet) rapidly (<10ns) heats up the soot particles in the measurement zone from the local ambient flame temperature to above the carbon vaporization temperature (~4000 K). (Among the materials formed in combustion, only soot is significantly heated by the laser pulse. This is because other materials such as ash and liquid absorb only a negligible amount of energy and volatile materials are believed to vaporize in the laser heating process [15].) The heated particles then incandesce and this blackbody radiation (LII signal) is collected by a camera that is fitted with an appropriate optical band pass filter. The function of the filter is to isolate the LII signal (shorter wavelength) produced by the laser heated soot particles from the radiation of the background flame (longer wavelength).
Several studies have demonstrated that LII signal is linearly related to the soot mass concentration in the measurement zone [65] [74] [82] [83]. Using gas samples of known concentrations [15] [84] or a flame [82] [83] [85], a calibration can be performed to generate a constant for the relationship shown in Equation (2.4). Based on this calibration constant, LII signals measured in future experiments can be converted into absolute soot concentration values.

\[
\text{Soot Concentration (mg/m}^3) = \text{LII Signal (counts) x Calibration Const.} \quad (2.4)
\]

Besides measuring soot concentration, several studies have applied the method of time-resolved LII (TIRE-LII) to determine the size of soot primary particles [66] [85] [86]. The concept behind TIRE-LII is that larger particles will take longer time to cool down than smaller ones and thus will have a lower signal decay rate. Readers interested in TIRE-LII experiments are referred to work such as those by Will et al. [66] [86] as this subject is beyond the scope of this study.

2.4.4 Laser Induced Incandescence: Fundamental Theory

The governing principle behind LII is the conservation of energy. The mechanisms for energy transfer are illustrated in Figure 2.4.

![Figure 2.4 Energy Exchange Mechanisms during an LII Process](image)

Quantitatively, this energy exchange is described in Equation (2.5).

\[
Q_{\text{absorbed}} - Q_{\text{conduction}} - Q_{\text{vaporization}} - Q_{\text{radiation}} = \Delta \text{Energy}_{\text{soot}} \quad (2.5)
\]
There are two stages in an LII experiment: heating and cooling. During the laser heating stage, cooling effects due to conduction, vaporization, and radiation are insignificant as heating takes place over a short period of time (<10ns). Thus, by neglecting the cooling terms in Equation (2.5), an expansion of the laser absorption and internal energy term gives [87]:

\[
C_a F_o q(t) N_p = \frac{1}{6} \pi d_p^3 N_p \rho_s \frac{dT}{dt}
\]

where \( C_a \) is the absorption cross section of a soot particle (nm\(^2\)), \( F_o \) is the laser fluence (mJ/mm\(^2\)), \( q(t) \) is the temporal power density of the laser (1/s), \( N_p \) is the number of particles present in the measurement volume, \( d_p \) is the diameter of a soot particle (nm), \( \rho_s \) is the density of soot (kg/m\(^3\)), \( c_s \) is the specific heat of soot, \( T \) is temperature (K), and \( t \) is time (s).

Rearranging and integrating Equation (2.6) over the duration of the laser pulse gives the peak soot temperature at the end of the laser pulse [87]:

\[
T_{\text{max}} = \left( \int_0^{\tau_{\text{max}}} q(t) dt \right) \left( \frac{6\pi E(m) F_o}{\lambda \rho_s c_s} \right) + T_g
\]

where \( T_{\text{max}} \) is the peak soot temperature at the end of the laser pulse, \( E(m) \) is the complex refractive index of soot, \( \lambda \) is the wavelength of laser sheet (nm), \( \tau_{\text{max}} \) is the duration of the laser pulse (s), and \( T_g \) is the ambient gas temperature (K).

When laser heating stops, cooling effects dominate as heat is transferred back to the surroundings. (As the heating and cooling process take place over a short period of time, soot oxidation effects are relatively minor. Soot oxidation during the 10-20 ns of heating and cooling are conventionally ignored in previous applications of LII to combustion. Also, the effects of signal trapping are partly accounted for in the calibrations.) The time resolved temperature profile for a soot particle in the cooling stage is as follows [87]:
\[ T(t) = (T_{\text{max}} - T_g) \exp \left[ - \frac{3K_a \alpha (\gamma + 1) N_p}{2 f_{\text{MFP}} \rho \varepsilon_a d_p N_p} \left( \frac{N_p}{f_a} \right)^{1/\varepsilon_a} t \right] + T_g \]  

(2.8)

where \( k_a \) is the heat conduction coefficient of soot (J/(msK)), \( \alpha \) is the thermal accommodation coefficient of soot, \( \gamma \) is the ratio of specific heats, \( f \) is the Eucken factor (a measure of vibrational thermal conductivity), \( \lambda_{\text{MFP}} \) is the mean free path (nm), \( f_a \) is a pre-factor constant [87], \( \varepsilon_a \) is an exponent constant [87], and \( t \) is the delay time between the laser pulse and LII signal acquisition (s).

Based on Planck's radiation law and the temperature profile obtained from Equation (2.8), a time resolved LII signal profile is given by [88]:

\[ I(t, \lambda) = \left\{ \frac{8\pi^3 c^2 h}{\lambda_{\text{LII}}^6 \rho_s} \exp \left( \frac{-hc}{\lambda_{\text{LII}} kT(t)} \right) - 1 \right\}^{-1} E(m) \Delta \lambda \rho_1 N_p d_p^3 \]  

(2.9)

where \( c \) is the speed of light (m/s), \( h \) is the Planck's constant ((kgm^2)/s), \( \lambda_{\text{LII}} \) is the center wavelength of the optical filter, \( k \) is the Boltzmann's constant ((kgm^2)/(s^2K)), \( \Delta \lambda \) is the LII detection bandwidth of the optical filter (nm), and \( t \) is the delay time between the laser pulse and LII signal acquisition (s). \( t \) is usually held constant for soot concentration measurements and variable in TIRE-LII measurements.

As shown, LII signal is linearly related to soot mass concentration (i.e. mass of soot particles \( \rho N_p d_p^3 \)) present in the volume probed by the laser sheet) at any instant in time. Typically, the \( \left\{ \frac{8\pi^3 c^2 h}{\lambda_{\text{LII}}^6 \rho_s} \exp \left( \frac{-hc}{\lambda_{\text{LII}} kT(t)} \right) - 1 \right\}^{-1} E(m) \Delta \lambda \) term in this relationship is empirically determined via a LII signal calibration.
2.5 Summary

A review of the process of soot formation and oxidation has been provided. Several strategies for reducing soot emissions were outlined. The second part of this review presented the advantages of using LII to measure soot concentration over the use of traditional soot diagnostics technique. This was followed by a discussion on the concept and theory behind LII.
3.0 LASER INDUCED INCANDESCENCE (LII) CALIBRATION

3.1 Introduction

LII can readily provide a relative measure of soot concentration in a flow. If a quantitative measure is desired, however, the LII system must be calibrated to establish a relationship between the detected LII signal and soot concentration. To deduce this relationship, which is typically linear [15] [64] [74], gas samples of different, but known, soot concentration were measured using LII. The detected LII signal intensity was then paired with the corresponding soot concentration in the sample to generate a data point. A linear fit through a number of data points would produce a calibration curve.

3.2 LII System and Various Calibration Instruments

The LII system (LaVision Soot Master) used in this study consisted of a laser source, a set of laser optics, two intensified CCD cameras, and a control unit. This system was calibrated with gas samples produced by a graphite aerosol generator (GAG) and a propane-diffusion flame (PDF). Note that the same LII results should be observed even though the GAG and PDF would generate particles of different compositions (i.e. synthetically prepared graphite vs. combustion generated soot).

3.2.1 LII System: Laser Source

The laser system used in this study was a Nd:YAG dual cavity pulsed laser (Big Sky Ultra PIV 200). The specifications of the two lasers are as shown in Table 3.1. The use of a 532 nm laser wavelength can help minimize interference from possible fluorescence of various species in the exhaust [61]. Note that throughout this study, both lasers were operated at their maximum (100%) power output level.
Table 3.1 Laser Specifications

<table>
<thead>
<tr>
<th>Beam Parameters</th>
<th>Laser 1</th>
<th>Laser 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength (nm)</td>
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<td>532</td>
</tr>
<tr>
<td>Power (mJ/pulse)</td>
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<td>200</td>
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<tr>
<td>Beam Diameter (mm)</td>
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<td>Pulse Width – FWHM (ns)</td>
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<tr>
<td>Pulse Rate (Hz)</td>
<td>10</td>
<td>10</td>
</tr>
</tbody>
</table>

3.2.2 LII System: Laser Optics

Two quartz spherical lenses and a quartz cylindrical divergence lens (50 mm focal length) were used to focus and transform the laser beam into a sheet for making planar-LII (PLII) measurements. Quartz was chosen because of its high transmittance (>95%) at the 532 nm wavelength range.

The light sheet used in this study had a thickness of approximately 0.8 mm and a width of approximately 10 cm. To orient and direct this laser sheet to the measurement zone, a LaVision 90° Steering Mirror was used.

All the aforementioned lenses and mirror were integrated into a single assembly that was directly attached to the laser. A typical setup is illustrated in Figure 3.1. This arrangement significantly facilitated the process to align these optical components.
3.2.3 LII System: Intensified Charge-Coupled Device (ICCD) Camera

Two ICCD cameras were used in this study (LaVision NanoStar S-20 Intensified Imaging System series). An ICCD camera is a CCD camera coupled with an image intensifier to improve camera sensitivity. These ICCD cameras were used to acquire monochromatic images of 1280 x 1024 pixels with a resolution of 12 bits. Each camera was fitted with a 105 mm focal length lens (Nikon Micro Nikkor; F/2.8) and an interference filter with a bandwidth of 70 nm, centered on 400 nm. As discussed in Chapter 2, the reason for using a filter with a shorter wavelength than the laser excitation wavelength was to suppress interference from the background flame and other particles present in the measurement zone. The camera settings used throughout this study are as follows:

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Setting (Same for Both Cameras)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gate (Exposure of the Intensifier)</td>
<td>200ns</td>
</tr>
<tr>
<td>Gain (Signal Intensification Level)</td>
<td>99</td>
</tr>
<tr>
<td>F-#</td>
<td>4</td>
</tr>
</tbody>
</table>

3.2.4 LII System: System Control Unit

All lasers and cameras were connected to a programmable timing unit (LaVision PTU 9), which was controlled by a software package integrated with the LII system (LaVision DaVis Version 7.1).

3.2.5 LII System: LII Test Section

Two LII test sections were used as an optically accessible container to hold the calibration gas samples:

1. A borosilicate tube (BT): The tube (Kimble Kimax KG-33 series) has an outer diameter of 70 mm and a wall thickness of 3 mm.
2. The shock tube optical section (STOS): The windows of the STOS are made from fused quartz and are 28 mm thick. Details of the STOS design can be found in [89].
Since different materials were used in making the two test sections (borosilicate vs. quartz), a correction was needed to account for the difference in optical attenuation across the two mediums before calibration results obtained from different setups could be compared. This correction is based on the Beer-Lambert Law and is shown in Appendix B.

3.2.6 Soot Concentration Measurement: Aethalometer

In this calibration, an Aethalometer (Magee Scientific series AE21) was used to measure soot concentration in the gas samples. It was installed immediately downstream of the LII test section to minimize particle losses during transportation.

The Aethalometer uses a continuous filtration and optical transmission technique to measure black carbon (BC) concentration [90]. Inside the Aethalometer are a quartz filter, an 880 nm wavelength light source, a flow meter, and two detectors. The function of each part is briefly described in Table 3.3.

<table>
<thead>
<tr>
<th>Part</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz Filter</td>
<td>Collects the particulates contained within the gas sample</td>
</tr>
<tr>
<td>880 nm Light Source</td>
<td>Generates a light which passes through the filter</td>
</tr>
<tr>
<td>Flow Meter</td>
<td>Measures the volume of gas sampled by the Aethalometer</td>
</tr>
<tr>
<td>Detector 1</td>
<td>Measures the level of light attenuation across a clean spot on the filter to establish a background attenuation value</td>
</tr>
<tr>
<td>Detector 2</td>
<td>Measure the actual attenuation across a spot on the filter with collected particulates</td>
</tr>
</tbody>
</table>

Both the actual and background light attenuation across the filter were measured once every minute by the two detectors. Based on the incremental optical attenuation and the volume of gas filtered between each measurement, the mass concentration of BC in the gas stream was determined.

It should be noted that, during this calibration, the following two issues with the Aethalometer were encountered and resolved:
Issue 1: When the gas sample was heavily loaded with soot particles, the filter in the Aethalometer would saturate very quickly (less than two minutes, which corresponded to less than two measurements). Although the Aethalometer could automatically replace a saturated filter with a clean one, each filter change would cause a 20 minute interruption in the data collection process [90].

Solution: A dilution loop was installed to filter the gas sample measured by the Aethalometer. As shown in Figure 3.2, it consisted of a pump, two filters, a flow control valve, and a flow meter. With this loop, a portion of the gas sample was filtered, and the cleaned gas was used to dilute the gas sample.

Because of this dilution, a dilution factor must be multiplied to the Aethalometer data to determine the original soot concentration in the flow. This dilution factor was calculated based on the flow rates set at the dilution loop and the Aethalometer.

Issue 2: Due to non-linearity in the Aethalometer, the measured BC concentration was observed to decrease with time, even if the concentration in the gas sample was constant over the time considered. As discussed in previous studies [56] [57] [91], this non-linearity was the result of a "Scattering Effect" (enhanced light absorption across the filter due to multiple scattering at the fibers of a clean filter) and a "Shadowing Effect" (increased underestimation of black carbon in a loaded filter).
Solution: The data obtained in this calibration were corrected for the Scattering and Shadowing effects according to the steps outlined in Weingartner [91]. This correction can be found in Appendix A.

3.2.7 Soot Source: Propane Diffusion Flame

A soot extraction system was built to collect calibration gas samples from a PDF. A schematic of the soot extraction system is shown in Figure 3.3. A ¼” (0.152” inner diameter) stainless steel tube was placed immediately above the flame. Two pumps were used in parallel to extract a combined volumetric flow rate of 21.5 LPM. At this flow rate, a flow velocity of approximately 30 m/s was attained in the ¼” tube. Such a high flow rate was necessary because:

- The flame must be extinguished before complete combustion occurs to generate soot. Thus, a high flow velocity at the tip of the tube was required to apply a sufficiently high strain rate to extinguish the flame [92].
- The extracted gas sample must be cooled quickly to avoid thermophoretic losses (deposition of particles driven by a temperature gradient [93]). This was done by drawing excess air at room temperature into the tube to quench the soot samples, as suggested in the literature [93] [94] [95].

![Figure 3.3 Soot Extraction System](image)

Soot concentration in the extracted sample was controlled by adjusting the flow rate of propane supplied to the burner. Higher propane flow rate would result in higher soot concentration at the output, at the expense of reduced flame stability. In this calibration,
the range of propane flow rate used was chosen as a balance between flame stability and the amount of soot generated. As summarized in Table 3.4, gas samples of four different soot concentrations were generated to calibrate the LII system. As mentioned in Section 3.2.6, these concentrations were measured using an Aethalometer.

<table>
<thead>
<tr>
<th>Test</th>
<th>Propane Flow Rate (LPM)</th>
<th>Soot Concentration (mg/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.20</td>
<td>7.63</td>
</tr>
<tr>
<td>3</td>
<td>0.21</td>
<td>17.30</td>
</tr>
<tr>
<td>4</td>
<td>0.22</td>
<td>47.09</td>
</tr>
</tbody>
</table>

### 3.2.8 Soot Source: Graphite Aerosol Generator

A graphite aerosol generator (Palas model GFG-1000) was used to produce the second type of soot particles for this calibration. Inside the GAG are two electrodes coated with graphite. During operation, a spark is struck across the two electrodes to vaporize a small amount of graphite. A constant stream of argon gas then carries the vaporized graphite out of the GAG. During transportation, the vaporized graphite re-condenses back to solid carbon, creating a particle-laden gas stream. Soot concentration in the GAG output was controlled by adjusting the argon flow rate and electrode spark frequency. In this calibration, six levels of soot concentration were used, as shown in Table 3.5.

<table>
<thead>
<tr>
<th>Test</th>
<th>Argon Flow Rate (LPM)</th>
<th>Spark Frequency (Hz)</th>
<th>Output Concentration (mg/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>4.10</td>
<td>175</td>
<td>4.88</td>
</tr>
<tr>
<td>3</td>
<td>4.60</td>
<td>333</td>
<td>8.33</td>
</tr>
<tr>
<td>4</td>
<td>4.72</td>
<td>450</td>
<td>10.60</td>
</tr>
<tr>
<td>5</td>
<td>5.00</td>
<td>666</td>
<td>14.00</td>
</tr>
<tr>
<td>6</td>
<td>5.24</td>
<td>800</td>
<td>15.90</td>
</tr>
</tbody>
</table>

The output concentrations shown in Table 3.5 were quoted from the manufacturer [96]. As a check, the Aethalometer was used to measure the soot concentration in the GAG output. The results are listed in Table 3.6.
Table 3.6 Expected and Actual GAG Output Soot Concentration

<table>
<thead>
<tr>
<th>Test</th>
<th>GAG Specified (mg/m³)</th>
<th>Aethalometer Measured (mg/m³)</th>
<th>Aethalometer - GAG (mg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>4.88</td>
<td>5.79</td>
<td>0.91</td>
</tr>
<tr>
<td>3</td>
<td>8.33</td>
<td>10.26</td>
<td>1.93</td>
</tr>
<tr>
<td>4</td>
<td>10.60</td>
<td>11.80</td>
<td>1.20</td>
</tr>
<tr>
<td>5</td>
<td>14.00</td>
<td>15.96</td>
<td>1.96</td>
</tr>
<tr>
<td>6</td>
<td>15.90</td>
<td>18.79</td>
<td>2.89</td>
</tr>
</tbody>
</table>

The difference between the quoted and actual concentrations was observed to be around 20%. Possible causes of this discrepancy included uncertainty in the dilution loop flow meters, in the Aethalometer measurements, and in the Aethalometer data interpretation. Because of these uncertainties, only the quoted GAG concentrations shown in Table 3.5 were used to calibrate the LII system; the measured data shown in Table 3.6 were simply a reference for comparison.

3.3 Calibration Set-up

Table 3.7 lists the three setups implemented in this calibration. Each was performed to fulfill a different purpose. The first two configurations (Set-up PDF+BT and Set-up GAG+BT) were conducted to demonstrate the reliability of using LII to measure soot concentration. The third configuration was conducted to generate a calibration constant suitable for interpreting LII signals measured in a shock tube.

Table 3.7 Calibration Set-up

<table>
<thead>
<tr>
<th>Setup</th>
<th>Particle Source</th>
<th>LII Test Section</th>
</tr>
</thead>
<tbody>
<tr>
<td>Set-up PDF+BT</td>
<td>Propane diffusion flame</td>
<td>Borosilicate tube</td>
</tr>
<tr>
<td>Set-up GAG+BT</td>
<td>Graphite aerosol generator</td>
<td>Borosilicate tube</td>
</tr>
<tr>
<td>Set-up GAG+STOS</td>
<td>Graphite aerosol generator</td>
<td>Shock tube optical section</td>
</tr>
</tbody>
</table>

Depending on the setup employed, gas samples were produced according to the concentrations specified in either Table 3.4 or Table 3.5. Each sample was then subjected to 4500 LII measurements to generate an average LII signal that corresponded
to the soot concentration within the gas. Once all measurements were made, the data were plotted to produce a calibration curve.

**Set-up 1: Propane Diffusion Flame and Borosilicate Tube**

Set-up PDF+BT is illustrated in Figure 3.4. As shown, a portion of the extracted soot sample was passed through a cylindrical borosilicate tube for LII measurements. The gas sample was then diluted and measured by the Aethalometer. The placement of various LII system components is shown in the insert of Figure 3.4.
**Set-up 2: Graphite Aerosol Generator and Borosilicate Tube**

Instead of using a propane flame, the GAG was used as a particle source in this second setup. As shown in Figure 3.5, the gas samples containing synthetically produced graphite particles were passed through the borosilicate tube, which were then diluted and measured by the Aethalometer. It should be noted that Set-up GAG+BT had the same LII component placement as the one shown in the insert of Figure 3.4.

![Figure 3.5 Set-up 2: Graphite Aerosol Generator and Borosilicate Tube](image)
Set-up 3: **Graphite Aerosol Generator and the Shock Tube**

In this setup, the STOS was used in place of the borosilicate tube. Gas samples from the GAG were passed through the STOS for LII measurements. The placement of various LII system components is shown in the insert of Figure 3.6.

![Diagram of Set-up 3: Graphite Aerosol Generator and the Shock Tube Optical Section](image)

*Figure 3.6 Set-up 3: Graphite Aerosol Generator and the Shock Tube Optical Section*
3.4 Results and Discussion

For each setup, the detected LII signal intensities were plotted against the corresponding soot concentrations listed in Table 3.4 and Table 3.5. A linear regression through these points generated a calibration curve for that particular setup. When fitting the calibration data, the fitted line was forced through the origin because detected LII signal must be zero when soot concentration was zero. The results are shown in Figure 3.7.

![Soot Concentration Vs. LII Signal](image)

**Figure 3.7 Calibration Curves**
(PDF = Propane Diffusion Flame; GAG = Graphite Aerosol Generator)
(STOS = Shock Tube Optical Section; BT = Borosilicate Tube)
(NC = Not Corrected for Different Attenuations; C = Corrected)

The following three observations were made from Figure 3.7:

1. As expected, the relationship between LII signal and soot concentration is linear.
2. Set-up GAG+BT and Set-up PDF+BT generated the same calibration curve, although it should be noted that the soot concentration in the gas samples generated from the PDF might possibly be subjected to around 20% uncertainty in the Aethalometer measurements.
3. The data series labeled as "GAG+STOS (NC)" represents the uncorrected LII signals obtained from Set-up GAG+STOS. The term "uncorrected" means the higher signal attenuation level through the thicker (compared to the BT wall) STOS window was not considered. Thus, it was expected that weaker LII signals would be observed from the uncorrected data. To account for this difference in attenuation, a correction was performed based on the steps outlined in Appendix B. The corrected results are shown in the data series labeled as "GAG+STOS (C)", which are in good agreement with the other two calibration runs.

From Figure 3.7, the following relationship was established to convert LII signals detected from measurements made inside a borosilicate tube to soot concentration values.

\[
Soot \text{ Concentration (mg/m}^3) = LII \text{ Signal (counts)} * 0.52
\]  

(3.1)

Using the attenuation constant found in Appendix B, Equation (3.1) was modified for use with LII measurements made inside the STOS.

\[
Soot \text{ Concentration (mg/m}^3) = [LII \text{ Signal (counts)} * 8.044] * 0.52
\]  

(3.2)

3.5 Conclusions

An empirical relationship between soot concentration and LII signal was developed. The calibration involved the use of three different experimental configurations and two types of soot particles: synthetically produced graphite and combustion generated soot. The following points were observed:

1. The calibration results showed linearity between LII signal and soot concentration.
2. The same calibration curve was obtained regardless of how the gas samples were measured and generated. This implies the LII system is a robust instrument for soot concentration measurements.
4.0 STATISTICAL EXPERIMENTAL DESIGN

4.1 Introduction

The first formal application of statistical experimental design was performed by Sir Ronald A. Fisher. In the 1920s, he developed the three basic principles of experimental design: randomization, replication, and blocking to increase the efficiency of his experiments in agriculture. Fisher also implemented statistical concepts such as factorial design and analysis of variance to maximize the information obtained from his research.

The development of response surface methodology (RSM) by Box and Wilson [97] is another milestone on statistical experimental design. Originally, Box applied the technique of RSM to his work in the chemical and process industry. Over the years, RSM has been modified and used in various fields, including in internal combustion engine research [98] [99] [100] [101] [102]. Seabrook [98] and Ghauri [99] both applied the central composite rotatable design (CCRD), a modified version of RSM, to their research on emission reduction through valve timing optimization and exhaust gas recirculation. Knafl [101] applied the central composite faced (CCF) design to study the effects of injection pressure and injection timing on NOx emissions, soot emissions, and fuel efficiency of a production type medium duty diesel engine.

The following discussion is divided into three sections. It begins with an introduction to the concept of central composite designs. Then, the procedures for developing a test matrix for this study are presented. Finally, it summarizes the various statistical tools used to analyze the results of this study.

4.2 Central Composite Designs

In an experiment, particularly one that involves response optimization, the variable being studied is likely to be dependent on several factors. Ideally, a full factorial experiment
should be conducted to test all possible combinations of independent variables. However, full factorial experiments are often impractical to carry out because, as shown in Equation (4.1), the number of tests required increases exponentially as the number of independent variables and variable levels increases.

\[ N = L^V \] (4.1)

where \( N \) is the number of experiments required in a full factorial test, \( L \) is the number of variable levels tested, and \( V \) is the number of independent variables tested.

To reduce the number of tests required, experimenters often resort to changing and testing one variable while holding all others constant. However, the conclusions reached in this type of experiment are often incorrect as the interactions between variables are neglected. Figure 4.1, adapted from Seabrook [98], illustrates the problem with this type of experiment.

![Arbitrary Response Surface](image)

**Figure 4.1 Hypothetical "One Variable at a Time" Experiment (Adapted from Seabrook [98])**

In this hypothetical test, suppose the true optimum of the system is located at \( A = 50 \) and \( B = 30 \), as indicated by the contours in Figure 4.1. However, if an experimenter decides to test the two variables individually, he will find Variable A is optimized at \( A = 20 \) and \( B = 60 \), as indicated by the dots in the figure. This means the "One Variable at a Time"
approach will indicate an optimum level different from the true value. This discrepancy is observed because the interaction effects between variables are neglected in the "One Variable at a Time" experiment. This example illustrates that interaction effects between variables are important as systems may respond in a misleading way when only one variable is tested at a time.

To improve experimental efficiency and quality, the central composite design (CCD) was developed by Box and Wilson [97]. As an example, to test four variables at five levels, a CCD experiment requires only 31 tests to determine the main effects and second order interactions between all variables, whereas a full factorial experiment requires 625 \( N=5^4 \) tests. Also, since variable interactions are considered, a CCD experiment can more accurately predict the optimum response than the "One Variable at a Time" experiment.

There are two parts to a CCD experiment. First, a test matrix must be designed to meet the requirements of a CCD. Second, a regression analysis must be performed on the experimental data to generate a response function. This response function can then be used to identify the optimal operating condition in a process or to estimate a response at any variable combinations not tested in the experimental space.

A CCD consists of a factorial cube bounded between levels -1 and +1, center points at level 0, and star points at levels \(-\alpha\) and \(+\alpha\), as shown in Figure 4.2. The value of \(\alpha\) and the number of center points to be repeatedly tested depends on the type of CCD chosen for the experiment and are specified in Mason [108]. These specified values must be used when constructing the test matrix to ensure accuracy in the approximation and efficiency in generating the response surface.
There are three types of CCD: Circumscribed (CCC), Inscribed (CCI), and Faced (CCF). These designs differ from each other in terms of the location of the star points and the boundaries of the factorial cube, as shown in Figure 4.3.

The CCF design was chosen for this study as it required only three levels of tests for each factor (-1, 0, +1), whereas the other designs required five levels (-α, -1, 0, +1, +α). With fewer levels, both the preparation time and the probability for mistakes in test preparation are reduced [108].

4.3 Experimental Design Procedures

In this study, the effects of fuel composition, fuel injection pressure, pre-combustion temperature, and pre-combustion pressure on soot formation were quantified in a CCF designed experiment. The CCF matrix shown in Table 4.1 was constructed as follows [108]:

---

Figure 4.2 Illustration of a Three-variable CCRD (Adapted from Stat-Ease [103])

Figure 4.3 Various Central Composite Designs (Adapted from MathWorks-Design of Experiments [107])
1. A fractional factorial \((m - 1)^k\) layout was constructed, where \(m\) and \(k\) represented the number of variable levels (3) and the number of variables (4), respectively.

2. Eight \((2 \times k)\) star points were added along the coordinate axes on all faces of the factorial cube. Each pair of star points was denoted as follows:

\[
\begin{align*}
(\pm 1, & \quad 0, \quad 0, \quad 0) \\
(0, & \quad \pm 1, \quad 0, \quad 0) \\
(0, & \quad 0, \quad \pm 1, \quad 0) \\
(0, & \quad 0, \quad 0, \quad \pm 1)
\end{align*}
\]

3. Three \((m)\) repeat observations were added to the design center:

\[(0, \quad 0, \quad 0, \quad 0)\]

4. Table 3.2 was constructed to show the \(27 (2^k + 2k + m)\) points in the test matrix.

### Table 4.1 CCF Design (Coded) Matrix

<table>
<thead>
<tr>
<th>Test Point</th>
<th>Fuel Composition (%N(_2) in ethene)</th>
<th>Fuel Injection Pressure (bar)</th>
<th>Pre-combustion Temperature (K)</th>
<th>Pre-combustion Pressure (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>2</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>4</td>
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<td>1</td>
<td>1</td>
<td>1</td>
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<td>16</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>17</td>
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<td>19</td>
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<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
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<td>21</td>
<td>0</td>
<td>0</td>
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<td>0</td>
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<td>22</td>
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<td>0</td>
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<td>26</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>27</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
For the four variables listed in Table 4.1, the levels -1, 0 and +1 were defined as:

<table>
<thead>
<tr>
<th>Variables</th>
<th>Level -1</th>
<th>Level 0</th>
<th>Level +1</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Fuel Composition (%N₂ in ethene)</td>
<td>0</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>B. Fuel Injection Pressure (bar)</td>
<td>60</td>
<td>70</td>
<td>80</td>
</tr>
<tr>
<td>C. Pre-combustion Temperature (K)</td>
<td>1200</td>
<td>1300</td>
<td>1400</td>
</tr>
<tr>
<td>D. Pre-combustion Pressure (bar)</td>
<td>35</td>
<td>30</td>
<td>25</td>
</tr>
</tbody>
</table>

As an additional step (not required by the CCF design), Table 4.1 was divided into three blocks, one for each of the three fuel mixtures tested. Within each block, the order for testing each point was rearranged to facilitate the experiment. Substitution of the definitions listed in Table 4.2 generated the following test matrix (in the order tested):

<table>
<thead>
<tr>
<th>Test Point</th>
<th>Fuel Composition (%N₂)</th>
<th>Fuel Injection Pressure (bar)</th>
<th>Pre-combustion Temperature (K)</th>
<th>Pre-combustion Pressure (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>60</td>
<td>1200</td>
<td>35</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>60</td>
<td>1200</td>
<td>25</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>60</td>
<td>1400</td>
<td>35</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>60</td>
<td>1400</td>
<td>25</td>
</tr>
<tr>
<td>17</td>
<td>0</td>
<td>70</td>
<td>1300</td>
<td>30</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>80</td>
<td>1400</td>
<td>35</td>
</tr>
<tr>
<td>8</td>
<td>0</td>
<td>80</td>
<td>1400</td>
<td>25</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>80</td>
<td>1200</td>
<td>25</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>80</td>
<td>1200</td>
<td>35</td>
</tr>
<tr>
<td>13</td>
<td>20</td>
<td>80</td>
<td>1200</td>
<td>35</td>
</tr>
<tr>
<td>14</td>
<td>20</td>
<td>80</td>
<td>1200</td>
<td>25</td>
</tr>
<tr>
<td>15</td>
<td>20</td>
<td>80</td>
<td>1400</td>
<td>35</td>
</tr>
<tr>
<td>16</td>
<td>20</td>
<td>80</td>
<td>1400</td>
<td>25</td>
</tr>
<tr>
<td>18</td>
<td>20</td>
<td>70</td>
<td>1300</td>
<td>30</td>
</tr>
<tr>
<td>9</td>
<td>20</td>
<td>60</td>
<td>1200</td>
<td>35</td>
</tr>
<tr>
<td>10</td>
<td>20</td>
<td>60</td>
<td>1200</td>
<td>25</td>
</tr>
<tr>
<td>12</td>
<td>20</td>
<td>60</td>
<td>1400</td>
<td>25</td>
</tr>
<tr>
<td>11</td>
<td>20</td>
<td>60</td>
<td>1400</td>
<td>35</td>
</tr>
<tr>
<td>20</td>
<td>10</td>
<td>80</td>
<td>1300</td>
<td>30</td>
</tr>
<tr>
<td>21</td>
<td>10</td>
<td>70</td>
<td>1200</td>
<td>30</td>
</tr>
<tr>
<td>22</td>
<td>10</td>
<td>70</td>
<td>1400</td>
<td>30</td>
</tr>
<tr>
<td>24</td>
<td>10</td>
<td>70</td>
<td>1300</td>
<td>25</td>
</tr>
<tr>
<td>23</td>
<td>10</td>
<td>70</td>
<td>1300</td>
<td>35</td>
</tr>
<tr>
<td>25</td>
<td>10</td>
<td>70</td>
<td>1300</td>
<td>30</td>
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<tr>
<td>26</td>
<td>10</td>
<td>70</td>
<td>1300</td>
<td>30</td>
</tr>
<tr>
<td>27</td>
<td>10</td>
<td>70</td>
<td>1300</td>
<td>30</td>
</tr>
<tr>
<td>19</td>
<td>10</td>
<td>60</td>
<td>1300</td>
<td>30</td>
</tr>
</tbody>
</table>
It should be noted that full randomization of the 27 test points was not practical. Due to the limited amount of fuel available, experiments with high injection pressures must be conducted first. As an attempt to minimize bias, however, only one of the 27 test conditions listed in Table 4.3 was tested per day to allow sufficient time for all the experimental equipments to recover before being used at another test condition.

Note that each of the 27 test conditions consisted of five experiments, as shown in Table 4.4 (i.e. a total of 27 x 5 = 135 experiments were completed in 27 days). The purpose of the first two trials was to determine an average ignition delay time with reference to the fuel injector trigger signal. The procedures for determining ignition delay are deferred to Chapter 5. Once the delay was found, the timing of the two ICCD cameras was varied according to Table 4.4 for the three LII trials.

<table>
<thead>
<tr>
<th>Repeat</th>
<th>ICCD Camera 1 Triggered After:</th>
<th>ICCD Camera 2 Triggered After:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Delay Trial A</td>
<td>Not Used</td>
<td>Not Used</td>
</tr>
<tr>
<td>Delay Trial B</td>
<td>Not Used</td>
<td>Not Used</td>
</tr>
<tr>
<td>LII Trial 1</td>
<td>Ignition Delay+0.5 ms</td>
<td>Ignition Delay+2.0 ms</td>
</tr>
<tr>
<td>LII Trial 2</td>
<td>Ignition Delay+1.0 ms</td>
<td>Ignition Delay+2.0 ms</td>
</tr>
<tr>
<td>LII Trial 3</td>
<td>Ignition Delay+1.5 ms</td>
<td>Ignition Delay+2.0 ms</td>
</tr>
</tbody>
</table>

As shown in Table 4.4, each test point would produce three LII images captured at a time of 2.0 ms after the start of ignition (ASOI), with referenced to the injection signal. Special emphasis was placed on acquiring LII images at 2.0 ms ASOI because, temporally, this time bin should be the closest to the end of combustion. Thus, the soot concentration detected at 2.0 ms ASOI should be the most representative of the amount of soot emitted.

By varying the camera timings, a temporal sequence of LII images was obtained for each test condition, as indicated by Figure 4.4. The purpose of acquiring LII images at different times was to measure the changes in soot concentration within the fuel jet throughout the combustion process.
4.4 Statistical Analysis for RSM Experiments

4.4.1 Multiple Regression Analysis

A second-order (with interaction) model was evaluated in a multiple regression analysis to generate a response function that described the test results of this study. This analysis was performed using a MATLAB code developed in this research, which can be found in Appendix C. The regression model is of the following form:

\[
y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_4 + \beta_5 x_1 x_2 + \beta_6 x_2 x_3 + \beta_7 x_3 x_4 + \beta_8 x_4 x_4
\]

where \( y \) is the estimated soot concentration (mg/m\(^3\)) at 2.0 ms ASOI, \( \beta_0 \) to \( \beta_{14} \) are the regression constants of the model, \( x_1 \) to \( x_4 \) are the coded form of the four independent variables listed in Table 4.2, and \( e \) is the residual (error) of the regression. The residuals are assumed to be normally distributed.

Equation (4.2) is commonly used to describe the results of experiments designed based on RSM [109] [110]. It is because this model can straightforwardly account for all main effects, second order effects, and second-order interactions between the variables of interest. For example, although a different form of the model may be used to capture the effects of higher-order interaction terms (e.g. \( x_1 x_2 x_3 \)), interpretation of this higher-order model can become difficult unless the relationship in question is known \textit{a priori} [111].
Once the coefficients in Equation (4.2) were evaluated, it was used to create a series of contour plots for result presentation. When producing these plots, two variables were varied while the other two were held constant at their center points.

4.4.2 Model Checking: Residuals and Coefficient of Determination

The residual term \( e \) shown in Equation (4.2) is defined as the difference between the observed response \( y_i \) and the predicted response \( \hat{y}_i \). To identify outliers in the results and to check the model for adequacy, the residual for each test \( e_i = y_i - \hat{y}_i \) was standardized (by dividing all residuals by their average standard deviation) and plotted against the model predicted response \( \hat{y}_i \). In a residual plot, such as the one shown in Figure 4.5, the standardized residuals should be randomly scattered about zero and should lie between -3 and +3 [112] [113]. Any trends observed in this plot may suggest that an inappropriate regression model is used to generate the response surface [111] [113]. When that happens, the residuals can be plotted against a different axis, such as interaction effects (e.g. \( x_i x_j \)), to search for problems with the regression model.

Furthermore, in this research, model residuals were plotted against other parameters such as nitrogen addition, fuel injection pressure, pre-combustion temperature, pre-combustion pressure, and variations in ignition delay to evaluate their influence on the effectiveness of the model, an example of one such plot is shown in Figure 4.6.
Another useful parameter for evaluating the global fit of a regression model is the coefficient of determination ($R^2$). It is defined as the proportion of variability in a data set that is accounted for by the model [111], as shown in Equation (4.3). Generally, a regression model is acceptable if $R^2 > 0.5$ [111].

$$R^2 = 1 - \frac{SSE}{SST} = 1 - \frac{\sum (y_i - \hat{y}_i)}{\sum (y_i - \bar{y})}$$  \hspace{1cm} (4.3)

where $y_i$ is the observed response, $\hat{y}_i$ is the predicted response, and $\bar{y}$ is the average observed response.

### 4.4.3 Error Analysis: Standard Error of Predicted Response

The standard error of the response surface was calculated to assess the quality of the predicted response as well. It is defined as follows [112]:

$$s_{\hat{y}(x)} = s \sqrt{x^{(m)}(X'X)^{-1}x^{(m)}}$$  \hspace{1cm} (4.4)
where \( s \) is the square root of the mean square error of the response surface \( (s = \sqrt{MS_E}) \), \( x^{(m)} \) is a vector with values outlining the point of interest for calculating the standard error \( (x^{(m)} = [1, x_1, x_2, x_3, x_4, x_1, x_2, x_1, x_2, x_3, x_1 x_3, x_2 x_4, x_3 x_4, x_4]) \), and \( X \) is a matrix with values outlining the 27 conditions tested, as follows:

\[
X = \begin{bmatrix}
1 & x_1 & x_2 & \cdots & x_4 x_4 \\
1 & x_1 & x_2 & \cdots & x_4 x_4 \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
1 & x_1 & x_2 & \cdots & x_4 x_4
\end{bmatrix}
\]  \hspace{1cm} (4.5)

4.4.4 Model Analysis: Significance of Parameters

The significance of each parameter on modeling the detected soot concentration can be evaluated by inspecting its test of significance \( (t) \) statistic. The \( t \)-statistic is defined as shown in Equation (4.6). By definition, a highly influential parameter is indicated by a high \( t \)-statistic. For example, in a system with 12 degrees of freedom, any parameter that has a \( t \)-statistic higher than 2.179 is considered as influential at a 95% confidence level.

\[
t_{\beta_i} = \frac{\hat{\beta}_i}{s_{\beta_i}}
\]  \hspace{1cm} (4.6)

where \( t_{\beta_i} \) is the \( t \)-statistic assigned to parameter \( i \), \( \beta_i \) is the estimated regression constant for parameter \( i \), and \( s_{\beta_i} \) is the estimated standard error for \( \beta_i \).

4.5 Summary

The benefits of using RSM as an experimental design technique were presented. This was followed by a discussion on the steps involved in generating a RSM-designed test plan for this research. Finally, various statistical tools available for interpreting and evaluating the results of RSM experiments were provided.
5.0 SHOCK TUBE COMBUSTION EXPERIMENTS

5.1 Introduction

The goal of this study was to quantify the effects of nitrogen addition to ethene on soot emission under various combustion conditions. To reach this goal, LII experiments were conducted in a shock tube, according to the test matrix outlined in Chapter 4. Each LII image captured from the experiments was digitally processed to enhance its quality and to extract relevant information. The extracted data was statistically analyzed according to the procedures outlined in Chapter 4 to generate a set of response functions to illustrate the relationship between soot emission and the combustion parameters examined.

5.2 Experimental Apparatus

In this experiment, soot generated from combustion inside a shock tube was measured using LII. Using a reflected-shock technique, air inside the shock tube was heated and compressed to the engine-relevant conditions outlined in Table 4.2.

A schematic of the shock tube facility is shown in Figure 5.1. The LII system was positioned with reference to the shock tube optical section (STOS) as indicated. Also, as shown in the figure, an electronically controlled injector was installed at the end of the STOS to inject fuel into the shock tube for combustion.
The stainless steel shock tube was 7.90 m long with an inner diameter of 5.9 cm. It was separated into a 3.11 m driver section and a 4.79 m driven section (including the STOS) by a double-diaphragm intermediate section, as shown in Figure 5.1. This intermediate section consisted of two 0.76 mm thick lexan diaphragms that were installed in series and were separated by a 66 cm$^3$ chamber. Along the shock tube, four flush-mounted dynamic pressure transducers (PCB Pizeotronics 112B11 series) and a data acquisition system (Wavebook 512 series; 140 kHz sampling rate per channel) were installed to detect the
passage of an incident shock wave. In addition, a vacuum sensor (Auto Tran 860 series) and a high-pressure sensor (Eclipse data instruments) were used to monitor the initial gas pressure in the driven and driver section, respectively, before each experiment. Voltage outputs from these two pressure sensors were displayed with a multimeter (Circuit-Test DMR-3600 series).

The fuel injection system used in this study consisted of a fuel injector (Westport J-42 series), a customized injector controller (Westport Innovations), and a control program (Westport WCut series). The injector was a magneto-restrictive unit with a central hole of 0.31 mm diameter. It was mounted at the end of the optical section and was on the center line of the shock tube, as shown in Figure 5.1. The WCut software was used to control the duration of each injection and the delay between the detection of a trigger signal and the start of injection. In the experiments, injection duration was fixed at 0.5 ms and injection delay was fixed at 0.2 ms. Fuel supply pressure was regulated according to the test matrix outlined in Table 4.3. Also, the J-42 was used to inject the three fuels tested in this study:

- Ethene (99.9% purity)
- Ethene and nitrogen (Praxair Certified: 10.01% nitrogen and 89.99% ethene)
- Ethene and nitrogen (Praxair Certified: 19.99% nitrogen and 80.01% ethene).

As mentioned in Section 1.1, ethene was selected as the baseline fuel because its high tendency to generate soot makes it suitable for demonstrating the capabilities of a new LII system.

As discussed in Chapter 4, the LII images acquired in this study were captured at specified times with reference to an average ignition delay. To determine this average, two preliminary trials were performed for each test condition considered in this study prior to conducting the three LII experiments.

Ignition delay was measured using a high frame rate digital camera (Vision Research Phantom V7.1 CMOS series) equipped with a 50 mm F/1.2 Nikkor lens to record the natural luminescence of the combustion process. The camera was set to capture images
of 80 pixels by 800 pixels in size to match the STOS window aspect ratio, which provided a spatial resolution of 0.2 mm by 0.2 mm per pixel. It was operated at a frame rate of approximately 31,100 fps, which resulted in a time interval of approximately 32 μs in between frames. The effective integration time was set at 2 μs per frame. In this study, the camera and its internal clock were simultaneously triggered by the same signal that triggered the fuel injector. As shown in Figure 5.2, by searching for the frame in which the emergence of a flame kernel was first observed, the ignition delay was found from the camera output as an elapsed time from the injector trigger signal (800 μs in this case).

![Figure 5.2 Typical Image Sequence Captured to Identify the Start of Ignition](image)

The identified average ignition delay for each experimental condition is presented in Appendix G. Also, the effect of nitrogen addition, P_i, T_0, and P_0 on ignition delay is study using response surface methodology in Appendix G, which shows the addition of nitrogen can increase ignition delay, whereas an increase in P_i and T_0 can reduce ignition delay.

The average ignition delay for each condition was used to establish the timing sequence for the two LII cameras. (A more detailed discussion on image acquisition timing was
provided in Section 4.3.). In this experiment, Camera 1 (shown in Figure 5.1) was set to capture images at 0.5 ms, 1.0 ms, and 1.5 ms after the average start of ignition (ASOI) timing, whereas Camera 2 was setup to capture images at 2.0 ms ASOI.

5.3 Experimental Procedure

To prepare for a shock tube experiment, air was first evacuated from the driver, driven, and intermediate sections of the shock tube using a vacuum pump (Cenco HYVAC 7 series). Then, the driven section was filled with air (Praxair medical grade) and both the driver and intermediate section were filled manometrically with a mixture of helium (Praxair 99.9% purity) and air (Praxair medical grade). The amount of air and helium and the initial pressure filled in the driver and driven section was determined based on the desired pressure and temperature behind the reflected shock wave by solving 1-D conservation equations for mass, momentum, and energy across the shock using a method discussed by Huang [115] [116]. Qualitatively, the initial pressure in the driver section was always higher than that in the intermediate section, which was always higher than that in the driven section. The pressure in the intermediate section was set to ensure the pressure difference across each diaphragm was below its burst strength.

Once the shock tube had been charged to the desired pressure, an experiment would begin by venting the gas in the intermediate section to atmospheric pressure, resulting in the rupture of the two lexan diaphragms (as the pressure difference across each diaphragm became higher than the burst strength). The subsequent sudden expansion of the driver gas sent a shock wave towards the optical section. Also, when the diaphragms ruptured, a command was issued to the injection system to charge the fuel to the desired pressure. As the shock wave passed by the first dynamic pressure transducer (closest to the driver section), a signal was generated to activate the Wavebook data acquisition system. Moments later (~2 ms), as the shock was detected to pass by the last dynamic pressure transducer (closest to the injector), a trigger signal was generated by an instrument control program (LabVIEW 7 Express series) to activate the fuel injection system, the high-speed CMOS camera, and the LII system.
At the end of each experiment, signals from the dynamic pressure transducers were analyzed to calculate the velocity of the incident shock wave. Based on this velocity, the actual pressure and temperature achieved in the STOS during the experiment was determined. Huang [116] has shown that the actual temperature and pressure were in agreement with the expected conditions to within 1-2% and 3-4%, respectively.

Note that the shock tube was thoroughly cleaned after each experiment. Cleaning of the shock tube is essential because the rupture of the diaphragms produces and scatters fragments of lexan particles along its length. These particles must be removed in order to prevent them from affecting the next combustion process.

5.4 Experimental Results

A typical temporal sequence of LII images is shown in Figure 5.3. These images show the cross-sectional spatial distribution of soot concentration within a fuel jet. In this sequence, the injector orifice was located at the far left center of each image, with fuel being injected to the right. The image acquisition time is indicated on the left and the distance from the injector orifice is shown by the scale below the LII images. These images are false colored according to the color scale shown on the right.
Note that the LII image taken at 2.0 ms ASOI is not included in Figure 5.3. This is because the setup of this experiment required the two LII cameras to capture images from two different positions and angles. This could potentially lead to discrepancies in the measurements. Thus, in this study, data collected by Camera 1 were only compared against other measurements acquired by Camera 1 and never compared against those acquired by Camera 2 in order to ensure a fair comparison.

Along with the LII images, a high speed video of luminosity from the combustion process was recorded for each experiment. This video provides the spatial distribution of the line-of-sight integrated luminosity in the direction perpendicular to the laser sheet. As a reference, the frames that correspond to the LII images shown in the above sequence are included in Figure 5.4. Comparing between Figure 5.3 and Figure 5.4, the LII images are observed to have similar overall profile as the images taken with the high-speed camera.
In the following discussion, the experimental results are briefly presented to highlight the experimental variability encountered in this study and recommend a method to address this issue. A full discussion on experimental results is deferred to Section 5.5.

Figure 5.5 is a summary of the experimental data collected at 2.0 ms ASOI in this study, from which a high degree of run-to-run variability is observed. For example, at Test Point 9 (circled), the measured soot concentrations are observed to vary by close to a factor of two (from \( \sim 3800 \text{ mg/m}^3 \) to \( \sim 6800 \text{ mg/m}^3 \)).
On consideration, a high level of variability might be expected since:

1. LII measurements were made from a single plane through the center of the shock tube; thus, the probability of achieving good alignment between the soot pockets within a fuel jet and the thin laser sheet was not high. This might result in considerable shot-to-shot variation in the images taken because only the laser heated soot particles could generate LII signals; thus, a relatively sooty flame could appear less sooty if its soot pockets were misaligned with the laser.

Typically, this problem can be solved by averaging over a large number (>20) of LII images [77] [78] [79]. As testing with a large number of repeats in a shock tube would be impractically time consuming, therefore the experiments were limited to only three repeats at each test point.

When analyzing the data, the average of the three measurements collected at all test points was used to generate a response function (hereafter referred to as “average-soot model”). However, three measurements were clearly not sufficient to provide a statistically meaningful average. Thus, an additional approach to analyze the data was attempted: at each test point, the LII measurement with the maximum soot concentration was used to generate another response function (hereafter referred to as “most-soot model”). These most-soot images should provide a better indication of the soot concentration detected within a fuel jet when its soot pockets were well aligned with the laser sheet. Also, these images could better represent the behavior of sooty combustion regions that led to high soot concentration levels [76].

2. Another possible source of variability was the ignition delay in each combustion process. As discussed in Section 4.3, two trial runs were conducted for each combustion condition to determine an average ignition delay; the camera acquisition timing for the three repeated LII experiments was then set based on this average. As each combustion was unique, a different ignition delay was observed in each experiment. Thus, in reality, the three LII images at each test
point were never acquired at the same time (2.0 ms ASOI), as shown in Figure 5.6. This can potentially be problematic, especially when the acquisition time is near the onset of an oxidation process, as images taken prior to the start of soot oxidation may show higher concentration than those taken after.

Before developing a technique to mitigate this issue, it would be worthwhile to evaluate the possibility of ignition delay being a cause of experimental variability. To conduct this evaluation, the soot concentration detected in each LII measurement was plotted against both the actual image acquisition timing achieved (with respect to the start of ignition) and the ignition delay detected (with respect to the injection command signal) in the corresponding combustion process. The results are shown in Figure 5.7. From these figures, it appears unlikely that variability observed in the LII measurements were caused by variations in either the image acquisition timing or the ignition delay.
In short, misalignment between soot particles and the laser sheet might be a more significant factor (than the variations in image acquisition timing and ignition delay) in contributing to the shot-to-shot variations observed in the LII measurements. In response, it would be constructive to describe the data collected in this experiment using a most-soot model in addition to an average-soot model. It should be reminded that the concept of building a most-soot model was supported by the following argument: because this model was based on measurements in which soot particles were better aligned with the laser sheet, its trends might more robustly depict the overall soot concentration levels detected in typical combustion.

In addition to variability, extinction of the signal (trapping) by soot located between the emitting location and the camera can potentially affect the measured soot concentrations. An estimate of this effect can be found in Appendix H, which predicts that signal trapping can possibly attenuate the detected LII signals by less than 10%. As the calculation performed in Appendix H was based on the maximum soot concentration detected in this experiment (7000 mg/m³), however, the 10% attenuation is expected to be an upper bound estimate. Thus, it is unlikely that signal trapping is a significant source of bias or variability in the LII measurements.
5.5 Response Surface Model

Each LII image acquired was digitally processed to enhance its quality and to extract a value to represent the level of soot detected. Then, following the steps described in Section 4.4, a set of response functions was generated.

5.5.1 Digital Image Processing

All LII images were processed in four steps.

In the first step, each raw LII image was corrected for background noise (variations in the camera dark-current intensity). As dark-current intensity was a function of CCD temperature, it was subjected to variability in the temperature of the ambient air used for camera cooling. To account for this variability, a background image was taken prior to any collection of LII data. This background image was then subtracted from the LII images acquired in the experiments.

Secondly, a threshold was applied to each image. This was necessary to ensure all background noise was completely removed from the LII images. There was a risk involved in thresholding the images: information from the combustion process could be lost, particularly if a large region of low density soot was present. In order to prevent any significant loss of information, a suitable (and constant) threshold level was determined after visually inspecting all LII images.

Thirdly, a spatially averaged LII signal was determined for each thresholded image. Instead of averaging the pixel intensities over the entire field of view, a selective averaging method was used. The concept of this method is shown in Equation (5.1).

\[
\text{Average Signal} = \frac{\text{Sum of Thresholded LII Signal}}{\text{Number of Pixels with Signal Above the Threshold}} \tag{5.1}
\]
As a final step, averaged LII signals obtained from Equation (5.1) were multiplied by the calibration constant found in Section 3.4 to determine the corresponding soot concentration detected in that particular LII image. Once processed, this set of concentration data could be used as inputs to build four response functions.

5.5.2 Construction of the Response Functions

A minimum least-square regression was performed to identify the function coefficients of a second order polynomial model. Nitrogen addition, injection pressure, pre-combustion temperature, and pre-combustion pressure were used as input variables. The outputs of this regression analysis, which includes response functions, the corresponding coefficients of determination ($R^2$) and standard error of estimation ($s_{\hat{y}}(x)$), are as listed in Equation (5.2) (for 0.5 ms ASOI), Equation (5.3) (for 1.0 ms ASOI), Equation (5.4) (for 1.5 ms ASOI), Equation (5.5) (for 2.0 ms ASOI, most-soot model), and Equation (5.6) (for 2.0 ms ASOI, average-soot model).
\[ y = 3898.8 - 151.52x_1 - 36.883x_2^2 + 411.05x_3 + 113.52x_4 + 170.51x_1x_2 	ag{5.2} \]
\[ + 64.069x_1x_2 + 125.97x_1x_3 + 130.53x_1x_4 + 66.667x_2x_3 + 43.631x_2x_4 \]
\[ - 53.094x_2x_4 - 628.09x_3x_3 - 104.99x_3x_4 - 23.593x_4x_4 \]
\[ R^2 = 0.826 \quad s_{\hat{y}(x)} = 120.6 \text{mg/m}^3 \]

\[ y = 3750.2 - 95.409x_1 + 76.448x_2^2 - 16.897x_3 - 4.195x_4 + 108.71x_1x_2 \tag{5.3} \]
\[ - 13.682x_1x_2 - 26.991x_1x_3 - 63.659x_1x_4 + 141.69x_2x_2 - 54.97x_2x_3 \]
\[ + 17.955x_2x_4 - 100.61x_3x_3 - 37.139x_3x_4 - 88.706x_4x_4 \]
\[ R^2 = 0.621 \quad s_{\hat{y}(x)} = 61.2 \text{mg/m}^3 \]

\[ y = 3622.6 - 333.66x_1 + 94.471x_2^2 + 48.096x_3 + 86.121x_4 + 11.382x_1x_2 \tag{5.4} \]
\[ - 117.04x_1x_2 - 78.629x_1x_3 - 30.227x_1x_4 - 176.45x_2x_2 - 85.689x_2x_3 \]
\[ - 31.702x_2x_4 - 148.52x_3x_3 - 123.32x_3x_4 + 159.41x_4x_4 \]
\[ R^2 = 0.777 \quad s_{\hat{y}(x)} = 103.6 \text{mg/m}^3 \]

\[ y = 5623.2 - 590.8x_1 + 227.82x_2 - 188.93x_3 + 38.661x_4 + 27.23x_1x_2 \tag{5.5} \]
\[ - 29.067x_1x_2 - 234.77x_1x_3 - 212.81x_1x_4 - 165.16x_2x_2 - 181.83x_2x_3 \]
\[ + 269.71x_2x_4 - 36.745x_3x_3 + 189.77x_3x_4 + 101.8x_4x_4 \]
\[ R^2 = 0.567 \quad s_{\hat{y}(x)} = 320.3 \text{mg/m}^3 \]

\[ y = 4859.9 - 765.8x_1 + 164.49x_2 - 94.66x_3 + 177.83x_4 + 50.494x_1x_2 \tag{5.6} \]
\[ - 69.258x_1x_2 - 178.76x_1x_3 - 322.69x_1x_4 + 51.474x_2x_2 - 201.71x_2x_3 \]
\[ + 54.076x_2x_4 - 151.5x_3x_3 + 32.356x_3x_4 - 12.531x_4x_4 \]
\[ R^2 = 0.581 \quad s_{\hat{y}(x)} = 265.2 \text{mg/m}^3 \]

where \( y \) represents the model predicted soot concentration (\text{mg/m}^3) and \( x_1, x_2, x_3, \) and \( x_4 \) represent the coded form of the amount of nitrogen added to ethene, injection pressure, pre-combustion temperature, and pre-combustion pressure, respectively. It is reminded that the definition of these coded values can be found in Table 4.2.
With $R^2$ values greater than 0.5, the second order polynomial appears to be an acceptable model for building the response functions. These $R^2$ values are not high, however. The low $R^2$ values could be explained by the variability and uncertainties in the experiments and could potentially be improved by increasing the number of repeats at each test point, as mentioned in Section 5.4.

**Comparison between the Most-Soot and the Average-Soot Model:**

With two versions of response function describing the amount of soot detected at 2.0 ms ASOI, it would be beneficial to check if their behaviors would correlate with the each other. To conduct this comparison, both versions were used to predict a soot concentration at each of the 27 conditions tested. The two sets of predictions were then plotted against each other, as shown in Figure 5.8. If the two models correlate, the 27 pairs of predictions should fall close to a line that passes through the origin, and the slope of this line can be used to show that the predictions by the most-soot models are higher than those predicted by the average-soot model.

![Figure 5.8 Average-Soot Model vs. Most-Soot Model](image)

The linearity shown in Figure 5.8 implies that correlation is observed between the two models.
**Validation of the Response Functions:**

Although correlations between the most-soot and the average-soot model were observed, it would still be necessary to ensure that the predictions by these models were reasonable compared to measured data. Reliability of the response functions was investigated by comparing model predictions with additional LII measurements made at Test Point 17, 18, and 25 specified in Table 4.3; these points were selected to focus on checking the modeled effect of nitrogen addition on detected soot concentration. Nitrogen addition was tested in greater detail because its effect on soot emission was the main focus of this study. The results of this validation are shown in Figure 5.9.

![Figure 5.9 Model Validation Results](image)

(Combustion condition: injection pressure = 70 bar, pre-combustion pressure = 30 bar, pre-combustion temperature = 1300 K, nominal image acquisition time = 2.0 ms ASOI)

The response functions appear to reasonably fit the soot concentrations measured in this study. From Figure 5.9, the following observations are made:

- Agreement is observed between the validation data (shown as diamonds) and the model built from the set of most-soot model (Equation (5.5), solid line).
- When all eight measurements at each test point (three from experiment and five from validation) are considered, the average-soot model (Equation (5.6), dash line) appears to provide a reasonable fit as well.
- These observations show that the most-soot model (Equation (5.5), solid line) and the average-soot model (Equation (5.6), dash line) can respectively provide a
reasonable estimate of the amount of soot detected in a most-sooty and in an average-sooty combustion scenario.

- Further, higher soot concentrations were typically detected in the validation trial than the ones measured in the experiments, even though the test conditions were carefully replicated. With the data available, there is insufficient evidence to conclude whether the one set of data is more representative of the amount of soot detected in a typical combustion event than the other (i.e. validation data vs. experimental data); additional tests are necessary. Also, more LII measurements are needed to confirm whether the observed discrepancy between the two sets of data is due to actual physical effects or experimental variability.

With the reliability of the models established, a discussion on the trends shown by these response functions now follows. It should be noted that the following discussion is focused on results derived from Equation (5.5) (the most-soot model at 2.0 ms ASOI), unless otherwise stated. This is because the most-soot model may be more representative of combustion that lead to higher soot emissions, as discussed in Section 5.4.
5.5.3 Discussion of the Most-Soot Response Surfaces

The effects of the four combustion parameters on the amount of soot detected at 2.0 ms ASOI are illustrated by the response surfaces shown in Figure 5.10 to Figure 5.15. Additionally, contour plots derived from these response surfaces are included in the following figures to better show various trends in the results. It should be reminded that the response surfaces presented in the following discussion were derived from the most-soot model. (Note that the response surfaces derived from the average-soot model can be found in Section 5.5.6.)

When plotting the following response surfaces, two parameters were allowed to vary while the other two were fixed at their center points to individually show the effect of each parameter on detected soot concentration. While this arrangement can facilitate comparison of the trends observed in this study to the literature, it also implies the response surfaces presented in this section represent only a fraction of the results obtained in this study.
Figure 5.10 Contour Plot: Nitrogen Addition and Injection Pressure
(Pre-combustion Temperature = 1300 K, Pre-combustion Pressure = 30 bar)
Figure 5.11 Contour Plot: Nitrogen Addition and Pre-combustion Temperature (Injection Pressure = 70 bar, Pre-combustion Pressure = 30 bar)
Figure 5.12 Contour Plot: Nitrogen Addition and Pre-combustion Pressure
(Injection Pressure = 70 bar, Pre-combustion Temperature = 1300 K)
Figure 5.13 Contour Plot: Injection Pressure and Pre-combustion Temperature (% Nitrogen Addition = 10%, Pre-combustion Pressure = 30 bar)
Figure 5.14 Contour Plot: Injection Pressure and Pre-combustion Pressure (% Nitrogen Addition = 10%, Pre-combustion Temperature = 1300 K)
Figure 5.15 Contour Plot: Pre-combustion Temperature and Pre-combustion Pressure (% Nitrogen Addition = 10%, Injection Pressure = 70 bar)
**Effect of Nitrogen Addition:**

Figure 5.10, Figure 5.11, and Figure 5.12 show the estimated effect of nitrogen addition on detected soot concentration under combustion conditions with different injection pressures, pre-combustion temperatures, and pre-combustion pressures, respectively. Overall, as shown in these figures, addition of nitrogen to the fuel was observed to reduce the amount of soot detected. When the effect of nitrogen addition was considered alone (i.e., when the other parameters were held at their respective center point), a change from pure ethene to the 80% ethene/20% nitrogen mixture was observed to lower the detected soot concentration level by 19%. When the other parameters are individually added to the consideration, Figure 5.10 through Figure 5.12 indicate that the effect of fuel dilution is less sensitive to changes in injection pressure, but is more sensitive to changes in pre-combustion pressure and temperature. Specifically, from Figure 5.10, an increase in the nitrogen content in the fuel (from 0% to 20% by volume) is shown to consistently reduce soot concentration by 19% over the range of injection pressures tested. On the other hand, Figure 5.11 and Figure 5.12 show that nitrogen addition caused a greater reduction in detected soot concentration at higher pre-combustion temperature (12% at 1200 K vs. 26% at 1400 K) and lower pre-combustion pressure (12% at 35 bar vs. 24% at 25 bar).

These trends (i.e., reductions in soot due to nitrogen addition) are qualitatively consistent with those reported in previous studies conducted by Axelbaum [11], McTaggart-Cowan [12], and Gulder and Snelling [41]. As discussed in Section 2.3.2, a reduction in soot might be caused by a reduced soot formation rate and an improved late stage burn-up associated with an increased momentum transfer from the injection of a denser fuel mixture, a reduced availability of carbon in the combustion, and a reduced flame temperature due to fuel dilution.

The trends observed from Figure 5.10 to Figure 5.12 were based on information collected at 2.0 ms ASOI. In order to assess the effect of nitrogen addition on detected soot concentration during the earlier stages of the combustion process, Equation (5.2), (5.3), and (5.4) were used to describe the measurements made at 0.5 ms, 1.0 ms, and 1.5 ms. Based on these response functions, the effect of nitrogen addition to ethene on the
detected soot concentration over first three time bins could be determined. A case of 0% and 20% nitrogen addition (by volume) was considered. When generating Figure 5.16, the other three parameters were set to their center point value to prevent them from affecting the estimates. The results are shown in the following figure.

![Figure 5.16 Effect of Nitrogen Addition to Ethene over Time (Response Prediction)](image)

As shown, the models predict that nitrogen addition could lead to less soot being detected over the period of time considered. Based on this trend, it is possible that soot formation rate is reduced in combustion of the nitrogen-diluted fuel, perhaps due to a reduction in combustion temperature, a reduction in the amount of carbon present in the combustion process, and a change to the overall fuel/oxidizer ratio, as discussed in Section 2.3.2. Also, the addition of nitrogen appears to cause a relatively greater reduction in soot concentration at 1.5 ms ASOI, compared to the earlier timings. This trend suggests that a more complete combustion and an improved soot oxidation might be achieved for the nitrogen-diluted fuel; as discussed, these effects might be caused by an increased turbulence associated with injecting a higher density fuel mixture. More experiments are recommended to experimentally investigate the influence of fuel dilution on flame temperature and to verify the statistical significance of the trends shown in Figure 5.16.
**Effect of Pre-combustion Temperature:**

Figure 5.11, Figure 5.13, and Figure 5.15 show the estimated effect of pre-combustion temperature on the amount of soot detected within a fuel jet burning at different fuel compositions, injection pressures, and pre-combustion pressures, respectively. When the effect of pre-combustion temperature was considered alone (i.e. when the other parameters were held at their respective center point), an increase from 1200 K to 1400 K was observed to decrease soot concentration by 7%. Interestingly, when the other parameters are individually added to the consideration, these surface plots show that the effect of pre-combustion temperature on detected soot levels is more pronounced under certain conditions. Specifically, from Figure 5.11, for combustion of the diluted fuel (20% nitrogen), it is observed that an increase in pre-combustion temperature (1200 K to 1400 K) can lead to a 16% reduction in detected soot concentration, whereas the effect of temperature is not obvious in the combustion of pure ethene. Similarly, Figure 5.13 and Figure 5.15 respectively show that at low injection pressure (60 bar) and pre-combustion pressure (25 bar), the effect of increasing pre-combustion temperature (from 1200 K to 1400 K) is unnoticeable; however, its effect is more apparent at higher injection pressure (12% reduction at 80 bar) and pre-combustion pressure (13% reduction at 35 bar). In summary, these figures show that an increase in pre-combustion temperature causes a greater reduction in soot concentration when the levels of nitrogen addition, injection pressure, and pre-combustion pressure are high.

Qualitatively, the reductions in soot concentration associated with increases in pre-combustion temperature are expected. As discussed in Section 2.3.3, a high temperature may hinder the process of soot formation (by inhibiting PAH growth) and promote soot oxidation. These effects might explain the reductions estimated in these figures.
Effect of Pre-combustion Pressure:

Figure 5.12, Figure 5.14, and Figure 5.15 show the estimated effect of pre-combustion pressure on the amount of soot detected within a fuel jet burning at different fuel compositions, injection pressures, and pre-combustion temperatures, respectively. Among the four parameters examined in this study, the effect of pre-combustion pressure appears to be the most sensitive to changes in combustion conditions. Figure 5.12 shows that for combustion of the 20% nitrogen diluted fuel, a reduction in pre-combustion pressure (35 bar to 25 bar) is found to decrease the observed soot level by 7%, while for combustion of pure ethene, an 8% increase in soot concentration is observed. Likewise, Figure 5.14 and Figure 5.15 show that a decrease in pre-combustion pressure (35 bar to 25 bar) can reduce the detected soot levels at low injection pressure (by 8% at 60 bar) and pre-combustion temperature (by 5% at 1200 K); however, the same decrease in pre-combustion pressure is shown to raise the detected soot concentrations by 11% and 9% at high injection pressure (80 bar) and pre-combustion temperature (1400 K), respectively.

These alternating behaviors and the increases observed may be unexpected. Typically, with decreasing ambient pressures, the amount of soot detected in non-premixed gaseous fuel combustion should decrease rather than increase [49] [51] [52]. This is because an decrease in ambient pressure may decrease the reaction rates of soot formation; subsequently, as less soot is present at higher pressures, radiative cooling should be reduced, which may result in a hotter flame temperature to promote soot oxidation [51] [52]. Note that a possible explanation that addresses these unexpected and alternating trends will be suggested later in this section.
Effect of Injection Pressure:

Figure 5.10, Figure 5.13, and Figure 5.14 show the estimated effect of injection pressure on the amount of soot concentration detected within a fuel jet burning at different fuel compositions, pre-combustion temperatures, and pre-combustion pressures. When the effect of injection pressure was considered alone (i.e. when the other parameters were held at their respective center point), a decrease in injection pressure from 80 bar to 60 bar was found to reduce the detected soot concentration level by 8%. When the other parameters are individually added to the consideration, these figures indicate that the effect of injection pressure on the amount of soot detected is less sensitive to fuel composition, but is more sensitive to changes in pre-combustion pressure and temperature. Specifically, as shown in Figure 5.10, for all fuel compositions, a consistent 8% reduction in soot concentration is observed as injection pressure is decreased (80 bar to 60 bar). On the other hand, Figure 5.13 and Figure 5.14 respectively show that at high pre-combustion temperature (1400 K) and pre-combustion pressure (35 bar), the effect of decreasing injection pressure (80 bar to 60 bar) is not as apparent as the ones observed low pre-combustion temperature (14% reduction at 1200 K) and pre-combustion pressure (16% reduction at 25 bar).

The trends shown in these figures are unexpected. Decreases in injection pressure should typically lead to an increase in soot and vice versa. According to the discussion in Section 2.3.3, as injection pressure increases, the density of the injected fuel mixture should also be increased. Intuitively, it is expected that the increase in turbulence transfer associated with the injection of a denser fuel should improve air-fuel mixing and thus reduce soot formation by promoting a more complete combustion. Thus, the estimated reductions in soot associated with decreases in injection pressure may be unexpected. A possible explanation to this unexpected trend is suggested in the following discussion.
Other Effects Associated with Changes in Injection and Pre-combustion Pressure:

Considering the various strategies for soot reduction discussed in Section 2.3.3, the effects of injection pressure and pre-combustion pressure shown by the response surfaces appear counterintuitive. Is there another factor that can affect soot formation but has not been considered? One possibility is the changes in overall and local air fuel ratio (AFR) associated with changes in the two pressures. As mentioned, soot formation is favored under fuel rich combustion conditions. Thus, it is possible that changes in these pressures can create a richer combustion environment that promotes soot formation. To evaluate this possibility, the effect of these two pressures on both overall and local AFR is briefly discussed in this section.

To calculate an overall AFR, fuel flow rates (on a mass/injection basis) were determined for the range of injection pressures and pre-combustion pressures tested in this study; also, the mass of air in the combustion zone was calculated based on the air pressure filled in the driven section at the beginning of each experiment. The details of these calculations can be found in Appendix F. The results are shown in the following three graphs, which represent the three levels of pre-combustion temperature tested in this study. (A different overall AFR is observed at different pre-combustion temperature because the amount of air filled into the shock tube was a parameter that controlled the pre-combustion temperature achieved in a particular experiment.)
The interaction between overall AFR and the two pressures shown in Figure 5.17 is the same as the one suggested in Section 2.3.3: at constant pre-combustion pressure, an increase in injection pressure results in a richer overall AFR; on the other hand, at constant injection pressure, an increase in pre-combustion pressure results in a leaner overall AFR. Also, as shown in Figure 5.17, changes in the two pressures can affect overall AFR by up to a factor of approximately two. Thus, from Figure 5.17, a connection between injection pressure, pre-combustion pressure, and overall AFR is observed.

As combustion is a local phenomenon, knowledge of the effect of injection pressure and pre-combustion pressure on local AFR is desirable. To further this investigation, a mean centerline AFR was determined for each experiment at the time when ignition began. (As its name suggests, this parameter represents the average AFR along the centerline of a fuel jet). This calculation was carried out using a parameter scaling model developed by Sullivan et al. [117]. Details of this calculation can be found in Appendix F.
sample of the calculated results is summarized in Figure 5.18 (the rest of the results are provided in Appendix F).

![Figure 5.18 Mean Centerline AFR](image)

Figure 5.18 Mean Centerline AFR

Figure 5.18 shows that changes in either injection pressure or pre-combustion pressure can affect the mean centerline AFR. Also, Figure 5.18 is observed to show similar qualitative trends as those shown in Figure 5.17. For example, both the overall AFR (Figure 5.17) and the locally averaged AFR (Figure 5.18) are richest at a pre-combustion pressure of 80 bar and an injection pressure of 25 bar.

Another feature is observed when Figure 5.17 and Figure 5.18 are compared. From Figure 5.17, the AFR inside the shock tube is observed to be overall lean; from Figure 5.18, however, the AFR on the centerline of the fuel jet is observed to be rich. This characteristic is typical for non-premixed combustion, in which the air-fuel mixture is expected to be rich in the fuel jet and lean overall.

Interestingly, a connection is observed between the trends in AFR and the amount of soot detected in this study. For example, the conditions at which the mean centerline and overall AFR was richest matched the conditions at which the highest soot concentration was recorded. This connection suggests that AFR is a possible factor in controlling the amount of soot formed. Since AFR (both overall and local) have been shown to be influenced by injection pressure and pre-combustion pressure, this connection further
suggests that AFR may be a factor contributing to the mixed and unexpected effect of the two pressures on soot formation.

Changes in AFR might also be responsible for the non-monotonic trends observed in some of the response surfaces. For example, as discussed in Section 2.3.3, an increase in injection pressure should improve turbulent mixing of the gaseous jet, which should reduce soot formation; however, from Figure 5.13, it was observed that raising the injection pressure actually first increased the level of soot detected before it caused any reductions. Changes in AFR may be a possible explanation for this trend. As injection pressure was initially increased, local and overall AFR might become richer to cause an increase in the observed soot level. As injection pressure was increased further, however, improved turbulent mixing might dominate over the effect of AFR to cause the reduction observed in the response surface.

It should be noted that this discussion is only based on simplified estimates of the overall and mean centerline AFR. As combustion is a highly localized and complex phenomenon, a more detailed investigation (perhaps through computational fluid dynamics (CFD) modeling) is recommended.

**Limitations in Experimental Results:**
The results presented in the previous discussion are subjected to the following limitations:

- These results only represent the amount of soot detected during the combustion process. Because soot oxidation effects late in the combustion process (beyond the time frame studied) were not considered, the soot concentrations observed in this study may not correlate with the actual concentration of soot emitted as exhaust.

- The LII signals obtained in this study may not be representative of the actual soot concentration within the entire fuel jet as only a small fraction of the total volume in the combustion zone was sampled by the thin laser sheet.
5.5.4 Residual Analysis

To check for outliers and evaluate the effectiveness of the response function, predictions from the model were compared against experimental data, and the resulting residuals were standardized and plotted against model predictions. The results are shown in Figure 5.19. As shown, these residuals are randomly scattered about zero, indicating that the second order polynomial model was appropriate for fitting the data gathered in this study.

Moreover, Figure 5.19 shows that the four response functions built in this study have similar residuals, regardless of when the LII images were acquired. This means that the use of four response functions to implicitly demonstrate the effect of time on detected soot level is adequate. This is because if any trend is observed when comparing the four sets of residuals (such as when the residuals are particularly lower for a certain time bin),
the response function may need modifications to improve model fit by accounting for the effect of time explicitly.

Additionally, the residuals were plotted against the four independent variables tested in this study (i.e. nitrogen addition, \( P_n \), \( T_0 \), and \( P_0 \)) as well as variations in ignition delay to show if these parameters could influence the effectiveness of the model; the results are presented in Figure 5.20 and Figure 5.21, respectively. When generating the four plots in Figure 5.20, only one parameter was allowed to vary while the other three were held constant at the center point. Given the limited amount of data available, no statistically significant trends are observed from either Figure 5.20 or Figure 5.21 (i.e. the residuals are not significantly lower for a certain variable or at a certain variable level), although more data points may be needed to confirm this observation. This suggests that the model is effective in presenting the data collected from the experiments (i.e. the model is not biased towards describing a certain trend).

The residuals presented in Figure 5.20 and Figure 5.21 are observed to be mostly negative. This is because these residuals are obtained from comparing between the soot concentrations predicted by the most-soot model to those actually measured. As the most-soot model typically predicts a soot concentration higher than the average, this explains the negative residuals observed in these figures.
Figure 5.20 Effect of Fuel Dilution, $P_i$, $T_{co}$, and $P_o$ on Residuals

Figure 5.21 Effect of Variations in Ignition Delay on Residuals
5.5.5 Significance of Parameters

A $t$-statistic was calculated for each parameter to show its significance in the model. Variables that are more influential in the model have higher $t$-statistic values than the less-influential variables. The results are shown in Figure 5.22, which indicates nitrogen addition is the most influential parameter in estimating the detected soot concentration levels (excluding the constant of regression, which was not considered as a parameter in the model). Also, note that some of the interaction effects between variables (e.g. $x_1x_3$) were as influential as the main effects considered in the model (e.g. $x_2$). This observation confirms the need to account for the interaction effects between the variables tested in this study and justifies the use of RSM to design this experiment.

![Figure 5.22 T-statistic for Model Parameters](image-url)
5.5.6 **Comparison of the Most-Soot Model to Other Models**

The response surfaces derived from the average-soot model are presented in Figure 5.23 through Figure 5.28. As discussed in Section 5.4, the average-soot model was an alternate approach to describe the data collected in this experiment.

Note that in the following figures, an additional set of response surfaces (labeled as “random-model”) are shown as well. The “random-model” (Equation (5.7)) was constructed using the average of the six images obtained at each test condition as input data (regardless of when the images were acquired) – unlike the average-soot model, in which only the three images taken at 2.0 ms ASOI were averaged and used as inputs. Although this averaging technique has taken away the temporal resolution captured in the experimental results, it has enabled the random-model to show trends that are more general than the other two (i.e. the random-model can possibly be used to describe soot concentration levels detected at random times during a given combustion process).

\[
y = 4308.7 - 479.67x_1 + 104.58x_2 + 26.378x_3 + 121.49x_4 + 73.68x_1x_1 \\
- 45.739x_1x_2 - 85.987x_1x_3 - 155.24x_1x_4 + 31.054x_2x_2 - 117.03x_2x_3 \\
+ 15.898x_2x_4 - 221.95x_3x_3 - 15.684x_3x_4 + 1.5878x_4x_4
\]  

\[
R^2 = 0.555 \quad s. = 147.4mg / m^3
\]  

In the following discussion, the response surfaces derived from the most-soot model are compared to both the average-soot and random-model. The purpose of this comparison is to further evaluate the correlation between the most-soot and average-soot model. Additionally, the most-soot model is compared against the random-model in order to consider the robustness in its predictions (i.e. whether the most-soot model can reasonably estimate soot concentration levels at times other than 2.0 ms ASOI for a given condition). To facilitate this comparison, a set of contour plots are derived from the three models and can be found in Figure 5.23 through Figure 5.28. Also, note that the response surfaces of the most-soot model are repeated in the following figures for convenience.
Figure 5.23 Response Surface Comparison Based on Nitrogen Addition and $P_i$

(Top left: most-soot model  Top right: average-soot model)
(Center: random-soot model  Bottom: contour plot)
(Pre-combustion Temperature = 1300 K, Pre-combustion Pressure = 30 bar)
Figure 5.24 Response Surface Comparison Based on Nitrogen Addition and $T_o$,
(Top left: most-soot model  Top right: average-soot model)
(Center: random-soot model  Bottom: contour plot)
(Injection Pressure = 70 bar, Pre-combustion Pressure = 30 bar)
Figure 5.25 Response Surface Comparison Based on Nitrogen Addition and $P_0$ (Injection Pressure = 70 bar, Pre-combustion Temperature = 1300 K)

(Top left: most-soot model  Top right: average-soot model)
(Center: random-soot model  Bottom: contour plot)
Figure 5.26 Response Surface Comparison Based on $P_i$ and $T_o$
(Top left: most-soot model        Top right: average-soot model)
(Center: random-soot model        Bottom: contour plot)
(% Nitrogen Addition = 10%, Pre-combustion Pressure = 30 bar)
Figure 5.27 Response Surface Comparison Based on $P_i$ and $P_o$
(Top left: most-soot model  Top right: average-soot model)
(Center: random-soot model  Bottom: contour plot)
(% Nitrogen Addition = 10%, Pre-combustion Temperature = 1300 K)
Figure 5.28 Response Surface Comparison Based on $T_0$ and $P_0$
(Top left: most-soot model  Top right: average-soot model)
(Center: random-soot model  Bottom: contour plot)
(% Nitrogen Addition = 10%, Injection Pressure = 70 bar)
The following observations were made from the comparison of the three response functions:

- All three response functions (most-soot, average-soot, and random) generated similar response surfaces whenever nitrogen addition was plotted as an independent axis. This can be observed by comparing the response surfaces presented in Figure 5.23 through Figure 5.25. It can also be shown by the similar trends observed along a particular set of iso-contour lines presented in these figures (e.g. in Figure 5.23, for the \( P_i = 60 \text{ bar} \) case, the solid, dash, and dash-dot line all display similar trends). This observation indicates that nitrogen addition was perhaps a more influential parameter than the others (i.e. \( P_i, T_0, \) and \( P_0 \)) in the sense that it was capable of causing three separately derived models to show the same trends. This observation confirms the findings of the significance test conducted in Section 5.5.5.

- Since the most-soot, average-soot and random-model all show similar trends, it appears that the observed trends are insensitive to how the experimental data was interpreted. Thus, the most-soot model is expected to provide a reasonable estimate of the effect of nitrogen addition on the detected soot concentration level, at least on a qualitative basis.

- Less similar trends were observed from the other response surfaces (those without nitrogen addition plotted as an independent axis). Referring to the results of the significance test, this observation might be caused by the lower influence of these parameters (i.e. \( P_i, T_0, \) and \( P_0 \)) on the response functions. Given the data available, it remains undetermined whether a particular model is superior to the other two in describing the effects of \( P_i, T_0, \) and \( P_0 \) on soot concentration; additional validations are necessary.

Similar to the analysis presented in Section 5.5.5, a \( t \)-statistic was calculated for each parameter in the random-model to determine its influence. The results are shown in Figure 5.29. They are also repeated in Table 5.1 to highlight any changes in the \( t \)-statistic of each parameter among the three response functions (i.e. most-soot, average-soot, and random-model). As mentioned in Section 4.4.4, for a system with 12 degrees of freedom,
any parameter that has a t-statistic higher than 2.179 is considered as influential at a 95% confidence level.

From Figure 5.29, the effect of nitrogen addition is observed to have the highest level of significance among all the parameters considered. Also, from Table 5.1, nitrogen addition and other parameters such as $P_0$ and $P_1T_0$ are found to be more influential in the random-model than in the average-soot and most-soot model. However, not all parameters are more influential in the random-model; there are some parameters in Table 5.1 (e.g. $T_0$ and $N_2T_0$) that have a lower significance level in the random-model than in the most-soot model.

This change in significance level may be caused by the increase in the number of measurements used to generate a response function (i.e. the most-soot model was constructed from one LII measurement collected at each test condition whereas the average-model and random-model was built from the average of three and six measurements, respectively). As the sample size increases, its average may converge to a more statistically representative value or it may reveal that a particular parameter does not have an actual significant effect on the response function, which may respectively result in either an increase or a reduction in the significance level of that parameter. However, with the limited data available, the effect of sample size on the influence of each parameter suggested in this discussion could not be verified. Additional experiments are needed.
Table 5.1 T-statistics for the Most-Soot, Average-Soot, and Random-Model

<table>
<thead>
<tr>
<th>Parameter Definition</th>
<th>Most</th>
<th>Average</th>
<th>Random</th>
</tr>
</thead>
<tbody>
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<td>Constant</td>
<td>17.558</td>
<td>18.325</td>
<td>29.237</td>
</tr>
<tr>
<td>X1=N&lt;sub&gt;2&lt;/sub&gt;</td>
<td>2.884</td>
<td>4.515</td>
<td>5.089</td>
</tr>
<tr>
<td>X2=P&lt;sub&gt;i&lt;/sub&gt;</td>
<td>1.112</td>
<td>0.970</td>
<td>1.110</td>
</tr>
<tr>
<td>X3=T&lt;sub&gt;0&lt;/sub&gt;</td>
<td>0.922</td>
<td>0.558</td>
<td>0.280</td>
</tr>
<tr>
<td>X4=P&lt;sub&gt;0&lt;/sub&gt;</td>
<td>0.189</td>
<td>1.048</td>
<td>1.289</td>
</tr>
<tr>
<td>X1X1=N&lt;sub&gt;2&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.050</td>
<td>0.113</td>
<td>0.295</td>
</tr>
<tr>
<td>X1X2=N&lt;sub&gt;2&lt;/sub&gt;P&lt;sub&gt;i&lt;/sub&gt;</td>
<td>0.134</td>
<td>0.385</td>
<td>0.457</td>
</tr>
<tr>
<td>X1X3=N&lt;sub&gt;2&lt;/sub&gt;T&lt;sub&gt;0&lt;/sub&gt;</td>
<td>1.081</td>
<td>0.994</td>
<td>0.860</td>
</tr>
<tr>
<td>X1X4=N&lt;sub&gt;2&lt;/sub&gt;P&lt;sub&gt;0&lt;/sub&gt;</td>
<td>0.979</td>
<td>1.794</td>
<td>1.553</td>
</tr>
<tr>
<td>X2X2=P&lt;sub&gt;i&lt;/sub&gt;P&lt;sub&gt;i&lt;/sub&gt;</td>
<td>0.305</td>
<td>0.115</td>
<td>0.125</td>
</tr>
<tr>
<td>X2X3=P&lt;sub&gt;i&lt;/sub&gt;T&lt;sub&gt;0&lt;/sub&gt;</td>
<td>0.837</td>
<td>1.121</td>
<td>1.171</td>
</tr>
<tr>
<td>X2X4=P&lt;sub&gt;i&lt;/sub&gt;P&lt;sub&gt;0&lt;/sub&gt;</td>
<td>1.241</td>
<td>0.301</td>
<td>0.159</td>
</tr>
<tr>
<td>X3X3=T&lt;sub&gt;0&lt;/sub&gt;T&lt;sub&gt;0&lt;/sub&gt;</td>
<td>0.068</td>
<td>0.338</td>
<td>0.890</td>
</tr>
<tr>
<td>X3X4=T&lt;sub&gt;0&lt;/sub&gt;P&lt;sub&gt;0&lt;/sub&gt;</td>
<td>0.873</td>
<td>0.180</td>
<td>0.157</td>
</tr>
<tr>
<td>X4X4=P&lt;sub&gt;0&lt;/sub&gt;P&lt;sub&gt;0&lt;/sub&gt;</td>
<td>0.188</td>
<td>0.028</td>
<td>0.006</td>
</tr>
</tbody>
</table>

5.6 Conclusions

A set of shock tube experiments was conducted to study the effects of ethene dilution with nitrogen on the soot concentration detected within a combusting fuel jet under various engine-relevant conditions. Two sets of response functions were built to describe the data collected in this experiment, with one (Equation (5.5)) using the maximum soot concentration and the other (Equation (5.6)) using the averaged soot concentration detected at each test point as input data. These two functions were validated by
additional experiments at several selected test conditions. Agreement between the predicted response and measured results was observed and these two functions demonstrated their ability to provide a reasonable estimate of the amount of soot detected in either a “worst-case” or an “average” combustion scenario. A summary of the observations made from the most-soot model is as follows:

1. When fuel composition was changed from ethene to a mixture of 80% ethene/20% nitrogen (by volume), a reduction in soot concentration was observed. In addition, it was observed that the effect of fuel dilution on the amount of soot detected within a combusting fuel jet was relatively insensitive to changes in injection pressure, but was more sensitive to changes in pre-combustion pressure and temperature. Moreover, compared to the other parameters studied (injection pressure, pre-combustion temperature, and pre-combustion pressure), nitrogen addition was found to be the most influential factor concerning the estimated soot concentration within a burning jet.

2. When pre-combustion temperature was increased from 1200 K to 1400 K, a reduction in soot concentration was measured. This observation may be the result of reduced soot formation and enhanced oxidation at high ambient temperatures.

3. Decreasing the fuel injection pressure from 80 bar to 60 bar was observed to decrease the amount of soot detected. Although unexpected, this observation may be explained by a secondary factor that can affect soot formation; a possible candidate for this secondary factor is AFR.

4. Changes in pre-combustion pressure show mixed effects on the level of soot detected. Based on the response surfaces presented, a reduction in pre-combustion pressure (from 35 bar to 25 bar) can either increase or decrease the observed soot concentration, depending on the condition considered. Although these alternating trends were unexpected, they further suggested that changes to pre-combustion pressure might induce changes in other variables that could affect soot formation, such as local AFR.
5.7 Recommendations

1. The results of this study show the addition of nitrogen can reduce soot formation rate in the early stages of combustion. The cause of this reduction is not determined, although it may possibly be caused by a lower flame temperature in the combustion of diluted fuel. It is recommended that flame temperature be measured in future experiments to validate this concept. One possible technique for measuring flame temperature is two-color pyrometry.

2. The lower soot concentration detected during the later stages of combustion supports the suggestion to an improved soot burnout associated with adding nitrogen to the fuel. However, this rationale has not been formally confirmed in this study. Thus, this study suggests that soot burnout be investigated in greater detail in future experiments. One possible technique is the use of laser induced fluorescence to detect the presence of OH radical within the combustion zone. This is because the presence of OH radical can indicate the availability of a soot oxidizing environment.

3. It will be beneficial to further investigate the effect of fuel injection pressures and pre-combustion pressures on local AFR and soot formation. This may be done through CFD simulation and combustion modeling.
6.0 SUMMARY AND RECOMMENDATIONS

The effects of nitrogen addition to ethene, fuel injection pressure, pre-combustion temperature, and pre-combustion pressure on soot formation have been studied under engine-relevant conditions using laser induced incandescence (LII).

Chapter 2 provided an introduction to soot and LII. The process of soot formation and various principles for reducing soot emission were discussed. Also, a comparison between LII and other soot diagnostic techniques was presented, followed by a discussion on the theory behind LII.

Chapter 3 presented the calibration procedures performed to establish a quantitative relationship between LII signal intensity and soot mass concentration within the measurement region. Two sources of soot particles and three different setups were used in this calibration and all yielded the same result. This relationship is repeated in Equation (6.1).

\[ \text{Soot Concentration (mg/m}^3\text{)} = \text{LII Signal (counts)} \times 0.52 \]  \hspace{1cm} (6.1)

Chapter 4 discussed the use of response surface methodology to design a test matrix for this study. It also outlined the procedures for generating a set of response functions to estimate soot concentration for any combustion conditions defined within the experimental space.

Chapter 5 presented the experiments performed to study the effects of nitrogen addition, fuel injection pressure, pre-combustion temperature, and pre-combustion pressure on soot emissions. Soot mass concentration was measured using LII. Based on the experimental results, a set of response functions was built. A validation was performed to ensure the trends predicted by these empirically-fitted models agreed with additional measured data.
Using these models, a series of response surfaces were plotted and the following observations were made:

1. Changing the fuel composition from pure ethene to a mixture of 80% ethene/20% nitrogen (by volume) was observed to reduce soot. Results from this study also showed that a consistently lower soot concentration was detected temporally throughout the combustion process of the diluted fuel; this observation suggested that fuel dilution with nitrogen could potentially inhibit soot formation and improve late-stage combustion process by lowering combustion temperature, lowering the presence of carbon in the combustion, changing the overall fuel/oxidizer ratio, and increasing turbulent mixing through the injection of a denser fuel. Moreover, among the four variables tested in this research, the effect of nitrogen addition was found to be the most influential.

2. Increasing the pre-combustion temperature from 1200 K to 1400 K was observed to reduce soot concentration levels.

3. Decreasing the fuel injection pressure from 80 bar to 60 bar was found to reduce soot concentration levels. This observation is unexpected; results suggested that this reduction might be caused by the changes in both the overall and local air fuel ratio associated with changes in injection pressure.

4. Depending on the actual combustion condition considered, reducing pre-combustion pressure (from 35 bar to 25 bar) can either increase or decrease soot, depending on the exact condition considered. This alternating behavior further suggested that soot formation and oxidation might be affected by changes in overall and local AFR associated with changes in pre-combustion pressure (and injection pressure).

All the objectives set for this study were achieved. First, a quantitative relationship between LII signal and soot concentration was established through a LII system calibration. Secondly, response surface methodology was applied to design the experiment performed in this study and to analyze the results collected. Finally, the potential of using nitrogen as a fuel additive to achieve cleaner combustion was investigated.
Based on the observations made in this study, the following recommendations for future LII and soot emission research have emerged:

1. Given the variable nature of combustion, ideally, a large number of measurements should be obtained under each test condition to generate a statistically representative result. However, this is not possible for shock tube experiments as the study would become impractically time consuming. It is recommended, therefore, in place of the shock tube, future LII experiments be performed with a combustion device capable of generating a large quantity of data within a short period of time, such as an optical engine. The larger dataset should account for the effect of shot-to-shot variability observed.

2. It is recommended that future studies be performed at higher pre-combustion pressures to more closely replicate the combustion conditions found in current production engines. This is another reason to suggest a new combustion apparatus for future LII experiments as the maximum pre-combustion pressure tested in this study was limited to 35 bar by the physical design of the shock tube.

3. Also, future experiments should consider testing at higher fuel injection pressures and with fuel blends that are more commonly used by production engines, such as methane, methane/nitrogen, and methane/hydrogen.

4. It will be worthwhile to explore the use of LII for primary particle size measurements. A possible starting point would be to perform point-wise LII measurements on an ethene/nitrogen diffusion flame. This may provide an opportunity to examine the effect of fuel dilution on soot formation in greater detail.
REFERENCES


103


[95] Matter Engineering AG. *Preliminary Data Sheet, SKM 04127-15a.* 2004


APPENDIX A AETHALOMETER CORRECTION

As discussed within the main text, the use of the Aethalometer was complicated by the following effects:

- Scattering effect: "the enhanced light absorption across the filter due to multiple scattering at the fibers of a clean filter" [1].
- Shadowing effect: "the increased underestimation of black carbon as the filter is loaded" [1].

Due to these effects, the measured BC mass concentration was observed to decrease with time even when the actual concentration in the gas sample had remained constant. Thus, the data from the Aethalometer must be corrected before it could be of any use.

To correct the results, two factors were applied to the measured BC mass concentration, as shown in Equation (A.1).

\[ M_{BC,ACTUAL} = \frac{M_{BC,MEASURED}}{C[R(ATN)]} \]  

where \( M_{BC,ACTUAL} \) is the actual soot mass concentration present in the flow of interest, \( M_{BC,MEASURED} \) is the concentration measured by the Aethalometer, \( C \) is a calibration constant applied to the measured concentration to compensate for the Scattering effect, and \( R(ATN) \) is a calibration constant applied to compensate for the Shadowing effect [1].

A.1 Determination of \( M_{BC,MEASURED} \)

From the output of the Aethalometer, an attenuation coefficient can be determined. Attenuation coefficient is defined as:

\[ b_{ATN} = \frac{[A\Delta ATN]}{[Q\Delta t]} \]  

(\[A\Delta ATN] [Q\Delta t])
where $A$ is the cross sectional area of the sample spot on the filter (0.5 cm$^2$), $\Delta ATN$ is the incremental attenuation between two measurements, $Q$ is the flow rate set at the Aethalometer, and $\Delta t$ is the time between two measurements.

The measured BC mass concentration is related to the attenuation coefficient by:

$$M_{BC,\text{MEASURED}} = \frac{b_{ATN}}{\sigma_{ATN}}$$  \hspace{1cm} (A.3)

where $\sigma_{ATN}$ is 16.6 m$^2$/g for the Aethalometer used in this study.

### A.2 Determination of $C$ and $R(\text{ATN})$

The value of the Scattering correction factor ‘$C$’ was found to equal 2.09.

In Equation (A.1), $R(\text{ATN})$ is defined as:

$$R(\text{ATN}) = 1 - \frac{f - 1}{f} \left[ \frac{\ln(\text{ATN}) - \ln(10\%)}{\ln(50\%) - \ln(10\%)} \right]$$  \hspace{1cm} (A.4)

where $f$ is a correction factor that must be calculated for each Aethalometer measurement trial and $\text{ATN}$ is the attenuation across the filter at the time the reading was made. The value of $\text{ATN}$ can be found in the data output from the Aethalometer.

To calculate the value of $f$, the measured BC mass concentration found in Equation (A.3) were plotted against $\ln(\text{ATN})$, as shown in Figure A.1.
From this plot, a linear regression was performed to determine the slope and intercept of the best fit line through these data points. Based on the slope and intercept found, the value of $f$ is given by:

$$f = \frac{(0.62 \text{ Intercept}) + (1.44 \text{ Slope})}{(0.62 \text{ Intercept}) + (2.44 \text{ Slope})} \quad (A.5)$$

A.3 Results

In this study, three correction trials were performed using a PDF as the source of soot particles. During each trial, a gas stream with a constant BC concentration was passed through the Aethalometer for five minutes to generate six readings. With this set-up, the measured BC concentration should remain constant with time.

The uncorrected Aethalometer results are shown in Figure A.2. As expected, due to the Scattering and Shadowing effects, the measured BC mass concentrations were erroneously decreasing with time.
The corrected Aethalometer results are shown in Figure A.3. As expected, this correction procedure flattened out the data. The results of this correction were satisfactory because, with the steady source of soot used in this study, the measured BC concentration should be constant with time.
Also, the corrected BC mass concentration was approximately an order of magnitude higher than the uncorrected value. Similar observations were made when a GAG replaced the PDF as the particle source in subsequent correction trials. Comparing the corrected concentration to the expected concentration at the GAG output, the two values were in agreement to within 20%, which was reasonable. For convenience, Table 3.6 is repeated here.

<table>
<thead>
<tr>
<th>Test</th>
<th>Quoted Concentration (mg/m³)</th>
<th>Actual Concentration (mg/m³)</th>
<th>Difference (Actual/Quoted)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>4.88</td>
<td>5.79</td>
<td>1.19</td>
</tr>
<tr>
<td>3</td>
<td>8.33</td>
<td>10.26</td>
<td>1.24</td>
</tr>
<tr>
<td>4</td>
<td>10.60</td>
<td>11.80</td>
<td>1.11</td>
</tr>
<tr>
<td>5</td>
<td>14.00</td>
<td>15.96</td>
<td>1.14</td>
</tr>
<tr>
<td>6</td>
<td>15.90</td>
<td>18.79</td>
<td>1.18</td>
</tr>
</tbody>
</table>

A.4 References

APPENDIX B ATTENUATION CORRECTION

In this study, two LII test sections were used to calibrate the system: a borosilicate tube and the shock tube optical section. As the thickness of these two media was different, an attenuation correction must be performed before the results from the different trials could be compared.

This correction was based on the Beer-Lambert Law. This law relates the transmission of light to the optical properties of the medium through which the light is traveling, as shown in Equation (B.1).

\[ \tau = \exp(-\sigma d) \]  

(B.1)

where \( \tau \) is the transmittance of the medium, \( \sigma \) is the extinction coefficient of the medium, and \( d \) is the thickness of the medium.

B.1 Methods and Results

For a 1 mm thick borosilicate sample, the optical transmittance at 400 nm is approximately 92%, as shown in Figure B.1. Using Equation (B.1), an extinction coefficient of 83.39 m\(^{-1}\) was found.

![Figure B.1 Borosilicate: Transmission Properties](Adapted from Valley Design Corp. [1])
As the actual thickness of the borosilicate tube wall was 3 mm, Equation (B.1) was used again to determine its transmittance.

\[ \tau_{\text{borosilicate}} = \exp\left[-\left(83.39 \text{m}^{-1}\right)(3e - 3m)\right] = 0.7787 \]  \hspace{1cm} (B.2)

For a 1 mm thick quartz sample, the optical transmittance at 400 nm is approximately 92%, as shown in Figure B.2. Similarly, an extinction coefficient of 83.39m$^{-1}$ was found.

![Figure B.2 General Purpose Clear Fused Quartz: Transmission Properties (Adapted from Atlas Specialty Lighting [2])](image)

As the actual thickness of the shock tube optical window was 28 mm, Equation (B.1) was used to determine its transmittance.

\[ \tau_{\text{shock}} = \exp\left[-\left(83.39 \text{m}^{-1}\right)(28e - 3m)\right] = 0.0968 \]  \hspace{1cm} (B.3)

To compare the results from the shock tube trials to the borosilicate tube trials, the observed LII signals must be scaled as follows:

\[
 LII_{\text{borosilicate}} = LII_{\text{shock}} \left(\frac{\tau_{\text{borosilicate}}}{\tau_{\text{shock}}}\right) = LII_{\text{shock}} \left(\frac{0.7787}{0.0968}\right) = LII_{\text{shock}} (8.044) \]  \hspace{1cm} (B.4)
where $LII_{borosilicate}$ is the LII signals that would have been observed if the trials were performed using the borosilicate tube and $LII_{shock}$ is the actual LII signals observed in the shock tube trials.

Using Equation (B.4), the shock tube calibration results were corrected, as shown below.

<table>
<thead>
<tr>
<th>$LII_{shock}$ (Uncorrected Values Plotted on Figure 3.6)</th>
<th>$LII_{borosilicate}$ (Corrected Values Plotted on Figure 3.6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1.05</td>
<td>8.43</td>
</tr>
<tr>
<td>2.10</td>
<td>16.87</td>
</tr>
<tr>
<td>2.63</td>
<td>21.16</td>
</tr>
<tr>
<td>3.30</td>
<td>26.54</td>
</tr>
<tr>
<td>3.73</td>
<td>29.98</td>
</tr>
<tr>
<td>4.30</td>
<td>34.61</td>
</tr>
</tbody>
</table>

B.2 References


APPENDIX C MATLAB CODES FOR DATA ANALYSIS

%******************************************************************************
%Main Program for Data Analysis
%******************************************************************************

clear all
close all
imtool close all

pt_est = zeros(3,4);

%Open the file containing information on the processed images
dip_avg=load('dip_avg.txt');
dip_avg(:,5:7)=[ ];
full_resid = zeros (27,4);

%Run the regression analysis for the four sets of data (eg 0.5, 1.0, 1.5, 2.0ms
%after SOI)
for (timing =1:4)
    if (timing ==1)
        [coeff_1, full_std_error_1, R_sq_1, full_resid_out(:,timing)]= resp_surf(timing,dip_avg);
    end
    if (timing ==2)
        [coeff_2, full_std_error_2, R_sq_2, full_resid_out(:,timing)]= resp_surf(timing,dip_avg);
    end
    if (timing ==3)
        [coeff_3, full_std_error_3, R_sq_3, full_resid_out(:,timing)]= resp_surf(timing,dip_avg);
    end
    if (timing==4)
        [coeff_4, full_std_error_4, R_sq_4, full_resid_out(:,timing)]= resp_surf(timing,dip_avg);
    end
end
% Removed Back Elimination, 2D plots
% output SST
% original saved as Full IP and DA

function [full_coeff_out, full_std_error_out, R_sq_out, full_resid_out] = resp_surf (timing, dip_avg)
% User Input
% input # of observations
obs=27;
% input # of parameters to be initially estimated
par=15;
% input coded values of x1, in ascending order of test points
X1=[-1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1];
% input coded values of x2, in ascending order of test points
X2=[-1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1];
% input coded values of x3, in ascending order of test points
X3=[-1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1];
% input coded values of x4, in ascending order of test points
X4=[-1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1];
% input results, in ascending order of test points
Y=(dip_avg(:,timing))';
% input rejection criteria for significance test: t(.025,df)
rej=[2.179 2.160 2.145 2.131 2.120 2.110 2.101 2.093 2.086 2.080 2.074 2.069 2.064 2.060 2.056 2.052];

% Prepare Raw Data for Regression
A=X1;
B=X2;
C=X3;
D=X4;
E=X1.*X1;
F=X1.*X2;
G=X1.*X3;
H=X1.*X4;
I=X2.*X2;
J=X2.*X3;
K=X2.*X4;
L=X3.*X3;
M=X3.*X4;
N=X4.*X4;
Z=[A' B' C' D' E' F' G' H' I' J' K' L' M' N' Y'];

for (i=1:par)
  for (j=1:par)
    if((i==j) & (j==1))
      hatA(i,j)=obs;
    end
  end
end
elseif((i==l) & (j>=2))
    hatA(i,j)=sum(Z(:,j-l));
elseif((i>=l) & (j==0))
    hatA(i,j)=sum(Z(:,i-l));
else
    hatA(i,j)=(Z(:,i-l))^* (Z(:,j-l));
end
end
end

for (i=1:par)
    if(i==1)
        hatB(i)=sum(Z(:,15));
    else
        hatB(i)=(Z(:,i-l))^* (Z(:,15));
    end
end
hatB=(hatB)';

%hatA * coefficient = hatB, solve for coefficient

%-------------------
%Regression with Back Elimination
%-------------------

float_index = zeros(par,1);
%a vector that records the removed indices for each iteration

track = zeros(par,1);
%a vector that records the removed indices for ALL iterations

iteration = 0;%number of iterations performed
removed=0;%number of unimportant coefficients removed
condition = 1;%activates the following while loop

while (sum(condition)>0)

    if(not(iteration ==0))
        %skips backward elimination for the first iteration to get full
        %model

        %define the rejection criteria for this iteration
        t_rej = rej(iteration);
        %t = 5;%%%added Dec 09, 2006

        condition = t<t_rej & not(t==0);
        %determines if there are any unimportant coefficient remaining in
        %the model. If no more unimportant coefficient, terminate this
        %while loop.

        index = find(t<t_rej & not(t==0));
        %locate the unimportant coefficient in the present model

    end
end

120
if(sum(index)>0)
    %if there are unimportant coefficients, then list them out
    %using the following for loop.
    [row, column] = size(index);
    for (counter = 1:column)
        to_be_removed(counter)= t(index(counter));
    end

    %find the value of the variable to be removed
    [min_t, index] = min(to_be_removed);

    %find the location of the variable to be removed
    [row, index] = find(t==min_t);

    %in case there are two t-statistics that have the same value
    if(length(index)>1)
        index(2:length(index))=[];
    end

    if (min_t<t_rej)
        removed = removed +1; %record that another term is removed
        hatA(:,index)=[]; %remove the appropriate column in hatA
        hatA(index,:)=[]; %remove the appropriate row in hatA
        hatB(index,:)=[]; %remove the appropriate row in hatB
        Z(:,index-l)=[]; %remove the raw data from Z

        %keeping track of which variable has been removed
        countdown = removed;
        countup = 0;

        %if it is the first variable to be removed
        if (removed ==1)
            track(index)=1;
            float_index(removed)=index;
        end

        %if it is the second (and up) variable to be removed
        if (removed >1)
            float_index(removed)=index;

            %compares to the previously removed variables to
            %keep track of the indices of all removed variables
            while (countdown>1)
                countdown = countdown -1;
                countup = countup + 1;
                if(index>=float_index(removed - countup))
                    index = index +1;
                else
                    track(index)=1;
                end
            end
            track(index)=1;
        end
    end
clear countdown countup;
clear X diagH prediction estimate residual residual_sq;
clear SSE df s_sq s studentized_residuals diagC t;
clear coefficient to_be_removed;
end
end

debug the value of t_rej for plotting the test for significance
debg

% keep a copy of the full model
if(iteration ==0)
   full_coefficient = coefficient';
end

% Residual Analysis

% create a matrix: X
X=ones(obs,par-removed);
for (i=1:par-removed)
   if(i==1)
      X(:,i)=1;
   else
      X(:,i)=Z(:,i-1);
   end
end

diagH = diag(X * ((X' * X)^ -1) * X');

% create a matrix: prediction for each coefficient
prediction = ones(obs,par-removed);
for (i=1:obs)
   for (j=1:par-removed)
      if(j==1)
         prediction(:,j)=coefficient(j);
      else
         prediction(i,j)=coefficient(j)*Z(i,j-1);
      end
   end
end

for (i=1:obs)
   % the sum of each prediction term becomes an estimate of the
%regression function
estimate(i)=sum(prediction(i,:));
end

for (i=1:obs)
    residual(i)=Z(i,par-removed)-estimate(i);
    %the 'par-removed' column of vector Z contains the experimental %responses 'Y'. So 'Y minus estimate' gives residual.
    residual_sq(i)=(residual(i))^2;
end

%SSE
SSE=sum(residual_sq);
df=obs-(par-removed);

%SST
SST = Y*Y'-(sum(Y))^2/obs;

%R square value
R_sq= 1-SSE/SST;

%studentized residuals
for (i=1:obs)
    studentized_resid(i)=residual(i)/s/sqrt(1-diagH(i)); %result
    studentized_resid(i)=residual(i)/s; %standardized residual
end

if (iteration == 0 | condition ==0);
    %plot only the first and last iteration
    figure()
    plot(studentized_resid, 'dk','MarkerFaceColor', 'k');
    line((0:0.01:obs+3),-3,'Color','k');
    line((0:0.01:obs+3),3,'Color','k');
    axis([0 obs+3 -4 4]);
    xlabel ('Case Number','FontWeight','bold');
    ylabel ('Standardized ResiduaIs','FontWeight','bold');
    if (iteration ==0)
        title ('Standardized Residual Plot (Full Model)','FontWeight','bold');
    end
    if (condition ==0)
        title ('Standardized Residual Plot (Reduced Model)','FontWeight','bold');
    end
end

%output the residuals for the full model
if (iteration ==0)
    temp_residual = studentized_resid;
end
end
%------------------------
%Significance Test
%------------------------

diagC = diag((X' * X)^-1);

%calculates t-values for the remaining coefficients
for (i=1:par-removed)
    t(i)=coefficient(i)/s/sqrt(diagC(i));
    t(i)=abs(t(i));
end

if (iteration ==0 | condition ==0);
    %plot only the first and last iteration
    if(condition ==0);
        %if this is the last iteration, update the vector of t-values
        %to retain the same assignment for each variable (ie. variable
        %15 will always represent x4*x4.)
        for (counter=1:par)
            if(track(counter)==0)
                t_2(counter)=t(l);
                t(i) =[];
            end
            if(track(counter)==1)
                t_2(counter)=0;
            end
        end
        clear t counter;
    t = t_2;
    clear t_2;
end

figure ()
bar ((0:par-l),t);
xlabel ('Coefficient Number (\beta_0 to \beta_{14})','FontWeight','bold');
ylabel ('Test of Significance Value','FontWeight','bold');
if (iteration ==0)
    title ('Test of Significance Plot (Full Model)\,','FontWeight','bold');
end
if (condition ==0)
    title ('Test of Significance Plot (Reduced Model)','FontWeight','bold');
end
text (2, 20, ['Coefficient Definition:']);
text (2, 18.5, ['0 = constant']);
text (2, 17, ['1 = X1 = Nitrogen Addition']);
text (2, 15.5, ['2 = X2 = Injection Pressure']);
text (2, 14, ['3 = X3 = Pre-combustion Temperature']);
text (2, 12.5, ['4 = X4 = Pre-combustion Pressure']);
text (2, 11, ['5 = X1X1, 6 = X1X2, 7 = X1X3, 8 = X1X4, 9 = X2X2']);
text (2, 9.5, ['10 = X2X3, 11 = X2X4, 12 = X3X3, 13 = X3X4, 14 = X4X4']);
ymin = min(t);
ymax = max(t);
axis([-1 par+3 ymin-5 ymax+5]);
end

%representative error at center point of full model
if(iteration ==0)
xm = [1; 0; 0; 0; 0; 0; 0; 0; 0; 0; 0; 0; 0; 0; 0; 0; 0; 0; 0; 0; 0; 0; 0; 0];
full_error = t_rej*s*sqrt((xm'*(X'*X)\-l*xm));
full_std_error = s*sqrt((xm'*(X'*X)\-l*xm));
end

iteration = iteration +1;
end

for (counter=1:par)
%update the vector of coefficients in order to retain the same
%address for each coefficient. (ie. variable 15 will always
%represent x4*x4)
if(track(counter)==0)
    coefficient_2(counter)=coefficient(1);
    coefficient(1) =[];
end
if(track(counter)== 1)
    coefficient_2(counter)=0;
end
end

clear coefficient counter;
mod_coefficient = coefficient_2;
clear coefficient_2;

%---------------------------------------
%Contour Plot (only for the 2.0ms after SOI case)
%---------------------------------------
if (timing ==4)

%Depending on the "counter" specified, either the full or the reduced
%model can be plotted

clear counter;
for (counter = 1:2);
    if (counter ==1)
        coefficient = mod_coefficient;
    end
    if (counter ==2)
        coefficient = full_coefficient;
    end

    arrow_x = [0.8 0.6];
    arrow_y = [0.6 0.4];
    analysis=zeros(36,1);
end
\begin{verbatim}
x1ia=linspace(0,20,201); \%from -1 to +1
x2ia=linspace(60,80,201); \%from -1 to +1
x3ia=linspace(1200,1400,201); \%from -1 to +1
x4ia=linspace(35,25,201); \%from -1 to +1

x1i=-1:0.01:1;
x2i=-1:0.01:1;
x3i=zeros(1,201);
x4i=zeros(1,201);

for (i=1:201)
  for (j=1:201)
    regression_x1i_x2i(i,j) =
      coefficient(1)+coefficient(2)*x1i(i)+coefficient(3)*x2i(j)+coefficient(4)*x3i(i)+coefficient(5)*x4i(i)+coefficient(6)*x1i(i)*x1i(i)+coefficient(7)*x1i(i)*x2i(j)+coefficient(8)*x1i(i)*x3i(i)+coefficient(9)*x1i(i)*x4i(i)+coefficient(10)*x2i(j)*x2i(j)+coefficient(11)*x2i(j)*x3i(i)+coefficient(12)*x2i(j)*x4i(i)+coefficient(13)*x3i(i)*x3i(i)+coefficient(14)*x3i(i)*x4i(i)+coefficient(15)*x4i(i)*x4i(i);
  end
end

figure()
[C,h]=contour(x2ia, x1ia, regression_x1i_x2i,5);
clabel(C,h);
ylabel ('% Nitrogen Addition (%)','FontWeight','bold');
xlabel ('Injection Pressure (Bar)','FontWeight','bold');

figure()
meshc(x2ia, x1ia, regression_x1i_x2i);
ylabel ({'% Nitrogen Addition (%)'},'FontWeight','bold', 'FontSize',14);
xlabel ({'Injection Pressure (Bar)'},'FontWeight','bold', 'FontSize',14);
zlabel ('Estimated Soot Concentration (mg/m^3)'),'FontWeight','bold', 'FontSize',14);
set(gcf, 'color', 'white');
view([66 20]);

clear regression_x1i_x2i;
\end{verbatim}
figure()
[C,h]=contour(x3ia, x1ia, regression_x1i_x3i,5);
clabel(C,h);
ylabel ('% Nitrogen Addition (%)','FontWeight','bold');
xlabel ('Pre-Combustion Temperature (K)';'FontWeight','bold');

figure()
[C,h]=contour(x3ia, x1ia, regression_x1i_x3i,5);
clabel(C,h);
ylabel ('% Nitrogen Addition (%)','FontWeight','bold');
xlabel ('Pre-Combustion Temperature (K)';'FontWeight','bold');

figure()
meshc(x3ia, x1ia, regression_x1i_x3i);
ylabel ('% Nitrogen Addition (%)','FontWeight','bold');
xlabel ('Pre-Combustion Temperature (K)';'FontWeight','bold');

for (i=1:201)
    for (j=1:201)
        regression_x1i_x4i(i,j)=coefficient(1)+coefficient(2)*x1i(i)+coefficient(3)*x2i(i)+coefficient(4)*x3i(i)+coefficient(5)*x4i(j)+coefficient(6)*x1i(i)*x1i(i)+coefficient(7)*x1i(i)*x2i(i)+coefficient(8)*x1i(i)*x3i(i)+coefficient(9)*x1i(i)*x4i(j)+coefficient(10)*x2i(i)*x2i(i)+coefficient(11)*x2i(i)*x3i(i)+coefficient(12)*x2i(i)*x4i(j)+coefficient(13)*x3i(i)*x3i(i)+coefficient(14)*x3i(i)*x4i(j)+coefficient(15)*x4i(j)*x4i(j);
    end
end

figure()
[C,h]=contour(x4ia, x1ia, regression_x1i_x4i,5);
clabel(C,h);
ylabel ('% Nitrogen Addition (%)','FontWeight','bold');
xlabel ('Pre-Combustion Pressure (Bar)';'FontWeight','bold');

figure()
meshc(x4ia, x1ia, regression_x1i_x4i);
ylabel ('% Nitrogen Addition (%)','FontWeight','bold');
xlabel ('Pre-Combustion Pressure (Bar)';'FontWeight','bold');

for (i=1:201)
    for (j=1:201)
        regression_x1i_x4i(i,j)=coefficient(1)+coefficient(2)*x1i(i)+coefficient(3)*x2i(i)+coefficient(4)*x3i(i)+coefficient(5)*x4i(j)+coefficient(6)*x1i(i)*x1i(i)+coefficient(7)*x1i(i)*x2i(i)+coefficient(8)*x1i(i)*x3i(i)+coefficient(9)*x1i(i)*x4i(j)+coefficient(10)*x2i(i)*x2i(i)+coefficient(11)*x2i(i)*x3i(i)+coefficient(12)*x2i(i)*x4i(j)+coefficient(13)*x3i(i)*x3i(i)+coefficient(14)*x3i(i)*x4i(j)+coefficient(15)*x4i(j)*x4i(j);
    end
end

figure()
[C,h]=contour(x4ia, x1ia, regression_x1i_x4i,5);
clabel(C,h);
ylabel ('% Nitrogen Addition (%)','FontWeight','bold');
xlabel ('Pre-Combustion Pressure (Bar)';'FontWeight','bold');
for (i=1:201)
    for (j=1:201)
        regression_x2i_x3i(i,j) = coefficient(1) + coefficient(2)*x1i(i) + coefficient(3)*x2i(i) + coefficient(4)*x3i(j) + coefficient(5)*x4i(i) + coefficient(6)*x1i(i)*x1i(i) + coefficient(7)*x1i(i)*x2i(i) + coefficient(8)*x1i(i)*x3i(j) + coefficient(9)*x1i(i)*x4i(i) + coefficient(10)*x2i(i)*x2i(i) + coefficient(11)*x2i(i)*x3i(j) + coefficient(12)*x2i(i)*x4i(i) + coefficient(13)*x3i(j)*x3i(j) + coefficient(14)*x3i(j)*x4i(i) + coefficient(15)*x4i(i)*x4i(i);
    end
end

figure()
[C,h]=contour(x3ia, x2ia, regression_x2i_x3i,5); clabel(C,h);
ylabel ('Injection Pressure (Bar)', 'FontWeight','bold');
xlabel ('Pre-Combustion Temperature (K)', 'FontWeight','bold');

figure()
meshc(x3ia, x2ia, regression_x2i_x3i);
ylabel ('Injection Pressure (Bar)', 'FontWeight','bold', 'FontSize',14);
xlabel ('Pre-Combustion Temperature (K)', 'FontWeight','bold', 'FontSize',14);
zlabel ('Estimated Soot Concentration (mg/m^3)', 'FontWeight','bold', 'FontSize',14);
set(gcf, 'color', 'white');
view([66 20]);

clear regression_x2i_x3i;

for (i=1:201)
    for (j=1:201)
        regression_x2i_x4i(i,j) = coefficient(1) + coefficient(2)*x1i(i) + coefficient(3)*x2i(i) + coefficient(4)*x3i(i) + coefficient(5)*x4i(j) + coefficient(6)*x1i(i)*x1i(i) + coefficient(7)*x1i(i)*x2i(i) + coefficient(8)*x1i(i)*x3i(i) + coefficient(9)*x1i(i)*x4i(j) + coefficient(10)*x2i(i)*x2i(i) + coefficient(11)*x2i(i)*x3i(i) + coefficient(12)*x2i(i)*x4i(j) + coefficient(13)*x3i(i)*x3i(i) + coefficient(14)*x3i(i)*x4i(j) + coefficient(15)*x4i(i)*x4i(i);
    end
end

figure()
[C,h]=contour(x4ia, x2ia, regression_x2i_x3i,5);
clabel(C,h);
ylabel ('Injection Pressure (Bar)', 'FontWeight','bold');
xlabel ('Pre-Combustion Pressure (Bar)', 'FontWeight','bold');

figure()
meshc(x4ia, x2ia, regression_x2i_x4i);
ylabel ('Injection Pressure (Bar)', 'FontWeight','bold', 'FontSize',14);
xlabel ('Pre-Combustion Pressure (Bar)', 'FontWeight','bold', 'FontSize',14);
zlabel ('Estimated Soot Concentration (mg/m^3)', 'FontWeight','bold', 'FontSize',14);
clear regression_x2i_x4i;

x1i=zeros(1,201);
x2i=zeros(1,201);
x3i=1:0.01:1;
x4i=1:0.01:1;

for (i=1:201)
    for (j=1:201)
        regression_x3i_x4i(i,j) = coefficient(1)+coefficient(2)*x1i(i)+coefficient(3)*x2i(i)+coefficient(4)*x3i(i)+coefficient(5)*x4i(j)+coefficient(6)*x1i(i)*x1i(i)+coefficient(7)*x1i(i)*x2i(i)+coefficient(8)*x1i(i)*x3i(i)+coefficient(9)*x1i(i)*x4i(j)+coefficient(10)*x2i(i)*x2i(i)+coefficient(11)*x2i(i)*x3i(i)+coefficient(12)*x2i(i)*x4i(j)+coefficient(13)*x3i(i)*x3i(i)+coefficient(14)*x3i(i)*x4i(j)+coefficient(15)*x4i(j)*x4i(j);
    end
end

figure()
[C,h]=contour(x4ia, x3ia, regression_x3i_x4i,5);
clabel(C,h);
ylabel ('Pre-Combustion Temperature (K)','FontWeight','bold');
xlabel ('Pre-Combustion Pressure (Bar)','FontWeight','bold');

figure()
meshc(x4ia, x3ia, regression_x3i_x4i);
ylabel ('Pre-Combustion Temperature (K)', 'FontSize',14);
xlabel ('Pre-Combustion Pressure (Bar)', 'FontSize',14);
zlabel ('Estimated Soot Concentration (mg/m{^3})', 'FontSize',14);
set(gcf, 'color', 'white');
view([66 20]);
clear regression_x3i_x4i;
end
end

% output results back to main program
full_coeff_out=full_coefficient;
full_std_error_out = full_std_error;
R_sq_out = R_sq;
full_resid_out = temp_residual;
APPENDIX D MATLAB CODES FOR IMAGE PROCESSING

% Main Program for Image Processing

clear all
close all
imtool close all

% results from 27 test points were processed
no_of_points = 27;
canny_out = zeros(no_of_points, 7);

for (test_point = 1:no_of_points)
    % image processing with the function "dipcanny"
    cd('C:\Documents and Settings\user1\Desktop\Thesis\Chapter 5 Experimental Image Processing\Codes')
    canny_out(test_point,:) = dipcanny(test_point);

    % display the progress on screen
    test_point
end

%dip_avg = average soot concentration using an adaptive method
% output the average into a text file for subsequent regression analysis
% Average concentration
% Output into a text file

dlmwrite('dip_avg.txt', dip_avg, 'delimiter', tab, 'precision', 6, newline)
% Function: dipcanny
% This function identifies the shock tube contamination particles by:
% 1. Canny edge detection
% 2. Signal intensity thresholding
% This function then removes the particles from the image and calculates an
% average soot concentration value.

function canny_out = dipcanny (test_point)

% Sets current working directory
if(test_point<10)
    dirname = sprintf ('C:\Documents and Settings\user1\Desktop\Thesis\Chapter 5 Experiment\Images\0%d_', test_point);
end
if(test_point>=10)
    dirname = sprintf ('C:\Documents and Settings\user1\Desktop\Thesis\Chapter 5 Experiment\Images\%d ', test_point);
end

avg_conc = zeros(3,4);

for (image_number=1:6)
    % Sets current working directory and load image
    if (image_number ==1)
        dirname2 = [dirname, sprintf('%d', image_number)];
        cd(dirname2);
        picture = imread('B00001.tif');
        picture = picture(568:787,176:1075);
        row = 1;
        column =2;
    end

    if (image_number ==2)
        dirname2 = [dirname, sprintf('%d', image_number)];
        cd(dirname2);
        picture = imread('B00001.tif');
        picture = picture(421:640,1:900);
        row = 1;
        column = 4;
    end

    if (image_number ==3)
        dirname2 = [dirname, sprintf('%d', image_number)];
        cd(dirname2);
        picture = imread('B00001.tif');
        picture = picture(568:787,176:1075);
        row = 1;
        column =2;
    end

end
if (image_number == 4)
    dirname2 = [dirname, sprintf('%d', image_number)];
    cd(dirname2);
    picture = imread('B00001.tif');
    picture = picture(421:640,1:900);
    row = 2;
    column = 4;
end

if (image_number == 5)
    dirname2 = [dirname, sprintf('%d', image_number)];
    cd(dirname2);
    picture = imread('B00001.tif');
    picture = picture(568:787,176:1075);
    row = 1;
    column = 3;
end

if (image_number == 6)
    dirname2 = [dirname, sprintf('%d', image_number)];
    cd(dirname2);
    picture = imread('B00001.tif');
    picture = picture(421:640,1:900);
    row = 3;
    column = 4;
end

picture = double (picture);

% calculate results
attenuation = 0.7787/0.0968;
calibration = 0.52;
intensity_temp = 0;
pixel_temp = 0;

% After inspecting the images, a threshold of 410 was found suitable for
% removing all contamination signal.
threshold = 410;
show_image = zeros (219,899);
for (i = 1:220)
    for (j = 1:900);
        if (picture(i,j)>threshold)
            picture (i,j) = picture (i,j);
            intensity_temp = intensity_temp + picture(i,j);
            pixel_temp = pixel_temp + 1;
            show_image (i,j) = picture (i,j);
        end
    end
end

% The calibration constant and the constant for correcting optical
% attenuation were multiplied to the average pixel intensity observed in
% each image. The result was a soot concentration in mg/m^3.
avg_conc(row,column)=intensity_temp/pixel_temp*attenuation*calibration;

clear picture

% output results
for (counter = 1:7)
    if (counter == 4)
        canny_temp(counter) = max (avg_conc(:,counter)); % mean
    elseif (counter == 5)
        canny_temp(counter) = avg_conc(1,4);
    elseif (counter == 6)
        canny_temp(counter) = avg_conc(2,4);
    elseif (counter == 7)
        canny_temp(counter) = avg_conc(3,4);
    else
        canny_temp(counter) = avg_conc(1,counter);
    end
end

canny_out = canny_temp;
### APPENDIX E SHOCK TUBE OPERATING PROCEDURE

<table>
<thead>
<tr>
<th>Step</th>
<th>Action</th>
</tr>
</thead>
</table>
| 1    | Switch on  
- Power supply X8 (Reset if blink)  
- Computer X3  
- Cameras and Lasers |
| 2    | Record Ambient T & P  
- Volt meter  
  - High pressure sensor  
  - Low pressure sensor  
- Barometer |
| 3    | Shut off air sampling valve |
| 4    | Clean  
- Wet cloth X1  
- Air jet X4 |
| 5    | Start computer programs  
- DaVis  
  - New Project, set file name, Soot Master  
  - Right Click "Properties", "Import Calibration"  
  - Search for: "Shock tube, Properties, Calibration.SET"  
  - Acquire Background image  
- Labview  
  - Labview (Shock tube icon); ignore error  
  - Click "RUN"  
- W Cut  
  - select file, "Continue"  
  - View, Real time data, single pulse test setup  
  - Input delay: Set to 0.2ms (minimum allowed)  
  - Input width: Set to 2ms  
- Waveview  
  - Load, D:/Mike/waveview6CH.cfg  
  - Click "Scope" icon  
  - Click "Acquire One Shot" icon  
  - Check if it is "Armed" |
| 6    | Put diaphragm back, torque |
| 7    | Fuel  
- Open shut off valve  
  - For first test of the Day  
  - Manually trigger injector  
  - Recharge fuel supply line, see above  
- Close shut off valve  
- Vent fuel  
- Install injector, torque |
<table>
<thead>
<tr>
<th>Step</th>
<th>Action</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td><strong>Vacuum</strong>&lt;br&gt;Open all valves, shut supply line&lt;br&gt;Connect clip to yellow wire&lt;br&gt;Turn on pump until vacuum is reached&lt;br&gt;Shut off valve to pump, pump off</td>
</tr>
<tr>
<td>9</td>
<td><strong>Driver gas composition</strong>&lt;br&gt;Excel&lt;br&gt;Input T &amp; P in blue cells&lt;br&gt;VdrAtm = High P sensor&lt;br&gt;VdmAtm = Low P sensor&lt;br&gt;VdmVac = After pumping&lt;br&gt;No, No&lt;br&gt;shknew C++&lt;br&gt;execute (Ctrl + F5) 2, Enter, Enter&lt;br&gt;Excel&lt;br&gt;Worksheet: Test prep&lt;br&gt;Click Macro button, No&lt;br&gt;Worksheet: Diaphragm&lt;br&gt;Vvac = Low P sensor&lt;br&gt;Vpos = High P sensor&lt;br&gt;2 reading for air&lt;br&gt;2 reading for He (higher P)</td>
</tr>
<tr>
<td>10</td>
<td><strong>Fill</strong>&lt;br&gt;Rotate 3-way valve to air bottle&lt;br&gt;Open air bottle to 80psi&lt;br&gt;Open needle valve to charge air to value from program&lt;br&gt;Read current pressure from volt meter&lt;br&gt;Shut off gray valve&lt;br&gt;Shut off valve to sensor branch (T off driver section)&lt;br&gt;Change to green wire&lt;br&gt;Fill air to 2nd voltage value&lt;br&gt;Close air bottle&lt;br&gt;Open release valve between bottles&lt;br&gt;Rotate 3-way valve to He bottle&lt;br&gt;Open He to 600psi&lt;br&gt;Open needle valve to charge intermediate to value from program&lt;br&gt;Shut off valve to intermediate section&lt;br&gt;Open needle valve to charge driver to value from program&lt;br&gt;Close He bottle</td>
</tr>
<tr>
<td>Step</td>
<td>Action</td>
</tr>
<tr>
<td>------</td>
<td>--------</td>
</tr>
<tr>
<td>11</td>
<td>LII Trigger</td>
</tr>
<tr>
<td>12</td>
<td>Test</td>
</tr>
<tr>
<td>13</td>
<td>Data processing</td>
</tr>
</tbody>
</table>
F.1 Calculations and Results

Fuel Flow Rate:
A fuel mass flow calibration was performed by the injector manufacturer. The results are listed in Table F.1.

<table>
<thead>
<tr>
<th>Back Pressure (bar)</th>
<th>Fuel Pressure (bar)</th>
<th>Ethene Mass Flow (mg/injection)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>150</td>
<td>3.35</td>
</tr>
<tr>
<td>35</td>
<td>120</td>
<td>2.70</td>
</tr>
<tr>
<td>35</td>
<td>100</td>
<td>2.25</td>
</tr>
<tr>
<td>30</td>
<td>150</td>
<td>3.42</td>
</tr>
<tr>
<td>30</td>
<td>120</td>
<td>2.75</td>
</tr>
<tr>
<td>30</td>
<td>100</td>
<td>2.28</td>
</tr>
<tr>
<td>25</td>
<td>150</td>
<td>3.00</td>
</tr>
<tr>
<td>25</td>
<td>120</td>
<td>2.71</td>
</tr>
<tr>
<td>25</td>
<td>100</td>
<td>2.28</td>
</tr>
</tbody>
</table>

These data was then extrapolated to provide a mass flow that corresponds to the injection pressures tested in this study. The results are shown in Table F.2.

<table>
<thead>
<tr>
<th>Back Pressure (bar)</th>
<th>Fuel Pressure (bar)</th>
<th>Ethene Mass Flow (mg/injection)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>60</td>
<td>1.78</td>
</tr>
<tr>
<td>35</td>
<td>70</td>
<td>1.92</td>
</tr>
<tr>
<td>35</td>
<td>80</td>
<td>2.06</td>
</tr>
<tr>
<td>30</td>
<td>60</td>
<td>1.38</td>
</tr>
<tr>
<td>30</td>
<td>70</td>
<td>1.61</td>
</tr>
<tr>
<td>30</td>
<td>80</td>
<td>1.83</td>
</tr>
<tr>
<td>25</td>
<td>60</td>
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</tr>
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<td>1.59</td>
</tr>
<tr>
<td>25</td>
<td>80</td>
<td>1.81</td>
</tr>
</tbody>
</table>
Mass of Air inside the Driven Section:

When preparing the shock tube for an experiment, ambient temperature and the initial air pressure inside the driven section was recorded. Also, the internal volume of the driven section was already known based on its dimensions (4.79m long with an inner diameter of 5.9 cm). Based on these data, the mass of air inside the driven section was calculated using the ideal gas law. The results are listed in Table F.3.

<table>
<thead>
<tr>
<th>Pre-combustion Temperature (K)</th>
<th>Pre-combustion Pressure (bar)</th>
<th>Mass of Air (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1200</td>
<td>25</td>
<td>8494</td>
</tr>
<tr>
<td>1200</td>
<td>30</td>
<td>10617</td>
</tr>
<tr>
<td>1200</td>
<td>35</td>
<td>12741</td>
</tr>
<tr>
<td>1300</td>
<td>25</td>
<td>7432</td>
</tr>
<tr>
<td>1300</td>
<td>30</td>
<td>8494</td>
</tr>
<tr>
<td>1300</td>
<td>35</td>
<td>10617</td>
</tr>
<tr>
<td>1400</td>
<td>25</td>
<td>6370</td>
</tr>
<tr>
<td>1400</td>
<td>30</td>
<td>7432</td>
</tr>
<tr>
<td>1400</td>
<td>35</td>
<td>9556</td>
</tr>
</tbody>
</table>

From Table F.3, it is observed that the mass of air inside the driven section decreases as pre-combustion temperature increases. This is because the pre-combustion temperature achieved in each experiment was controlled by the amount of air filled within the driven section.
Overall Air/Fuel Ratio:

Based on the mass of air inside the shock tube and the mass of fuel injected, an overall AFR was calculated for each experimental condition. The results are listed in Table F.4 (a graphical summary of the results can be found in Figure 5.17).

<table>
<thead>
<tr>
<th>Pre-combustion Temperature (K)</th>
<th>Pre-combustion Pressure (bar)</th>
<th>Fuel Injection Pressure (bar)</th>
<th>Mass of Ethene Injected (mg/injection)</th>
<th>Mass of Air in the Driven Section (mg)</th>
<th>Overall AFR</th>
</tr>
</thead>
<tbody>
<tr>
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<td>8494</td>
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</tr>
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<td>8494</td>
<td>4429</td>
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<td>6614</td>
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<td>80</td>
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<td>80</td>
<td>1.814</td>
<td>10617</td>
<td>5854</td>
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<td>6370</td>
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<td>60</td>
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<td>9556</td>
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<td>9556</td>
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<td>35</td>
<td>80</td>
<td>1.814</td>
<td>9556</td>
<td>5268</td>
</tr>
</tbody>
</table>
Mean Centerline AFR:

Equation (F.1) [1] was used to determine a local average AFR (on the centerline of the fuel jet) at the time when ignition began.

\[
AF = \frac{M_o}{M_f} \left( \frac{1}{X_f} - 1 \right)
\]  

(F.1)

where \( M_o \) is the molecular weight of the oxidizer (air), \( M_f \) is the molecular weight of the fuel, and \( X_f \) is the mean fuel mole fraction, which is defined as:

\[
X_f = \frac{k_x X_{fo} \left( \frac{d}{U_n \tau_{ign}} \right)^{1/2} \left( \frac{P_n}{P_o} \right)^{1/4}}{\Gamma}
\]  

(F.2)

where \( k_x \) is a constant \( (k_x = 5.1) \), \( X_{fo} \) is the initial mole fraction at the nozzle exit \( (X_{fo} = 1) \), \( \Gamma \) is a constant \( (\Gamma = 3) \), \( d \) is the injector nozzle diameter \( (d = 0.31 \text{ mm}) \), \( U_n \) is the jet velocity at the injector nozzle exit (calculated by assuming sonic conditions at the nozzle exit), \( \tau_{ign} \) is the ignition delay with respect to the actual start of fuel injection, \( P_n \) is the fuel pressure at the nozzle exit, and \( P_o \) is the (pre-combustion) pressure of the oxidizer.

To determine the value of \( \tau_{ign} \), a nominal mechanical injection delay was subtracted from the average of the three ignition delays detected at each test condition (as shown in Table F.5), this mechanical injection delay \((\tau_{ign} = 0.37 \text{ ms})\) was determined based on data collected from a similar injector in a series of schlieren experiments [2].
Table F.5 Ignition Delay Data

<table>
<thead>
<tr>
<th>Test Point</th>
<th>Detected Ignition Delay (ms)</th>
<th>Avg. Delay wrt. Injection Command (ms)</th>
<th>( \tau_{\text{IGN}} ) - Delay wrt. Start of Injection (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Trial 1</td>
<td>Trial 2</td>
<td>Trial 3</td>
</tr>
<tr>
<td>1</td>
<td>1.245</td>
<td>0.976</td>
<td>1.321</td>
</tr>
<tr>
<td>2</td>
<td>1.324</td>
<td>1.332</td>
<td>1.340</td>
</tr>
<tr>
<td>3</td>
<td>0.658</td>
<td>0.665</td>
<td>0.700</td>
</tr>
<tr>
<td>4</td>
<td>0.651</td>
<td>0.677</td>
<td>0.694</td>
</tr>
<tr>
<td>5</td>
<td>1.059</td>
<td>1.145</td>
<td>1.075</td>
</tr>
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<td>1.267</td>
<td>0.927</td>
<td>1.346</td>
</tr>
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<td>0.660</td>
<td>0.698</td>
</tr>
<tr>
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<td>0.662</td>
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<td>0.703</td>
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<td>0.949</td>
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<td>1.079</td>
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<td>0.956</td>
<td>1.490</td>
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<td>0.746</td>
<td>1.023</td>
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<td>0.726</td>
<td>0.721</td>
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<td>0.716</td>
<td>0.654</td>
<td>0.637</td>
</tr>
<tr>
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<td>0.739</td>
<td>0.829</td>
<td>0.742</td>
</tr>
<tr>
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<td>0.858</td>
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<td>0.947</td>
<td>1.153</td>
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<td>0.663</td>
</tr>
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<td>23</td>
<td>0.810</td>
<td>0.810</td>
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</tr>
<tr>
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<td>0.634</td>
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<tr>
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<td>0.800</td>
<td>0.687</td>
<td>0.731</td>
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<tr>
<td>27</td>
<td>0.764</td>
<td>0.694</td>
<td>0.640</td>
</tr>
</tbody>
</table>

Using Equation (F.1) and (F.2), a mean centerline AFR was found for each of the 27 test points considered. The results of this calculation are shown in Table F.6 (a small subset of the results is graphically presented in Figure 5.18).
Table F.6 Mean Centerline AFR at Start of Ignition

<table>
<thead>
<tr>
<th>Test Point</th>
<th>( t_{\text{ign}} ) (ms)</th>
<th>Injection Pressure (bar)</th>
<th>Pre-combustion Pressure (bar)</th>
<th>Mean Centerline AFR</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>35</td>
<td>1.655</td>
</tr>
<tr>
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<td>0.304</td>
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<td>0.615</td>
</tr>
<tr>
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<td>0.304</td>
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<td>25</td>
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</tr>
<tr>
<td>5</td>
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<td>0.810</td>
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<td>1.266</td>
</tr>
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<tr>
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<td>0.348</td>
</tr>
<tr>
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<td>35</td>
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</tr>
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<td>60</td>
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<td>70</td>
<td>30</td>
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</table>

**F.2 References**


APPENDIX G IGNITION DELAY DATA

G.1 Introduction
Ignition delay is a measure of the time between fuel injection and the start of ignition (in this research, ignition was defined as the moment at which the flame was first observed). The ignition delay of a non-premixed combustion process consists of two parts: a physical delay and a chemical delay. For gaseous non-premixed combustion, physical delay is defined as the time needed for the injected fuel to establish a combustible mixture by mixing and heat transfer (for liquid fuel combustion, evaporation is another contributing factor). Chemical delay is defined as the time needed to form radicals in the pre-combustion process and is typically presented in the form of an Arrhenius equation, such as [1]:

\[
\tau(\mu s) = 10^{-11.9} \cdot 10^{34200/T} \cdot \left[ C_2H_4 \right]_o^{0.3} \cdot \left[ O_2 \right]_o^{1.1} \cdot \left[ Ar \right]_o^{0.4}
\] (G.1)

where \( \tau \) is the chemical delay, \( T \) is the ambient temperature, \( k, a, a, b, \) and \( c \) are empirical constants, and \([ \cdot ]_o\) denotes the initial reactant concentrations. Although Equation (G.1) was developed with argon as the fuel diluent (rather than nitrogen), it can nevertheless be used to facilitate the discussion on various factors that can affect chemical delay in the next section.

G.2 Effect of Nitrogen Addition, \( P_i, T_0, \) and \( P_0 \) on Ignition Delay
As discussed in Section 5.2, the ignition delay in each shock tube experiment was obtained by inspecting a sequence of images captured by a high frame rate digital camera. The results are summarized in Table G.1. In addition, these points are plotted against the nitrogen content in the fuel, injection pressure, pre-combustion temperature, and pre-combustion pressure to highlight any trends between ignition delay and these parameters, as shown in Figure G.1.

143
<table>
<thead>
<tr>
<th>Test Point</th>
<th>Delay 1</th>
<th>Delay 2</th>
<th>LII 1</th>
<th>LII 2</th>
<th>LII 3</th>
</tr>
</thead>
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</tr>
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<td>1.324</td>
<td>1.332</td>
<td>1.340</td>
</tr>
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<td>0.658</td>
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<td>0.700</td>
</tr>
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<td>0.677</td>
<td>0.694</td>
</tr>
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</tr>
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<td>0.660</td>
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(Delay 1 & 2: Ignition delay for the two experiments performed to find the average ignition delay)  
(LII 1, 2, & 3: Ignition delay for the three experiments where LII images were taken.)
Figure G.1 Effect of Nitrogen Addition, $P_i$, $T_0$, and $P_0$ on Ignition Delay

The most apparent trend shown in Figure G.1 is that an increase in pre-combustion temperature ($T_0$) is observed to reduce ignition delay. This is expected since a high temperature environment is considered as a possible ignition source [2]. This trend is qualitatively consistent with that reported in the literature [3] [4]. Further, from Figure G.1, the other three parameters (i.e. nitrogen addition, injection pressure ($P_i$), and pre-combustion pressure ($P_0$)) do not appear to have any significant effects on ignition delay.

To further analyze the effect of these four parameters on ignition delay, a response function was generated. Using the average of the five ignition delay timings for each test condition listed in Table G.1 as input data, this response function was built according to the statistical technique presented in Section 4.4.1. The results are as follow:
where $\tau_{\text{ag}}$ represents ignition delay and $x_1$, $x_2$, $x_3$, and $x_4$ correspond to the definitions provided in Table 4.2.

From Equation (G.2), a series of response surfaces was created to illustrate the effects of nitrogen addition, $P_i$, $T_0$, and $P_0$ on ignition delay. Similar to the method used in Section 5.5.3, when plotting each of the following response surface, only two parameters were allowed to vary while the other two where fixed at their center points.

Ignition delay ranged from 0.6 to 1.6 ms over all conditions studied. The variability at nominally identical conditions was almost this large as well, but the response surface suggested that several trends were significant. Increasing pre-combustion temperature or injection pressure decreased the ignition delay, consistent with the findings of Sullivan et al. [5] for methane-ethane blends tested in the same shock tube apparatus used in this research. The response surfaces suggest that nitrogen addition may increase the ignition delay, but this trend appears less robust. Two standard errors from the response surface is 0.16 ms – only slightly less than the variations apparently produced by changing nitrogen concentration.

Further, the following observations were made from the response surfaces to specifically highlight the effect of each of the four parameters on ignition delay:

- The addition of nitrogen appears to increase ignition delay. This is expected because, as shown in Equation (G.1), the addition of nitrogen increases the concentration of diluent and reduces the concentration of fuel in the reactants, which should increase the chemical delay, and ultimately, the ignition delay.

- An increase in injection pressure appears to shorten ignition delay. This is expected since a higher injection pressure should increase the relative velocity
between the fuel and oxidizer. This should reduce the time required for the injected fuel to form a combustible mixture, resulting in a shorter physical delay.

- An increase in pre-combustion temperature appears to reduce ignition delay, as expected. At higher pre-combustion temperature, reaction rates, diffusion rates, heat transfer to the fuel jet should be increased. These factors may combine to reduce the duration of the physical delay, which would result in a shorter ignition delay for the overall combustion process as temperature is increased.

- Clear trends that indicate the effects of pre-combustion pressure on ignition delay are not observed from the response surfaces. From Equation (G.1), an increase in pre-combustion pressure is expected to reduce chemical delay by increasing in oxidizer concentration in the shock tube. However, in the following response surfaces, some of the trends show that an increase in pre-combustion pressure would lead to an increased ignition delay. These unexpected results may be caused by the variability in the ignition delay data. Additional experiments to further investigate the effect of pre-combustion pressure on ignition delay are recommended since a sample of five data points may not be sufficient to account for the observed variability.
G.3 Conclusions
Based on the ignition delay data collected in this research, a response function was developed. From the response surfaces, the addition of nitrogen to ethene was observed to increase ignition delay, whereas an increase in injection pressure and pre-combustion...
temperature was found to reduce ignition delay. Also, with the limited data available, the
effect of pre-combustion pressure on ignition delay could not be determined.

G.4 References


2007.

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[4] Afify, E., N. Korah, and D. Dickey. The Effect of Air Charge Temperature on
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APPENDIX H ESTIMATING THE EFFECT OF SIGNAL TRAPPING

Signal trapping is defined as attenuation of the LII signal due to soot particles present between the LII signal emitting location and the camera. It can be approximated – on an order-of-magnitude basis – by applying the Beer-Lambert Law. Using this law, signal extinction can be estimated by:

\[ Ext = 1 - \exp(-cLk_{ext}) \]  \hspace{1cm} (H.1)

where \( c \) is the mass concentration of soot (approximated by 7000 mg/m\(^3\), which is the highest of all the soot concentration measurements made in this research), \( L \) is the radius of the fuel jet (approximately 4 mm, as shown in Figure 5.3), and \( k_{ext} \) is the attenuation coefficient of combustion generated soot (4 m\(^2\)/g) [1]. Substituting these values into Equation (H.1), signal trapping was estimated to result in an attenuation of approximately 10%. As this calculation was based on the maximum soot concentration detected in this study (i.e. 7000 mg/m\(^3\)), the 10% attenuation in LII signal is expected to be an upper bound estimate. Therefore, signal trapping is unlikely to be a significant source or variability or bias in the soot measurements.

H.2 References