THE DEVELOPMENT AND APPLICATION OF AEROSOL SHOCK TUBE METHODS FOR THE STUDY OF LOW-VAPOR-PRESSURE FUELS

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ABSTRACT

This thesis describes a new facility and method of experimentation, which can be used to study the combustion chemistry of low-volatility fuels in the gas phase. Two main goals are described: first, the development of the aerosol shock tube and procedures; and second, a demonstration of its capabilities.

There is a lack of high-quality, accurate chemical kinetics data for the oxidation of large hydrocarbons, which are important for modeling diesel, rocket, or jet engines among other combustion systems. While conventional shock tubes are very effective reactor vessels for low-molecular-weight gaseous fuels (n-alkanes up to five carbon atoms), larger fuel molecules exist as low-volatility liquids/solids, and the vapor-pressures of these fuels are not large enough for high or even moderate fuel loadings. Heating the shock tube has extended the use of shock tubes to carbon numbers of 10 to 12, but beyond that, the high temperatures prior to the shock initiation can decompose the fuel, and (for fuel mixtures like diesel) can cause fractional distillation. The question is then: how can we study low-vapor-pressure fuels in a shock tube?

The solution presented here, which avoids the problems associated with heating, is called the aerosol shock tube. In the aerosol shock tube, the fuel is injected as an aerosol of micron-size droplets. Then a series of shock waves first evaporate the fuel and subsequently raise the resultant purely gas-phase mixture to combustion-relevant
temperatures. With proper selection of the shock strength and timing, this process effectively decouples the mass and heat transfer processes associated with evaporation from the chemical mechanism of combustion. This enables the study of extremely low-volatility fuels, never before studied in a purely gas-phase form in a shock tube.

The first application of this new facility was to measure the ignition delay time for many previously inaccessible fuels in the gas-phase. In this thesis, we have measured ignition delay times for the pure surrogate fuel components n-decane, n-dodecane, n-hexadecane, and methyl decanoate as well as for multi-component fuels such as JP-7 and multiple different blends of diesel fuel. Taken over a range of conditions, these measurements provide sensitive validation targets for their respective chemical mechanisms. These data showed agreement with past heated shock tube experiments for fuels in which premature fuel decomposition is not an issue (n-decane and low concentration n-dodecane). However, when comparing heated and aerosol shock tube ignition delay times for fuels that require significant heating, like n-hexadecane, the existing heated shock tube data demonstrated evidence of premature decomposition.

The second application to the study of chemical kinetics was to measure the concentration of important species during the decomposition and oxidation of select low-vapor-pressure fuels. These species time-histories provide much more information for kinetic mechanism refinement. Experiments were performed to measure the important OH radical and the stable intermediate C$_2$H$_4$ for both n-hexadecane and diesel.

The number of important low-vapor-pressure fuels that require high-quality validation targets is large, and our new method for providing this data has proven very effective. This work enables the development of the next generation of accurate chemical mechanisms and will be essential to their success.
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# CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ABSTRACT</strong></td>
<td>IV</td>
</tr>
<tr>
<td><strong>ACKNOWLEDGEMENTS</strong></td>
<td>VI</td>
</tr>
<tr>
<td><strong>CONTENTS</strong></td>
<td>VII</td>
</tr>
<tr>
<td><strong>LIST OF FIGURES</strong></td>
<td>XI</td>
</tr>
<tr>
<td><strong>LIST OF TABLES</strong></td>
<td>XIX</td>
</tr>
<tr>
<td><strong>CHAPTER 1: INTRODUCTION</strong></td>
<td>1</td>
</tr>
<tr>
<td>1.1 Distillate Fuels</td>
<td>2</td>
</tr>
<tr>
<td>1.2 Surrogate Fuels</td>
<td>6</td>
</tr>
<tr>
<td>1.3 Shock Tubes</td>
<td>9</td>
</tr>
<tr>
<td>1.4 Aerosol shock tube</td>
<td>11</td>
</tr>
<tr>
<td>1.5 Conclusions</td>
<td>13</td>
</tr>
<tr>
<td><strong>CHAPTER 2: COMBUSTION STUDIES IN THE AEROSOL SHOCK TUBE</strong></td>
<td>14</td>
</tr>
<tr>
<td>2.1 Aerosol Generation</td>
<td>15</td>
</tr>
<tr>
<td>2.2 Loading the Aerosol into the Shock Tube</td>
<td>18</td>
</tr>
<tr>
<td>2.3 Measuring Shock Speed</td>
<td>19</td>
</tr>
<tr>
<td>2.4 Fuel Measurement</td>
<td>21</td>
</tr>
<tr>
<td>2.4.1 In-Situ Measurement of Droplets</td>
<td>22</td>
</tr>
<tr>
<td>2.4.2 Gas-Phase Laser Absorption</td>
<td>22</td>
</tr>
<tr>
<td>2.4.3 Fuel Spectroscopy</td>
<td>23</td>
</tr>
<tr>
<td>2.4.4 FTIR/Heated Cell Measurements</td>
<td>24</td>
</tr>
<tr>
<td>2.4.5 Shock tube measurements of high temperature cross Section</td>
<td>27</td>
</tr>
<tr>
<td>2.5 Calculation of Equilibrium Shock Jump Conditions</td>
<td>30</td>
</tr>
<tr>
<td>2.5.1 Validation of AEROFROSH</td>
<td>31</td>
</tr>
</tbody>
</table>
2.6 Applications of Measurements Behind Reflected Shock Waves ..........34
2.7 Conclusions .........................................................................................36

CHAPTER 3: UNIFORMITY IN THE AEROSOL SHOCK TUBE 37
3.1 Introduction ..........................................................................................38
3.2 Aerosol Shock Tube Generation II .......................................................40
  3.2.1 Experimental Apparatus .................................................................40
  3.2.2 Calculation of Loading Pressures ....................................................43
3.3 Results ...................................................................................................45
  3.3.1 Nebulizer Performance .................................................................45
  3.3.2 Mixing Tank Loading Uniformity ....................................................46
  3.3.3 Shock Tube Loading Uniformity ......................................................49
3.4 Shock Wave Experiments .................................................................53
  3.4.1 Fuel Loading Uniformity ...............................................................53
  3.4.2 Ignition Delay Time Measurements ...............................................58
3.5 Conclusions ..........................................................................................59

CHAPTER 4: APPLICATION 1 - IGNITION DELAY TIMES 60
4.1 Introduction ..........................................................................................61
4.2 Low-Vapor-Pressure Fuels .................................................................62
  4.2.1 n-Decane .......................................................................................62
  4.2.2 n-Dodecane ..................................................................................62
  4.2.3 n-Hexadecane ..............................................................................63
  4.2.4 Diesel (DF-2) ...............................................................................63
  4.2.5 Methyl Decanoate .......................................................................63
4.3 Experimental Setup ................................................................................63
4.4 Results ...................................................................................................65
  4.4.1 n-Decane .......................................................................................67
  4.4.2 n-Dodecane ..................................................................................68
  4.4.3 n-Hexadecane ..............................................................................72
  4.4.4 Methyl Decanoate .......................................................................74
  4.4.5 Diesel ...........................................................................................75
4.5 Conclusions ................................................................................................... 79

CHAPTER 5: APPLICATION 2 - SPECIES TIME-HISTORIES 80

5.1 Introduction ................................................................................................. 81

5.2 Experimental Setup .................................................................................. 82
   5.2.1 Aerosol Shock Tube ............................................................................. 82
   5.2.2 Laser Absorption ................................................................................ 83

5.3 Results and Discussion ........................................................................... 85
   5.3.1 n-Hexadecane Oxidation .................................................................... 86
   5.3.2 Diesel Oxidation ................................................................................ 89

5.4 Conclusions ............................................................................................... 92

CHAPTER 6: CONCLUSIONS 93

6.1 Facility and Method ................................................................................ 93

6.2 Ignition Delay Times ............................................................................... 94

6.3 Species Time-Histories .......................................................................... 94

6.4 Future Work .............................................................................................. 95
   6.4.1 Negative Temperature Coefficient .................................................. 95
   6.4.2 Biofuels ............................................................................................ 96
LIST OF FIGURES

Figure 1.1: Distillation curves for common distillate fuels as well as a soybean derived bio-diesel................................................................. 3

Figure 1.2: Past ignition delay time measurements normalized to 6 atm and an equivalence ratio of 0.5. Many techniques and facilities were used to measure these ignition delay times.......................................................... 4

Figure 1.3: Chain length distribution of n-alkanes present in two different batches of diesel fuel [12]................................................................. 6

Figure 1.4: Fuel surrogate vapor pressures. Heated shock tube temperature limits partial pressure of fuel that can be added to mixtures......................... 8

Figure 1.5a-c: a. Shock tube prior to shock. Driver is filled till diaphragm breaks. b. Incident shock travels into driven section followed by contact surface. Expansion wave travels into driver. c. The incident shock is reflected at the endwall and forms a reflected shock which travels in opposite direction creating combustion-relevant conditions................................................................. 10

Figure 1.6: Aerosol shock tube prior to initiation of shock. Liquid or solid particles are loaded uniformly in the driven section to experiment on low-volatility fuels........ 12

Figure 2.1: Cross-section schematic of nebulizer in operation. The nebulizer uses a vibrating piezoelectric transducer to pinch off droplets and create a fog........ 16

Figure 2.2: 12-disk nebulizer bank in operation. Fuel is n-dodecane. ...................... 17

Figure 2.3: Experimental setup used to measure droplet size distributions for various fuels – Malvern Spraytec™ (Model RTS5214).............................. 17

Figure 2.4: Droplet size distributions for water and representative fuels used in this study................................................................. 18

Figure 2.5: Schematic of first-generation aerosol shock tube (AST I) filling method. Aerosol spatial uniformity was insufficient for high quality combustion experiments. Chapter 3 discusses an improved design........................................ 19

Figure 2.6: Attenuation of shock velocity in a dry argon shock. Attenuation rate is 2.1%/m. Shock conditions: P₁ = 0.26 atm, T₁ = 295 K, P₂ = 1.6 atm, T₂ = 715 K... 20
Figure 2.7: Attenuation of shock velocity in a n-dodecane aerosol. Attenuation rate is 3.6%/m. Shock conditions: $P_1 = 0.18$ atm, $T_1 = 294$ K, $P_2 = 1.4$ atm, $T_2 = 695$ K, $X_f = 0.63\%$, $X_{O_2} = 21\%$, balance Ar, Droplet loading by volume: 10.0 ppmv (volume of liquid per volume of gas).

Figure 2.8: Schematic of Mie-scattering diagnostic for measurement of liquid volume concentration.

Figure 2.9: Schematic of gas phase laser absorption measurements.

Figure 2.10: Experimental setup for measuring cross sections in a heated cell with an FTIR.

Figure 2.11: Methyl decanoate spectra measured at various temperatures in a heated cell using a FTIR.

Figure 2.12: Summary of cross section measurements at 3.39 µm for various fuels measured using the heated cell and FTIR.

Figure 2.13: Cross section measurements of n-dodecane at 3.39 µm extended to high temperatures using the aerosol shock tube.

Figure 2.14: Cross section measurements of JP-7 at 3.39 µm extended to high temperatures using the aerosol shock tube.

Figure 2.15: Example of fuel measurement behind an incident shock wave. The red trace shows droplet scattering and absorption. The black trace shows only droplet scattering. Arrival of the incident shock occurs at 0 µs and arrival of the reflected shock occurs at 500 µs. Conditions: 21% O$_2$ in Ar with $X_f$ (n-dodecane mole fraction) = 0.00680, $T_2 = 617$ K, $P_2 = 1.11$ atm, $T_5 = 993$ K, $P_5 = 4.23$ atm. Measurement location is 10 cm from endwall.

Figure 2.16: Comparison of AEROFROSH calculations to those made by Guha in 1992 [18] and Marble made in 1968 [19] for a shock traveling in pure water of varying initial quality.

Figure 2.17: Comparison of measured pressure (2 cm from the endwall) with those predicted by AEROFROSH.

Figure 2.18: Comparison of measured temperature using a two-wavelength fuel diagnostic with calculated temperature.
Figure 2.19: Comparison of measured temperature using a two-line CO$_2$ technique with calculated temperature. ................................................................. 33

Figure 2.20a,b: a. Plots of pressure versus time measured 2 cm from the endwall in AST I for mixtures of n-dodecane / 21% O$_2$ / Ar at various temperatures $\Phi = 1.0$, $P = 6.0$ atm. b. Summary of ignition delay times plotted on an Arrhenius plot. ....................... 35

Figure 3.1a-d: (a) Diagram illustrating components of AST II and initial pressures set for operation. (b) Aerosol mixture being prepared in the mixing plenum. (c) Endwall gate valve and ball valve opened and aerosol mixture expanded into the test section. (d) Endwall gate valve and ball valve closed and the driven gate valve opened; the shock tube is ready for initiation of the shock wave. ............................................................ 42

Figure 3.2: Schematic of filling process for second generation aerosol shock tube. Initial pressures in the test section ($V_{TS}$) and mixing tank ($V_{MT}$) are both $P_A$ and are separated from the dump tank ($V_B$) by a ball valve, which is at a lower pressure $P_B$. When the ball valve is opened the pressures equalize to $P_1$. At this point the expansion is sufficient for the gas from the mixing tank to fill the test section. ........ 43

Figure 3.3: The optical setup on the mixing plenum to measure the uniformity and the loading. ........................................................................................................ 47

Figure 3.4: Uniformity in tank: water aerosol. Two lasers at 10 and 40 cm from the endwall. The discrepancy between the two measurements indicate the magnitude of the non-uniformities present in the mixture at a particular time. The coefficient of variation (COV=$\text{StDev}/\text{Ave}$) is plotted as a function of time. ................................. 48

Figure 3.5: Filling the tank to different concentrations: water aerosol. Various curves represent different lengths of time that the nebulizer and mixing fan was turned on. This shows the effects of leaving the nebulizer running for different amounts of time and the range of achievable concentrations (1-100 ppmv). ........................................ 49

Figure 3.6: Optical setup for measuring non-uniformities in AST II method of filling. 50

Figure 3.7: Plot of laser extinction measurements at three locations along the tube and the resulting coefficient of variation: water aerosol. AST II generates non-uniformities much smaller than AST I, in this case 2%. .................................................. 50

Figure 3.8a-c: These plots show measurements of aerosol concentration at three locations while filling the shock tube using the AST II filling method (a) 50 slpm fill
rate (b) 4.0 slpm fill rate (c) 1.0 slpm fill rate. The flow rate was varied by using various diameter orifices. The flow rate was varied by using various diameter orifices. The optimal flow rate range is between 2 and 5 slpm (gas velocity ~45 cm/s).

Figure 3.9: The relationship between the resulting non-uniformity to the flow rate with which the tube was filled. The flow rate was varied by using various diameter orifices. The optimal flow rate range is between 2 and 5 slpm (gas velocity ~45 cm/s).

Figure 3.10: Top View: Diagnostics used in aerosol tube experiments. Pressure measurements are used to measure shock speed and ignition delay time. Laser light at 650 nm can be used to measure liquid aerosol concentration. Laser light at 3.39 µm is used to measure gas phase concentration after the fuel has evaporated. Side View: Incident shock propagates into aerosol evaporating and mixing fuel and oxidizer. This region is called region 2.

Figure 3.11a-c: Three shock experiments highlighting region 2 post-evaporation uniformity for a range of fuel loadings all with n-dodecane in 21%O2/Ar. (a) Conditions: Xf (n-dodecane mole fraction) = 0.00680, T2 = 617 K, P2 = 1.11 atm, T5 = 993 K, P5 = 4.23 atm (b) Conditions: Xf = 0.0100, T2 = 584 K, P2 = 1.64 atm, T5 = 921 K, P5 = 6.25 atm (c) Conditions: Xf = 0.0150, T2 = 534 K, P2 = 1.62 atm, T5 = 838 K, P5 = 6.26 atm.

Figure 3.12: Ignition delay times for AST I [21] and AST II. AST II data produces significantly reduced scatter and slightly lower mean values than AST I data. Pressure and Φ (equivalence ratio) were normalized to 5.0 atm and Φ=0.5 using P^{-0.86} and Φ^{-1.51} dependences, respectively.

Figure 4.1: Schematic of the aerosol shock tube with pressure and laser diagnostics. The pressure sensors are used for shock speed measurement and ignition delay time determination, the mid-IR HeNe laser is used for absorption-based fuel measurements, the visible laser diode is used for droplet scattering measurements, and the emission measurement is used to measure ignition delay time.

Figure 4.2: Example of an ignition delay time measurement. This example was done with a DF-2 (Cl 43) / 21% O2 / argon mixture with Φ = 0.48, T5=1197K, and P5=7.21 atm. The diagnostics in the upper frame (a) are located 3 cm from the endwall, and in
the lower frame (b) are 5cm from the end wall: (1) Mie scattering extinction, (2) pressure, (3) CH* emission, (4) fuel absorption, and (5) Mie scattering extinction...

Figure 4.3: n-decane/Air ignition delay times. Data conditions ranging over P=4.6-5.2 atm and Φ=1.0-1.9 are scaled to P=5 atm, phi=1.0 using the Olchanski and Burcat correlation [61] (blue diamonds: data; blue line: correlation; black lines: best fit to Shen et al. [48]).

Figure 4.4: n-Dodecane/air and n-dodecane/21% O₂/Ar ignition delay times for fuel-lean mixtures (Φ=0.5) at various pressures.

Figure 4.5: Variation of n-dodecane/21% O₂/Ar ignition delay time with equivalence ratio scaled to 6.0 atm (4.01-8.63 atm).

Figure 4.6: Equivalence ratio dependence of the ignition delay times for n-dodecane at a) 1250K and b) 1000K, both at P=6.0 atm.

Figure 4.7: (a) Comparison of n-hexadecane ignition delay times at 4 atm and equivalence ratio of 1.0 for various oxygen concentrations. (b) Ignition delay time variation with pressure for stoichiometric n-hexadecane / 4% O₂ / Ar mixtures. (c) Ignition delay time variation with equivalence ratio at 4 atm for stoichiometric n-hexadecane / 4% O₂ / Ar mixtures.

Figure 4.8: Ignition delay times of methyl decanoate / 21% O₂ / Ar mixtures at Φ = 0.1 and P=8atm and the ignition delay times from the LLNL mechanism by Herbinet et al. [46].

Figure 4.9: Diesel ignition delay times for three different diesel fuels compared with simulations using the LLNL mechanisms for various surrogate mixtures. Mixtures have an oxygen concentration of 21% with P=6atm and Φ=0.5. Colored, square symbols indicate data taken with aerosol shock tube; black circles represent data taken in a heated shock tube by Penyazkov et al. [55].

Figure 4.10: Variation of ignition delay time with pressure (Φ=0.5) and equivalence ratio (P=6atm) for mixtures consisting of DF-2 (CI 43) / 21% O₂ / Ar.

Figure 4.11: Variation in ignition delay time with aromatic content of diesel fuel. Oxygen concentrations of 4% were used with Ar as the diluent. P=6atm and Φ=0.5. The two diesel fuel blend measurements were compared to simulations of mixtures of n-hexadecane and iso-cetane (CN 42, 46) using LLNL mechanisms [43, 44].
Figure 5.1: Schematic of aerosol shock tube (AST II) setup. The different regions in the tube are (from left to right): A - driver gas, B - incident-shock heated driven gas with no fuel, C - incident-shock heated test mixture with fuel, and D - reflected-shock heated test mixture. Figure 5.2: Diesel OH on-line and off-line laser absorption near 306.7 nm and the difference absorbance signal attributable solely to OH during diesel oxidation. The pre-ignition plateau corresponds to around 10 ppm of OH. Initial reflected shock conditions: ONLINE: 1198 K, 6.69 atm, 1228 ppm diesel; OFFLINE: 1193 K, 6.60 atm, 1197 ppm diesel both in 4% O2 / argon. Figure 5.3: OH and C2H4 species time-histories during n-hexadecane oxidation. Initial reflected shock wave conditions: Φ=1.2, 1267 K, 6.54 atm; initial test gas mixture: 497 ppm C16H34, 1% O2/argon. The constant UV simulation is based on a LLNL hexadecane mechanism by Westbrook et al. [43]. Figure 5.4: C2H4 species time-histories during n-hexadecane oxidation. Initial reflected shock wave conditions: Φ=0.8, 1170 K, 4.60 atm, 326 ppm C16H34, 1% O2/argon; Φ=1.2, 1267 K, 6.54 atm, 497 ppm C16H34, 1% O2/argon; and Φ=1.2, 1333 K, 6.77 atm, 493 ppm C16H34, 1% O2/argon. Modeled using the LLNL model by Westbrook et al. [43] with constant UV and accounting for facility dP/dt. Figure 5.5: OH species time-histories during n-hexadecane oxidation. Initial reflected shock wave conditions: Φ=0.8, 1170 K, 4.60 atm, 326 ppm C16H34, 1% O2/argon; Φ=1.2, 1267 K, 6.54 atm, 497 ppm C16H34, 1% O2/argon; and Φ=1.2, 1333 K, 6.77 atm, 493 ppm C16H34, 1% O2/argon. Modeled using the LLNL model by Westbrook et al. [43] with constant UV and accounting for facility dP/dt. Figure 5.6: OH and C2H4 species time-histories during diesel oxidation. Initial reflected shock wave conditions: Φ=0.54, 1198 K, 6.69 atm; initial test gas mixture: 1228 ppm diesel, 4% O2/argon. Constant UV simulations for single-component surrogate models shown are: n-heptane and n-dodecane which use the JetSurf mechanism and n-hexadecane which uses the LLNL mechanism. Figure 5.7: C2H4 species time-histories during diesel oxidation. Initial reflected shock wave conditions: Φ=0.8, 1119 K, 4.63 atm, 1761 ppm diesel, 4% O2/argon; Φ=0.5, 1198 K, 6.69 atm, 1228 ppm diesel, 4% O2/argon; and Φ=0.6 1373 K, 6.33 atm, 1380
ppm diesel, 4% O₂/argon. Modeled using the LLNL model by Westbrook et al. [43] for n-hexadecane as the fuel with constant UV and accounting for facility dP/dt. ... 91

Figure 5.8: OH species time-histories during diesel oxidation. Initial reflected shock wave conditions: Φ=0.8, 1119 K, 4.63 atm, 1761 ppm diesel, 4% O₂/argon; Φ=0.5, 1198 K, 6.69 atm, 1228 ppm diesel, 4% O₂/argon; and Φ=0.6 1373 K, 6.33 atm, 1380 ppm diesel, 4% O₂/argon. Modeled using the LLNL model by Westbrook et al. [43] for n-hexadecane as the fuel with constant UV and accounting for facility dP/dt. ... 91

Figure A.1: Examples of shock velocity attenuation for various window heating configurations. Note that the old heater raised the temperature in region 1 accelerating the shock near the endwall. ................................................................. 98

Figure A.2: New heated window mount prior to installing on shock tube. Copper tubes are wrapped with ring heaters which conduct heat to windows. The mount is cooled by flowing cool water through inside of mount. ................................................................. 99

Figure B.1: X-t diagram for shock aerosol interaction. Particle breakup occurs fastest with particle acceleration occurring more slowly. Evaporation and diffusion occur most slowly after which the flow is in equilibrium. The measurement location is selected such that all these processes have occurred to a sufficient extent upon arrival of the reflected shock. ................................................................. 101

Figure B.2: Evolution of gas phase fuel concentration. Assuming spherical symmetry and that the droplet instantaneously evaporates. In this case, it takes only 15 µs for the fuel concentration to be 95% uniform. ................................................................. 104

Figure B.3: Time to achieve 95% uniformity with varying volume fraction of liquid for monodisperse size distribution of various diameters. ................................................................. 105

Figure C.1: Picture of aerosol shock tube driver section and additional segments for extending driver length (Photo Courtesy of Matt Campbell). ................................................................. 109

Figure C.2: Pressure trace from pressure transducer located at 2 cm from the endwall on a test using a tailored driver mixture. At 0 ms the incident shock arrives followed closely by the reflected shock. In region 5 the pressure slowly increases by some non-ideal facility effects. At 6 ms the reflection off the contact surface arrives but with no significant pressure jump. The pressure trace is reasonably level until the arrival of the expansion wave at 11 ms. ................................................................. 110
Figure C.3: Figure 4.9 of ignition delay time plot vs. inverse of temperature showing the effect of modeling as constant UV or with a 0.2 atm/ms dP/dt. The effect becomes apparent at test times above 10 ms. ................................................................. 111

Figure D.1: Simplified schematic of the expansion process showing (a) the initial state and (b) the final state........................................................................................................ 112

Figure D.2: Measurements of final pressure (P₁) after expansion of gas/aerosol mixture into dump tank. Initial pressure in the aerosol mixing tank and test section (Pₐ) was around 700 torr and the initial pressure in the dump tank (P₉) was varied. Also shown are various models used to predict the expansion behavior. The hybrid model that assumes isothermal expansion and isentropic compression seems to predict the final pressure quite well................................................................. 113

Figure D.3: Plot indicating how to set initial pressures in the mixing tank/test section and the dump tank. For example, to achieve an equilibrium pressure (P₁) of 100 torr and expansion factor of 2, the mixing plenum and test section should be set initially to 185 torr (Pₐ) and the dump tank should be set initially to 62 torr (P₉). ................. 114
LIST OF TABLES

Table 2.1: Tabulated results from measurement of temperature using the CO$_2$ diagnostic. Results show good agreement between measured temperature and predicted temperatures using AEROFROSH............................................................. 34

Table E.1: Table shows ignition delay time data with associated conditions. See chapter 4 for analysis. ............................................................................................................. 119
Chapter 1: INTRODUCTION

In the United States, the combustion of fossil fuels accounts for over 80% of our energy usage at a cost of nearly $1 trillion per year [1]. Thus any marginal improvement in combustion efficiency can be translated into sizable savings economically as well as environmentally. To achieve this, we strive to understand the process of combustion at its most fundamental level. When modeling the combustion in engines, fluid transport and heat transfer are important. But combustion is ultimately controlled by chemistry, and therefore a chemical mechanism needs to be well-founded for a model or CFD package to be successful.

A chemical mechanism is a road map that elucidates the exact chemical pathways by which fuel and oxidizer are transformed into products. These pathways begin with the fuel molecules breaking apart. Much of the fuel used is in the form of very large hydrocarbon molecules; for example, gasoline, jet-A, diesel, and bio-diesel have average carbon numbers of roughly 7, 12, 16, and 18 (per molecule), respectively. The large molecular size makes the modeling and experimentation of chemical kinetic phenomena difficult: modeling, because the number of species and reactions formed during oxidation
increases; and *experimentation*, because these large molecules have low-volatilities and decoupling the evaporation process from the combustion process is very difficult.

### 1.1 Distillate Fuels

Low-vapor pressure fuels have been and still are very widely used in our society. Their low volatility at atmospheric conditions make these fuels attractive due to a lower risk of unintended explosion, however, it also makes them difficult to work with experimentally.

Diesel fuel is one of the most widely used petroleum-based fuels used today. It is common for large, high-output engines to operate on diesel fuels. Commercial trucks and SUV’s, large industrial equipment such as bulldozers, front-end loaders, dump trucks, boats, locomotives, submarines, electric-power generators, etc., all use diesel fuel. This is because the diesel cycle is more fuel efficient than the Otto cycle; however, some may argue that diesel engines are more harmful to the environment [2]. More recently clean diesel fuel has become more popular, and companies like Mercedes-Benz, Honda, Nissan, and Toyota are starting to produce passenger vehicles that run on diesel fuel in the US. Lower equivalence ratios, tougher standards on fuel composition, and better catalytic converters have all greatly improved the environmental aspects of using diesel fuel. Despite these advances, we still do not have an accurate detailed chemical mechanism that describes the combustion chemistry that takes place inside a diesel engine.

Diesel fuel is a type of distillate fuel created by refining crude oil. Crude oil is a mixture of thousands of hydrocarbon molecules. The refining and cracking process begins by raising the crude oil temperature. As the temperature rises some components start to change phase from a liquid to a gas. Each component has a different response to this temperature increase so the chemical composition of the liquid changes with time. The gas-phase molecules are condensed and then collected in a separate vessel. Depending on what temperature is chosen to start and end this process, crude oil can be separated into many different “cuts” and used for many different purposes. There are
certain standards which define a particular distillate, but nonetheless there is variability in every batch. Some examples of distillation curves for popular fuels are shown in Figure 1.1. The data shows the volume of liquid recovered by the condenser at a given temperature. Gasoline is a lower temperature cut between 50-200C, jet fuel is a slightly less volatile fuel which is cut between 150-250C, and diesel is one of the higher temperature fuels at 200-350C. Bio-diesel, also shown here, is not derived from crude oil, but is manufactured from plant matter. A typical soybean-derived bio-diesel is evaporated between 350-400C. There are many others, but these are the main types of fuels that are distilled from crude oil.

![Distillation curves for common distillate fuels as well as a soybean derived bio-diesel.](image)

Figure 1.1: Distillation curves for common distillate fuels as well as a soybean derived bio-diesel.

The high-temperature evaporation window of diesel is what makes it ideal to use in the diesel cycle and also what makes it very difficult to study. Combustion takes place at temperatures between 700-2500K, and at these conditions all of the components of diesel fuel are in the gas phase in equilibrium. Therefore in order to do a purely gas-phase combustion chemistry experiment, the fuel needs to undergo a phase change before the experiment. To do this we must heat the fuel up to at least 400 C to ensure it is completely in the gas phase. Although rapid oxidation does not occur at these temperatures, slow decomposition and pyrolysis can occur (and probably do occur in the distillation process).
Many of the previous studies of diesel fuel combustion suffer from the effects of evaporation, which complicate the interpretation of the measurement. Some researchers attempt to avoid this by pre-heating the fuel. Heating the fuel too much will prematurely decompose the fuel, whereas failing to raise the temperature high enough will fractionally distill the fuel, thereby altering the composition of the fuel in the gas phase.

An example of an experimental measurement that is intimately connected to the overall chemistry is the ignition delay time. This is the time that it takes for reactants at a certain pressure and temperature to auto-ignite. These measurements can provide crucial targets for the validation of kinetic models; however, for low-vapor-pressure fuels few studies of this type exist. The data that do exist are quite scattered. Representative data are shown in Figure 1.2.

Figure 1.2: Past ignition delay time measurements normalized to 6 atm and an equivalence ratio of 0.5. Many techniques and facilities were used to measure these ignition delay times.
The comparative study of diesel fuel ignition delay time is complicated by the different types of experiments performed over the years, and the simple lack of data on neat diesel itself.

The studies that have been published can be divided into two categories: those done with spray injectors in shock tubes, rapid compression machines (RCM) and engines; and those done with flow tube reactors. Kobori et al. [3] studied diesel surrogate sprays in a RCM (P=41-118 atm, Φ=1). Clothier et al. [4] studied diesel ignition delay times in a single-cylinder gasoline engine modified for diesel operation (P=16 atm, Φ=1). Boiko et al. [5] investigated the ignition of droplets (typically 2 mm diameter) behind reflected shock waves (P=23 atm, Φ=1). Tsuboi and Kurihara [6] studied sooting of a light-fuel-oil spray injected into a shock tube (P=10 atm, Φ=1). Mellor et al. [7] describe the fuel-spray shock tube work of Hurn and Hughes [8] for partially refined diesel fuels as well as other early work (P=35 atm, Φ=1). Tachina [9] studied diesel ignition in a flow reactor. Spadaccini and Tevelde [10] (P=10-30 atm, Φ=0.3-1) and Tevelde and Spadaccini [11] (P=3-5 atm, Φ=0.2-1) advanced this method and used a specialized flow reactor with fully evaporated flows to study diesel ignition times at elevated pressures. The range of these works is shown in Figure 1.2; the data have been normalized to 6 atm and an equivalence ratio Φ = 0.5 using the correlation of Spadaccini and Tevelde [10].

The ignition delay times generated using spray injectors in shock tubes and a RCM are longer than the flow reactor data, because they include the additional time needed to evaporate and mix/diffuse the fuel/air mixture, as well as for ignition to occur. These diesel injector spray studies provide information about the relative ignition properties of different fuels, but analysis of the data is complicated because the chemistry of ignition of these sprays is strongly convolved with the evaporation and flame droplet processes. As a consequence of the large size of the single droplets, the strongly varying spatial distribution, and highly non-uniform size distribution of the diesel injector sprays, details of the shock-spray interaction and the chemistry of these experiments are not easily quantified. On the other hand, the flow tube reactor data, represented by
Spadaccini and Tevelde [10,11] covers the lower temperature regime and attempts to remove the effects of evaporation by preheating the fuel. No shock tube diesel fuel ignition delay data appear to exist for pre-evaporated fuel mixtures.

1.2 SURROGATE FUELS

Along with the study of diesel fuel itself, it is important to also study the individual components of diesel fuel. Most crucial are those components that can appropriately represent the characteristics of diesel fuel. It is impossible to model every component of diesel fuel; therefore, commonly accepted representative surrogates are often used to model the combustion behavior in useful devices.

Distillate fuels can be thought of as being comprised of six different categories of hydrocarbons: normal-alkanes, iso-alkanes, cyclo-alkanes, alkenes, iso-alkenes, and aromatics. A good surrogate mixture includes representative fuel molecules from each of these categories. In the category of n-alkanes, the most prevalent molecule is n-hexadecane or cetane, whose molecular formula is C_{16}H_{34}. A plot of the weight fraction versus carbon number for the n-alkanes reveals a bell curve centered near C16. This is shown for two different batches of diesel fuel in Figure 1.3 (data taken from Farrell et al. [12]).

![Figure 1.3: Chain length distribution of n-alkanes present in two different batches of diesel fuel [12](image)](image)
If we look at the other fuel categories, we also find high carbon number components. For example in the iso-alkane category, iso-cetane (2,2,4,4,6,8,8 heptamethylnonane, an isomer of n-hexadecane) is also an important fuel for understanding diesel combustion. In fact, a mixture of just these two components (cetane and iso-cetane), is the most widely used representative mixture for the ignition behavior of diesel fuel. A mixture of cetane and iso-cetane makes up what is called the primary reference fuel (PRF) for diesel, which provides a standard definition for the cetane number of a fuel. To measure a particular fuel’s cetane number, the fuel’s ignition delay time is measured in a Cooperative Fuel Research (CFR) engine. Then the ignition delay time is matched with that of a particular mixture of cetane and iso-cetane. Cetane has a rapid ignition delay and it is arbitrarily given a cetane number (CN) of 100 whereas iso-cetane has a slower ignition delay and it has a value of 15 (the definition for the lower bound cetane number comes from alpha methyl naphthalene CN=0). The mixture cetane number is a weighted average of its components’ cetane numbers.

The other categories of diesel representative fuel components can be found in Farrell et al. [12]. For aromatics, n-decyl benzene and 1-methyl napthalene were recommended. Others have suggested the use of butylcyclohexane and decalin in the cyclo-alkane category. Another important component is tetralin.

There have been very few combustion studies of these representative fuel components. This again is primarily due to the fact that all of these components, like diesel fuel, have very low vapor pressures. For n-hexadecane there have been some rapid compression machine studies [13], but there has been only one shock tube study [14].

On the other hand, n-alkanes with carbon numbers one through four (i.e. methane (C1) through n-butane (C4)) are gas phase at atmospheric conditions, so these are relatively easy to study. n-Pentane (C5) through n-heptane (C7) are liquids at atmospheric conditions, but have high vapor pressures; therefore, it is still possible to fill a chamber with gaseous fuel up to the saturation vapor pressure at the temperature of the experiment (300K).
When the carbon number is raised even further the vapor pressure drops and this starts to limit the fuel loading to a point where it makes certain high fuel loading conditions inaccessible in shock tubes for fuels as small as n-octane (C8). One common method of dealing with this issue is to heat the entire experimental apparatus in order to raise the saturation vapor pressure of the fuel and avoid condensation. This is very effective and greatly extends the test space of fuels up to n-dodecane (C12), but becomes prohibitive at higher carbon numbers, because the fuel starts to decompose by cracking and pyrolysis when exposed to elevated temperatures for extended periods of time (e.g. the time it takes to make a mixture of fuel and oxidizer). This time varies based on the mixing tank used, but is typically on the order of hours to create a homogeneous mixture. Vapor pressures of selected species as a function of temperature are shown in Figure 1.4. For a typical mixture, partial pressures of 10 to 100 torr of fuel are generally needed.

Recently Penyazkov et. al. [14] has used a heated shock tube to study the ignition behavior of n-hexadecane (C16), and Ristori et al. [13] have studied ignition times of hexadecane (C16) in a rapid compression machine. Based on this work, n-hexadecane appears to be the limit of what is possible with heating. The accessible fuel loading conditions for a very heavy n-alkane, e.g. n-eicosane (C20), would be severely limited using a heated experiment. The need for a better method of testing low-vapor-pressure fuels is apparent for surrogates as well as for diesel.

![Figure 1.4: Fuel surrogate vapor pressures. Heated shock tube temperature limits partial pressure of fuel that can be added to mixtures.](image)

8
1.3 Shock Tubes

Shock tubes have been in use for more than a century and have been prolific in studies ranging from high energy physics and wind tunnels, to chemical kinetics. The study of chemical kinetics in combustion systems is well-suited for shock tubes. The shock tube provides a method to raise the temperature and pressure to a well-controlled value almost instantaneously. The gas is also stagnant and adiabatic providing experimental conditions behind the reflected shock that can be modeled as constant internal energy and constant volume (U, V) when there is negligible chemical energy released.

As shown in Figure 1.5a, a shock tube is basically a long closed tube, which is hermetically separated into two parts: a driver section and a driven section. At the partition between these two sections there is a diaphragm that is designed to burst at a specific pressure difference between the two sections. The driven section is filled with the test gas mixture, and the experiment is initiated by filling the driver with helium (and sometimes a mixture of helium and nitrogen) until the diaphragm bursts. At this point the sharp pressure difference at the rupture creates a shock wave (incident shock) which travels into the driven section, as well as an expansion fan that travels into the driver section (Figure 1.5b). The driven section is made long enough such that the shock wave can become stable and flat. Behind the incident shock the temperature of the driven gas is elevated within a few collisional pathlengths and is also accelerated toward the endwall (this is called region 2). When the incident shock reaches the end of the driven section it hits the endwall cap. This reflects the shock and a new “reflected” shock wave is created and travels in the opposite direction (Figure 1.5c). Because the endwall stops the flow, the reflected shock stagnates the gas headed toward the endwall. This deceleration caused by the reflected shock further heats and compresses the gas (this is called region 5, see Appendix B for an X-t diagram). Near the endwall the gas has stagnated at elevated pressures and temperatures with a well-defined time zero, where it can be easily
studied with various diagnostics. These conditions are only limited by the eventual return to equilibrium brought on by successive reflections of the expansion wave.

Much insight has been gained in the study of combustion using shock tubes. One can measure individual elementary reaction rates, ignition delay times, the high temperature properties of combustion relevant molecules, and much more. Gaydon and Hurle have written a seminal text on the operation and dynamics of shock tubes used for these purposes [15]. A few tens of research groups around the world operate shock tube laboratories to study combustion kinetics.

![Shock Tube Diagrams](image)

Figure 1.5a-c: a. Shock tube prior to shock. Driver is filled till diaphragm breaks. b. Incident shock travels into driven section followed by contact surface. Expansion wave travels into driver. c. The incident shock is reflected at the endwall and forms a reflected shock which travels in opposite direction creating combustion-relevant conditions.
1.4 AEROSOL SHOCK TUBE

The benefits of shock tube reactors can be utilized if we apply them to the study of low-vapor-pressure fuels. In this work, we have developed a method and facility for applying the shock tube technique to low-vapor-pressure fuels, which is called the aerosol shock tube. In this facility, the fuel is loaded in the form of an aerosol and the incident shock evaporates the fuel.

The aerosol shock tube concept is an extension of the conventional shock tube technique. Recall that the heated shock tube technique would involve heating the shock tube and mixing assembly to allow a higher fuel vapor pressure to exist. The problem with this method appears prior to the shock initiation in the shock tube or mixing tank when the fuel temperature is too high for too long. The fuel will begin to decompose prior to the combustion experiment during the mixing and filling of the shock tube. The aerosol shock tube method avoids this by reducing the amount of time that the fuel is at elevated temperature prior to the combustion experiment from hours to fractions of a millisecond.

We can reduce the heating time by taking advantage of the inherent gas-dynamics that occur in a conventional shock tube. In shock tubes, the gas mixture being studied undergoes two subsequent shock compressions, first an incident shock, which approximately doubles the temperature (~600K) in current experiments and next the reflected shock which again raises the temperature by another factor of two (~1200K). This intermediate step (region 2) can be taken advantage of in the case of low-vapor-pressure fuels. The temperatures in this region (500K-800K) can evaporate almost any distillate liquid fuel that is in use today (in approximately 100 µs, See Appendix B for details about shock-aerosol interactions). Then the reflected shock will bring the purely gas-phase mixture to combustion-relevant temperatures where the chemistry can be observed.

The difficulty becomes how we load the shock tube with liquid fuel prior to the initiation of the incident shock. The amount of gaseous fuel needed in the typical
combustion experiment is small (~1%) compared to the total amount of gas required. Furthermore, in liquid form, the density is about a factor of 1000 times higher. Thus, only tens of ppm of liquid fuel volume fraction is typically needed. This concentration can be achieved by aerosolizing the liquid fuel using ultrasonic nebulizers and then flowing it into the shock tube (Figure 1.6). Once the aerosol is in the shock tube, the shock is initiated. The incident shock propagates as it would normally, but at a slightly lower speed due to the fact that the heat of vaporization of the droplets acts as an enthalpy sink behind the shock wave. When a droplet is shocked it is quickly evaporated and diffusion rapidly levels out the spikes in concentration (Appendix B). This leaves behind a completely uniform, gas-phase mixture of combustible gases. Then, the reflected shock further raises the temperature to the point where combustion can take place in the test time available.

![Fuel Aerosol Suspended in Oxidizing Bath-gas](image)

Figure 1.6: Aerosol shock tube prior to initiation of shock. Liquid or solid particles are loaded uniformly in the driven section to experiment on low-volatility fuels.

This ideal operational view brings up some obvious questions of practicality and implementation. For example, how do we ensure uniformity in the initial distribution of aerosol? This question was one of the hardest obstacles to overcome in order to successfully implement this method. Any spatial non-uniformity in the initial aerosol would greatly affect the uniformity of the final mixture behind the reflected shock. In this thesis, I will first introduce the method of filling that was previously used when the aerosol shock tube was first envisioned as a facility for studying the interaction of aerosols with incident shock waves. We call this the first-generation aerosol shock tube (AST I). Then I will describe the testing and methodology involved in the second-
generation aerosol shock tube (AST II). The improvements made result in improved spatial uniformity of the aerosol in the initial mixture.

1.5 CONCLUSIONS

There is a definite need to expand current modeling efforts to larger fuel molecules; however, the experimental challenge of separating the evaporation process from the combustion process becomes difficult for these fuels. Little to no experimental data exist for distillate fuels such as diesel and bio-diesel. The data that does exist for diesel fuel is widely scattered, and a successful method has not yet emerged to separate the evaporation effects and examine the purely chemical phenomena that occur during the oxidation of this fuel.

Fuel surrogates have been identified; however, these compounds also suffer from the challenges associated with low volatility. Consequentially, there have been very few experiments probing the combustion chemistry of these low-volatility fuels. Some surrogates such as n-hexadecane have been studied in a heated shock tube, which uses elevated temperatures to increase the vapor pressure of the fuel to allow more fuel into the test mixture. However, these studies may be subject to premature decomposition.

We have developed a new method called the aerosol shock tube, which takes advantage of shock tube methodology while avoiding the problem of premature decomposition. The shock tube is loaded with an aerosol made up of liquid fuel droplets surrounded by a gaseous oxidizer and diluent. This aerosol is rapidly evaporated behind the incident shock, and then the reflected shock brings it up to combustion relevant temperatures.

This solution presents a unique approach to gas phase experimentation for low-vapor-pressure fuels. For this method to work properly with applications to combustion, many technical challenges must be solved. These issues will be discussed in the next two chapters.
Chapter 2: COMBUSTION STUDIES IN THE AEROSOL SHOCK TUBE

This chapter is devoted to the details of the aerosol shock tube and the challenges in making it a successful approach to study the combustion kinetics of low-vapor-pressure fuels. Aerosol shock tube operation begins with the aerosol generation. This process has been refined and well-characterized. Then the filling method is described. This dictates the spatial uniformity of the aerosol. Filling and uniformity will briefly be introduced for the first-generation filling technique, and then will be covered more completely for the second-generation technique later in Chapter 3. Essential measurements will then be discussed such as shock speed measurements, as well as fuel concentration measurements. These measurements are critical for calculation of the conditions (temperature and pressure) of the combustion experiment.
2.1 AEROSOL GENERATION

At the foundation of this method is the generation of liquid fuel aerosols. There are many different devices available for the generation of aerosols, all of which produce aerosols with different properties. For example in a diesel engine, the aerosol generator is incorporated in the fuel injectors. These fuel injectors employ a high-pressure pump that forces the fuel through a small orifice, and jetting leads to Rayleigh instabilities, which break up the jets into droplets. These droplets range from 10-100 µm in size. The terminal velocity is too fast for the aerosol shock tube, where the aerosol must stay suspended and not be lost to the walls of the shock tube. In order to make smaller droplets, which take longer to settle, a more advanced method is needed.

Many devices operate by the principle that a piezoelectric material will physically expand and contract under the influence of an alternating current up to very high frequencies. This effect can be utilized to create standing waves on the surface of a liquid that will pinch off into small droplets. If this frequency is on the order of a megahertz, the resulting droplet diameters are on the order of microns. This droplet size is more appropriate for the loading of an aerosol shock tube as the settling time is a few minutes. For the aerosol shock tube, we utilize an array of piezoelectric disks submerged in the liquid fuel to aerosolize large quantities of the fuel (See Figure 2.1 for a cut-away of one nebulizer). The devices that contain the piezoelectric disks are called ultrasonic nebulizers, and this process is referred to as nebulizing the fuel. The resultant droplet size distributions of the various fuels are measured using a Malvern Spraytec™ (Model RTS5214) particle sizer.
These banks of nebulizers (Mist Maker™ 12-disk Nebulizer Bank Model DK12NS) are located outside of the shock tube in a vacuum-sealed compartment. During operation the liquid surface is somewhat violent, and for optimal aerosol generation the ceiling of the compartment must not come in contact with the bulk surface of the fluid. This requires a ceiling height of at least six inches above the surface of the liquid. The piezoelectric transducers output so much energy that large spires or jets are sustained above each jet. These jets can reach heights of four inches. These large disturbances are a result of the localized forcing of the surface and a spatial low-frequency response. There also exist standing waves which represent the spatial high-frequency response to the vibration. These look like tiny lumps or hairs on the surface of the spires and are responsible for pinching off the droplets. The large jets are continually sloshing and breaking-up, and as a result some very large droplets are made (5 mm), but these immediately fall back into the liquid pool, and only the micron sized droplets remain. See Figure 2.2 for picture of a nebulizer bank in operation.
To accurately measure the droplet sizes the aerosol must be made and entrained in a gas flow to transport it to the particle sizer. The experimental setup is shown below in Figure 2.3, and the results of these measurements for water, n-dodecane, and diesel fuel are shown in Figure 2.4. These distributions are all approximately the same. This is due to the fact that droplet size is most intimately related to the nebulizer frequency, and not as sensitive to the liquid’s surface tension and density. The result is a mass mean droplet diameter around 4 µm with a spread between 1-10 µm.
2.2 Loading the Aerosol into the Shock Tube

Loading the aerosol into the shock tube homogeneously is a difficult task; the quality of our combustion measurements relies heavily on the homogeneity of the mixture. For aerosols, any small spatial non-uniformity translates into a large, gas-phase non-uniformity. I will first discuss the simpler first-generation method of filling used in AST I. The next chapter contains a description of the more complex improvement of this method used in AST II.

Once these micron-sized particles are created, their large settling times and their small Stokes Numbers allow for easy entrainment in the gas flow. The droplets track the flow of bathgas very closely. Typically the bathgas is a mixture of an inert gas Ar or N₂ and the oxidizer O₂ in a ratio that is prescribed by the combustion experiment. The bath gas flows into the nebulizer compartment at or below the level of the liquid fuel and bubbles to the surface. From there the gas-aerosol mixture flows through a two inch inner diameter conduit, then through poppet valves in the endwall into the shock tube, and continues flowing along the entire length of the driven section to an outlet port in the sidewall of the shock tube near the diaphragm (Figure 2.5). Once a steady state flow is
setup throughout the shock tube, the shock tube is considered loaded. To initiate a shock all the valves are closed and the flow is stopped, then the driver is filled until the diaphragm breaks and the shock is created.

Figure 2.5: Schematic of first-generation aerosol shock tube (AST I) filling method. Aerosol spatial uniformity was insufficient for high quality combustion experiments. Chapter 3 discusses an improved design.

A very important aspect of this design is the poppet valves at the endwall. These valves are specially designed such that when they are opened they create turbulence in the flow, and once closed they create a very flat endwall. The design used was similar to those in an internal combustion engine for the intake and output of gases. There are four poppet valves which fill the endwall cross-sectional area. The poppet valves are opened only slightly to create jets of high-speed bathgas that are mixed with the low speed gas near the edges of the opening. This mixing creates turbulence, and serves to fill all the voids and corners uniformly with aerosol laden bathgas. Further down the tube the turbulence dampens out and dissipates, and the result is plug flow. This plug flow exhibits some unwanted river effects (this is described in detail in Tom Hanson’s thesis [16]). Essentially as the aerosol makes its way down the tube the aerosol settles and sets up a dense flowing river of aerosol on the bottom of the shock tube while the top of the shock tube is void of aerosol.

2.3 **MEASURING SHOCK SPEED**

With the aerosol in the tube and the valves closed, the shock can be initiated by filling the driver and bursting the diaphragm (See Figure 4.1 for the experimental arrangement of the pressure transducers and Figure 2.6 and Figure 2.7 for representative
attenuation plots). The shock velocity is carefully monitored using fast pressure sensors that indicate the position and relative timing of the shock. By dividing the distance between transducers by the time interval, we can calculate the velocity. Typically the velocity of the shock decreases as it propagates through the driven section of the shock tube. This is due to the fact that there is viscous dissipation near the sidewall of the shock tube. The attenuation of the shock is typically linear with about 2%/m attenuation rate (Figure 2.6). It has been observed that when a shock encounters an aerosol, this further attenuates the velocity (Figure 2.7). The temperature is related to the square of the Mach number, so any error in the velocity measurement will drastically affect the temperature uncertainty. Thus having accurate spatially resolved velocity measurements is very important to making quality combustion chemistry measurements.

Figure 2.6: Attenuation of shock velocity in a dry argon shock. Attenuation rate is 2.1%/m. Shock conditions: \( P_1 = 0.26 \text{ atm}, T_1 = 295 \text{ K}, P_2 = 1.6 \text{ atm}, T_2 = 715 \text{ K} \).
Figure 2.7: Attenuation of shock velocity in a n-dodecane aerosol. Attenuation rate is 3.6%/m. Shock conditions: $P_1 = 0.18$ atm, $T_1 = 294$ K, $P_2 = 1.4$ atm, $T_2 = 695$ K, $X_f = 0.63\%$, $X_{O_2} = 21\%$, balance Ar, Droplet loading by volume: 10.0 ppmv (volume of liquid per volume of gas).

### 2.4 Fuel Measurement

In the aerosol shock tube the conventional method of fuel concentration measurement cannot be used. In the conventional method, the fuel concentration is determined manometrically when making the mixture in a separate mixing tank. The mixing tank is equipped with a pressure sensor, and the fuel is added to an empty mixing tank. The pressure is recorded, and then the next component is added. The pressure of each successive step is recorded, and the mixture mole fractions can be calculated using Dalton’s Law. The method of measuring pressure to indicate total mole fraction does not work in a multi-phase mixture.

In the aerosol shock tube to measure the amount of fuel, we have employed two methods. First we measure the amount of fuel in the liquid phase (via a size distribution measurement) and add it to the vapor pressure at the measured temperature of the shock tube. After verifying that all the fuel has evaporated behind the incident shock, the fuel absorbance can be measured for the resulting gaseous mixture. The measurement is typically made near the endwall in the same location that the combustion measurements are made.
2.4.1 **IN-SITU MEASUREMENT OF DROPLETS**

The first method was used extensively in the first-generation aerosol shock tube in the study of the shock-droplet interactions, typically in water aerosols [16]. Measurements were made using a Mie scattering light extinction technique in a forward-scattering orientation (Figure 2.8). Because the droplet size distribution was typically lognormal and varied only slightly in average size and spread, a minimum of three different lasers were required to fit the size distribution. The different wavelengths of light were generated using fixed wavelength laser diodes, and were combined to pass through the shock tube on the same beam path. We used five wavelengths optimized for sensitivity to the droplet sizes expected. The typical aerosol concentration ($C_v$) was between 5-20 ppmv.

\[ C_v = \frac{V_{liq}}{V_{gas}} \]

Figure 2.8: Schematic of Mie-scattering diagnostic for measurement of liquid volume concentration.

2.4.2 **GAS-PHASE LASER ABSORPTION**

The second method involves measuring the gaseous fuel concentration directly after it is evaporated. This can be done by measuring the fuel absorption of a particular resonant wavelength (Figure 2.9). This measurement requires using two lasers of different wavelength. One wavelength is resonant and measures the fuel absorption (Figure 2.9) which is related to the concentration through the Beer-Lambert Law.

\[ \alpha \equiv -\ln \left( \frac{I}{I_0} \right) = \frac{\sigma_{PL}}{RT} X_f \]

Equation 2.1
where $\alpha$ is the absorbance, $I$ is the intensity of the light through the shock tube, $I_o$ is the incident intensity, $\sigma$ is the cross section ($m^2$/mole), $P$ is the pressure, $L$ is the path length, $R$ is the universal gas constant, $T$ is the temperature, and $X_f$ is the cross section.

![Schematic of gas phase laser absorption measurements.](image)

Figure 2.9: Schematic of gas phase laser absorption measurements.

The second laser is at a non-resonant absorption wavelength (Figure 2.8) and indicates the presence of liquid droplets. The non-resonant wavelength is chosen such that there are no gaseous absorption features in the mixture that will absorb the light. This diagnostic is then only affected by the presence of a liquid phase. Just as in the droplet size diagnostic, the attenuation of light due to liquid droplets present in the mixture is caused by Mie scattering. This also means if there is any condensation on the windows this laser is affected, which is an indication that the data from the other laser is suspect. So this non-resonant laser also doubles as a window cleanliness monitor. Usually heating the windows resolves most condensation problems (See Appendix A for a more detailed explanation).

### 2.4.3 Fuel Spectroscopy

There is a resonant wavelength for most hydrocarbons in the mid-IR, where the CH stretch rovibrational band lies. This rovibrational band typically has three main peaks and these correspond to the CH$_2$ functional group, the CH$_3$ functional group, and a combined band. We take advantage of a transition in the HeNe laser that overlaps with this rovibrational band. There are only a few manufacturers that make very low noise
HeNe lasers with optics for transmitting 3.39 µm light. We use the Jodon™ HN-10-GIR. The laser linewidth is very narrow and near the center of the CH stretch band.

For larger molecular weight molecules of interest, which have many carbon-hydrogen bonds, the multitude of rovibrational states is so dense that the spectrum is not a function of pressure; however, there is a temperature dependence. Raising the temperature serves to populate higher energy transitions and effectively spread the population over a wider range of energies. The result is a smoothing of the feature. More specifically the peaks decrease and the tails increase (Figure 2.11). Because the HeNe laser sits on a point of inflection, the temperature dependence of the cross section is relatively weak, until about 500 K where it then decreases monotonically.

There is also another option for measuring fuel in the CH stretch band. A difference-frequency-generation (DFG) laser has been recently commercialized, which gives access to a range of wavelengths in this band. This is particularly useful because the fuel spectrum can be used to measure temperature, the fuel concentration in the presence of droplets, or window fouling as in Klingbeil et al. [17].

### 2.4.4 FTIR/Heated Cell Measurements

The measurement of cross section must be carefully made for each fuel that we study. We make these measurements in both heated cells and shock tubes and cross-correlate the data. In the heated cell we use a well-characterized oven to control the temperature. The fuel is evaporated into a heated tank. Because the maximum working temperature of the pressure transducer is lower than the temperatures needed to keep the fuel in the gas phase, a N₂ buffer was occasionally required in the gas line of the pressure transducer. This avoids condensation on the pressure sensor’s head.
The cell has two sapphire windows through which a collimated beam from an FTIR passes. The beam is then detected on a liquid-nitrogen-cooled MCT detector, a Thermo Scientific™ Model MCTA (Figure 2.10). The FTIR measures the cross section over the entire band (Figure 2.11). These measurements can be made very precisely up to 300°C (Figure 2.12); but in the time it takes to average over many scans (two minutes) at higher temperatures the fuel begins to decompose. One method of checking for this decomposition is to look at the integrated band strength at each temperature. The integrated band strength is defined as the integral of the absorbance over the entire band. If this is constant, then no CH bonds have broken and left the population. If it decreases at high temperature, then some CH bonds have been destroyed. This is further evidence that the fuel cannot spend a long time at elevated temperatures. Measurements can be made faster by averaging fewer scans, allowing measurements up to 500°C, but result in larger error bars. To go to even higher temperatures we need to use the aerosol shock tube, itself.
Results of measurements of the CH stretch band are shown in Figure 2.11 for methyl decanoate at several different temperatures. It becomes apparent that the HeNe laser at 3.39 μm wavelength does not have the largest cross section. In experiments with low fuel loading, it would be beneficial to the fuel sensitivity to select a wavelength slightly above 3.4 μm to maximize the cross section. This can be done using a DFG laser instead of a HeNe.

Most of the work in this thesis uses high fuel loadings, so low absorption is not as much of an issue, and the 3.39 μm cross sections are sufficiently strong. To summarize the data presented in Figure 2.11 for 3.39 μm, we plot the cross section at this wavelength versus temperature as in Figure 2.12. This plot shows the cross sections of many low-vapor-pressure fuels. Most fuels exhibit little temperature dependence in this temperature range. This is not the case if we extend our measurements to higher temperature using the aerosol shock tube.
Figure 2.12: Summary of cross section measurements at 3.39 μm for various fuels measured using the heated cell and FTIR.

### 2.4.5 Shock Tube Measurements of High Temperature Cross Section

A shock tube can access higher temperatures using step changes in temperature. The fuel concentration can be measured behind the incident shock, and then the known amount of fuel can be used to measure the cross section behind the reflected shock. First the cross-section is measured to as high a temperature as possible in the heated cell / FTIR setup (Figure 2.10). Next the shock tube is filled with a fuel aerosol. A shock is initiated such that region 2 (the conditions behind the incident shock) is at a temperature within the range of temperatures that were measured in the heated cell, but hot enough that the fuel completely evaporates in region 2. Then the purely gas-phase absorbance can be measured. When the reflected shock further heats the purely gas phase mixture (region 5) the concentration is not changed. By measuring the ratio of the absorbance of region 5 to that of region 2 (where the cross section is known) we can calculate the cross section in region 5 shown in the equation below (Equation 2.2).
\[ \sigma_5(T_5) = \frac{\alpha_5}{\alpha_2} \sigma_2(T_2) \]  

Equation 2.2

where \( \sigma(T) \) is the cross section usually measured in m\(^2\)/mole at a specified temperature, and \( \alpha \) is the absorbance (defined in Equation 2.1) as measured in the heated cell (lower temperature) and the shock tube (high temperature). The subscripts 2 and 5 refer to region 2 (behind the incident shock) and region 5 (behind the reflected shock).

This operation can be repeated for a wide range of temperatures and each of the regions can be made to overlap to check the self-consistency of these measurements, thereby measuring the cross-sections at temperatures ranging from 300K all the way to 1200K. See Figure 2.13 and Figure 2.14 for examples of the experimental data for n-dodecane and JP-7 respectively.

![Figure 2.13](image-url)

Figure 2.13: Cross section measurements of n-dodecane at 3.39 \( \mu \)m extended to high temperatures using the aerosol shock tube.
These high temperature cross sections exhibit increased scatter as compared to the low temperature measurements of cross section. The uncertainty of the heated cell measurements are around 3-5%, whereas the uncertainty of the high-temperature measurements is on the order of 10%. The measurements in the shock tube incorporate additional error due to the fact that at these high temperatures the fuel begins to decompose quickly. Thus we rely on a measurement of the absorption immediately after the arrival of the reflected shock, which is sometimes convoluted with the schlieren spike in absorption. This added scatter only affects the degree to which we know the high-temperature cross sections. It does not affect how well we know the fuel concentration, because we use the fuel concentration measurement from region 2.
2.5 **Calculation of Equilibrium Shock Jump Conditions**

Measurements of gas phase absorption are not all that is required to measure the fuel concentration. In Equation 2.1, the absorbance \( \alpha = -\ln(I/I_0) \) is measured in the shock experiment (Figure 2.15), \( \sigma \) is measured in the heated cell with the FTIR. But to find \( X_f \), we need to know \( T \) and \( P \). Typically \( T \) and \( P \) are found by measuring the shock velocity and applying the shock jump relations to find \( T \) and \( P \) in regions 2 and 5; however, to do that one needs to know the initial gas composition or \( X_f \). This introduces an extra unknown, and to solve this, an extra equation is required. This can be accomplished by coupling the conservation of mass, momentum and energy equations to the Beer-Lambert equation. The solution of this set of equations is done numerically with a program called AEROFROSH (Appendix F) by iterating the fuel concentration to find a solution that satisfies all the equations.

![Graph](image)

*Figure 2.15: Example of fuel measurement behind an incident shock wave. The red trace shows droplet scattering and absorption. The black trace shows only droplet scattering. Arrival of the incident shock occurs at 0 µs and arrival of the reflected shock occurs at 500 µs. Conditions: 21% O₂ in Ar with \( X_f \) (n-dodecane mole fraction) = 0.00680, \( T_2 = 617 \) K, \( P_2 = 1.11 \) atm, \( T_5 = 993 \) K, \( P_5 = 4.23 \) atm. Measurement location is 10 cm from endwall.*
2.5.1 Validation of AEROFROSH

AEROFROSH was tested against analytical solutions made by Ghua et al. [18] and Marble et al. [19] for a water aerosol being evaporated by a shock wave. Figure 2.16 shows the temperature behind an incident shock whose strength is such that the ratio of pressure behind the shock to the initial pressure is 3. This plot was made to replicate Figure 4 in Ghua’s work [18]. The initial quality of the water was varied to understand the effect on the post-shock temperature. Up to 6% (by mass) liquid, there is an inverse relationship between post shock temperature and quality. This is due to the enthalpy lost to the heat of evaporation. However, at higher qualities the post-shock temperature stays constant with increasing quality, because here the post-shock gas phase is in equilibrium with the liquid phase at the saturated vapor pressure, and as a result droplets remain. AEROFROSH calculations agree with Ghua within the operational range of the aerosol shock tube. Also at the limit of complete evaporation AEROFROSH agrees with the calculations in Ghua et al. [18] and Marble et al. [19].

![Figure 2.16: Comparison of AEROFROSH calculations to those made by Guha in 1992 [18] and Marble made in 1968 [19] for a shock traveling in pure water of varying initial quality.](image)
AEROFROSH was also used to predict the conditions in the aerosol shock tube. To validate the calculations, we measured pressure near the endwall, and compared the measured pressure to the calculated pressure. The measurements matched the calculations to within the measurement error of 3% (Figure 2.17).

![Figure 2.17: Comparison of measured pressure (2 cm from the endwall) with those predicted by AEROFROSH](image)

To increase the sensitivity of our validation target, temperature was measured using two methods. The first was done using two DFG lasers that probed two different wavelengths in the CH stretch band for n-dodecane. The pair chosen had a ratio of cross-sections that was dependent on temperature. This enabled a sensitive measurement with an error in temperature of 5% [17]. Figure 2.18 shows the agreement using this measurement technique is within the measurement error. It is, however, slightly disconcerting that at high temperatures we see that the error is not random and has a systematic offset. We believe that this is due to slight decomposition of the fuel. This prompted further study using a more stable molecule for this temperature measurement.
The second method of temperature measurement involved using a two-line CO$_2$ diagnostic, which is described in Ren et al. [20]. This method was much more accurate with an error of only $<2\%$ in temperature. Within the accuracy of the measurement, the calculations of conditions are correct using AEROFROS (Figure 2.19).

![Figure 2.18: Comparison of measured temperature using a two-wavelength fuel diagnostic with calculated temperature.](image)

![Figure 2.19: Comparison of measured temperature using a two-line CO$_2$ technique with calculated temperature.](image)
### Table 2.1: Tabulated results from measurement of temperature using the CO₂ diagnostic. Results show good agreement between measured temperature and predicted temperatures using AEROFROSH.

<table>
<thead>
<tr>
<th>Region 2</th>
<th>Region 5</th>
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<tbody>
<tr>
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<tr>
<td><strong>AEROFROSH</strong></td>
<td><strong>Measured</strong></td>
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<tr>
<td>K</td>
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<tr>
<td>687</td>
<td>689.5</td>
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<tr>
<td>678</td>
<td>667.2</td>
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<tr>
<td>583</td>
<td>591.5</td>
</tr>
<tr>
<td>528.5</td>
<td>533.4</td>
</tr>
</tbody>
</table>

### 2.6 Applications of Measurements Behind Reflected Shock Waves

Once we are confident that the calculated conditions behind the incident shock are correct, we can easily apply the shock-jump equations to solve for the conditions behind the reflected shock wave (assuming stagnated flow in this region). Then, with well-defined conditions, high quality combustion chemistry measurements behind the reflected shock can be made.

The main application of this facility is in providing validation targets for detailed chemical kinetic models. These can take the form of ignition delay times, emission, and/or species-time history measurements.

Ignition delay times provide a single number to test simulations of the entire mechanism. The ignition delay time is defined as the time in which it takes a certain gas phase mixture to auto-ignite at a given temperature and pressure. Because this time depends on all the intermediate reactions it is a good metric for mechanism validation. The ignition event is characterized by an exponential rise in the reaction rate governed by a thermal or radical chain reaction. This causes an exponential rise in the products, OH and CH as well as a rapid consumption of hydrocarbons. For energetic mixtures the pressure and temperature will rise very sharply.
Figure 2.2a,b: a. Plots of pressure versus time measured 2 cm from the endwall in AST I for mixtures of n-dodecane / 21% O$_2$ / Ar at various temperatures $\Phi = 1.0$, $P = 6.0$ atm. b. Summary of ignition delay times plotted on an Arrhenius plot.

Shown in Figure 2.2a are the pressure traces for a mixture of n-dodecane and 21% O$_2$ in Ar at various temperature. Each of these experiments can be plotted on an Arrhenius plot to show more clearly the temperature dependence (Figure 2.2b). In this case we used pressure to indicate ignition, but OH* and CH* emission can also be used. A comparison of the measured ignition delay time to the mechanism will reveal the success or failure of a kinetic model. The relative behavior of the model with changes in initial temperature and pressure can give insight into which elementary reactions or reaction pathways are missing or in need of adjustment.

The ignition delay time is very useful; however, it is only one parameter, and with a model that has so many parameters it is not enough to constrain the mechanism completely. Therefore we can also measure species time histories and compare those to the simulated species time-histories produced using the mechanism. These measurements provide an account of the evolution in time of the concentration of a certain molecule in the gas mixture. The comparisons are most useful when comparing a molecule that is involved in many of the key reactions of a mechanism. In some cases, these measurements provide the basis for a fitting scheme where the most sensitive reaction rates are perturbed to enforce fitting between the model and the measurements.
2.7 Conclusions

In this chapter we looked at the details of how the aerosol shock tube works, and how it can be used to make very useful measurements of the combustion chemistry of low-vapor-pressure fuels. The aerosol is generated using ultrasonic nebulizers and has a size distribution typically between 1-10 µm. The aerosol can be entrained in an oxidizing bath gas and flowed into the shock tube. The incident shock wave is used to evaporate and mix the fuel, and at this stage laser absorption is used to probe the CH stretch rovibrational band to measure the purely gas phase absorbance. With that information and the shock speed we use AEROFROSH, which couples the shock jump equations to the Beer-Lambert relation to calculate the conditions and fuel mole fraction. We verified that this calculation procedure matches measurements, ensuring the quality of these measurements. This method is shown to be a very useful tool for the study of chemical kinetics. However, the aerosol uniformity, which has not been discussed in great detail, will be discussed in the next chapter.
**Chapter 3: Uniformity in the Aerosol Shock Tube**

The improved, second-generation aerosol shock tube (AST II) has been developed for the study of the chemical kinetics of low-vapor-pressure fuels. These improvements enable a wider range of fuel concentrations and enhanced spatial uniformity relative to our initial aerosol shock tube design (AST I). In addition, the design of AST II limits the aerosol loading zone in the shock tube to a fixed region (1.2 m in length adjacent to the shock tube endwall). AST II achieves these improvements by using a separate holding tank to prepare the aerosol mixture and a slightly under-pressure dump tank to carefully pull the aerosol mixture into the tube in a plug-flow. This filling method is capable of producing room temperature test gas mixtures of n-dodecane with equivalence ratios of up to 3.0 in 21% O₂, three times the loading achievable in the earlier AST I that used a flow-through strategy. Improvements in aerosol uniformity were quantified by measuring the liquid volume concentration at multiple locations in the shock tube. The measurements made over a length of 1.1 m of shock tube indicate that the AST II method of filling produces non-uniformities in liquid volume concentration of less than 2%, whereas in the AST I method of filling the non-uniformities reached 16%. The
improved uniformity can also be seen in measurement of gas phase fuel concentration behind the incident shock wave after the liquid droplets have evaporated. Significant reduction in the scatter of ignition delay times measured using AST II have also been achieved, confirming the importance of uniform loading of the aerosol in making high-quality combustion measurements.

3.1 INTRODUCTION

Although shock tubes are normally used to study purely gas-phase phenomena, they have also been used to study aerosols [21-31]. The primary challenge, however, in studying aerosols in shock tubes is in achieving a spatially uniform distribution of aerosol test mixture. A spatially non-uniform aerosol mixture can degrade the quality of the shock tube data; in earlier studies [21-31], non-uniformity in the spatial distribution of the aerosol tended to complicate the interpretation of the measurements and the determination of incident and reflected shock test conditions.

The uniformity of the final (post-evaporation) gas mixture is highly dependent on the spatial uniformity of the initial aerosol concentration. High levels of uniformity are easily achieved in gaseous mixtures because gases occupy the entire volume. However, an aerosol/gas mixture does not behave in this ideal manner. During filling, the gas tends to accelerate faster than liquid droplets, leaving the droplets behind and thus creating a spatially non-uniform aerosol loading. Smaller droplets will track the gas flow better, but small diameters render high fuel loadings difficult. A balance must be met between the benefit of high fuel loadings as gained from using larger droplets and the benefit gained by having smaller droplets which track the gas-phase flow and more easily form uniform spatial distributions. Previous work has found this balance in droplets created by ultrasonic nebulizers with mass mean diameters of around 4-5 µm [21, 22].

Other researchers have also been concerned with filling a tube with aerosol. Some have used a direct-injection aerosol filling strategy. One such method is to use a point source or sources where fuel injectors spray the fuel directly into the shock tube either prior to arrival of the incident shock, after the incident shock or after the reflected
shock [24-28]. However, these methods produce extremely non-uniform conditions due to the fact that the spray comes out in a cone pattern and there are regions in the tube that are not filled completely. Another method is to prepare a mixture of aerosol in a separate volume, after which the aerosol mixture can be expanded into the shock tube through a tube connecting the two volumes with a valve to control the filling process [29-31]. These methods are better suited for smaller particle sizes, on the order of sub-microns, because the high acceleration of the gas at the small area orifice will result in significant lagging of larger diameter particles. No quantification of the spatial uniformity was found in the studies discussed above; however in ref. [31] a uniformity of around 20% rms was extracted from time-resolved drum-camera measurements.

There also have been a number of studies in which a uniform mixture of aerosol is created in a continuous flow scheme. In these schemes the aerosol is generated in a moving stream of gas and carried with the gas flow. The gas flow is made to pass turbulence-generating structures in order to mix the aerosol; this approach is commonly used in aerosol wind tunnels. In one study, ref. [32], non-uniformities as low as 11% over a 30x30 cm cross-section of the wind tunnel for aerodynamic droplet sizes of 10 µm were reported. Using a similar technique, Brown was able to achieve ±10% variation in aerosol concentration [33]. At very low pressures of 1-10 torr, other researchers have tried with partial success to minimize spatial non-uniformities [34, 35].

These continuous-flow filling techniques have also been used in shock tubes, For example, the first-generation aerosol shock tube, built in our laboratory, used a continuous-flow filling technique [21, 22, 36]. In this facility, the aerosol is created with an ultrasonic disk nebulizer submersed in a liquid fuel pool. A continuous flow of gas is established over the nebulizer, into a manifold, through the shock tube endwall, through the entire length of the shock tube driven section, and into a mechanical pump. The aerosol carried by this flow of gas into the manifold is accelerated through a series of slightly opened poppet valves in the shock tube endwall. The narrow passages of the poppet valves create turbulence which mixes the aerosol, creating a uniform aerosol near the endwall. As the mixture flows further away from the endwall the turbulence
dissipates and the aerosol tends to settle to the bottom of the tube resulting in non-uniformities. The uniformity has been measured using a light sheet and imaging the scattering at 90 degrees. The best uniformities seen with this method (variations of ±24%) were found at the greatest observation distance from the shock tube end wall (45 cm) in the study. Results from gas phase absorption of the fuel behind the incident shock indicate that this non-uniformity is lessened by the process of evaporation and diffusion, because variations as small as only ±1.7% were reported using the same filling techniques [21].

The goal of the current study is to develop a new method to introduce aerosol into the shock tube, with higher spatial uniformity (particularly over the last meter of shock tube length nearest the endwall), and with the flexibility to fill the shock tube with a wider range of aerosol loadings.

3.2 AEROSOL SHOCK TUBE GENERATION II

3.2.1 EXPERIMENTAL APPARATUS

A simplified schematic of the experimental setup is shown below in Figure 1a. The schematic shows a cross-section of the shock tube as viewed from the side. The driver section of the shock tube is separated from the driven section (8.4 m long and 10 cm square cross-section) by a thin polycarbonate diaphragm. The test section (1.2 m long and 10 cm square cross-section), which contains the aerosol, is separated from the rest of the driven section by a gate valve. The gate valve was specially designed to make a smooth interior when opened, and when closed restricts the aerosol from filling the entire driven section of the shock tube. Another gate valve at the end of the test section acts as the endwall when closed. When open, the endwall gate valve allows aerosol to flow into the test section from the aerosol mixing plenum (50 cm long and 24 cm diameter). The 83 liter dump tank is connected through a 5.5 mm orifice and ball valve to the test section and provides expansion volume as the aerosol is pulled into the test section.
The procedure for filling the shock tube in four steps is shown in Figs. 1a-1d. First, the gas pressures in all volumes are set (with all valves closed) with a mixture of oxidizer and diluent. The aerosol mixing plenum and the shock tube test section are set to pressure $P_A$. The pressure $P_B$ in the dump tank is set lower than $P_A$. The pressure in the rest of the driven section is set to the final desired pressure $P_1$ such that when the ball valve to the dump tank is opened and the pressures in the other volumes equilibrate, all pressures are equal to $P_1$. (Figure 3.1a) The equations for calculating the initial pressures are shown in Equations 3.1 and 3.2

Second, the aerosol mixture is created. Inside the aerosol mixing tank a fan is turned on that mixes the entire volume. The fan rotates at approximately 100 rpm and has six individual blades equally spaced along the axis of rotation with an overall blade diameter of 12.5 cm. An ultrasonic nebulizer array is then turned on generating liquid droplets which are quickly caught up in the mixed flow. The fan and nebulizers are left on until the liquid loading in the mixed gas reaches the desired level. Then the nebulizers are turned off. (Figure 3.1b) Some settling of large drops may then occur.

Third, the aerosol mixture is transferred into the test section of the shock tube. First, the endwall gate valve is opened, and because the pressure difference across this valve is zero, there will be no flow. Immediately following this, the ball valve is opened and gas begins to flow from the test section into the dump tank. As gas from the test section flows from the test section into the dump tank, the mixture of aerosol is pulled in as a plug flow into the test section. The pressures ($P_A$, $P_B$, and $P_1$) are set such that the dividing surface between the aerosol mixture and the non-aerosol gas propagates well past the ball valve into the dump tank. (Figure 3.1c)

Finally, the pressures in all the volumes equilibrate, to a value such that there is no pressure difference across the driven section gate valve. This valve can then be opened without any resulting flow; the endwall gate valve and ball valve are then closed. The result is a smooth-walled shock tube with a spatially uniform aerosol near the endwall. (Figure 3.1d) The shock wave experiment can then be initiated, typically within a few seconds.
Figure 3.1a-d: (a) Diagram illustrating components of AST II and initial pressures set for operation. (b) Aerosol mixture being prepared in the mixing plenum. (c) Endwall gate valve and ball valve opened and aerosol mixture expanded into the test section. (d) Endwall gate valve and ball valve closed and the driven gate valve opened; the shock tube is ready for initiation of the shock wave.
3.2.2 Calculation of Loading Pressures

The initial pressures in the shock tube and tanks must be set such that once equilibrated, the desired final pressure in the shock tube is reached. This final pressure, $P_1$, is the pressure of the gas that the incident shock wave will propagate into and is used in calculating the conditions behind the reflected shock wave. A schematic demonstrating the filling process and the relevant volumes is shown in Figure 3.2.

![Figure 3.2: Schematic of filling process for second generation aerosol shock tube. Initial pressures in the test section ($V_{TS}$) and mixing tank ($V_{MT}$) are both $P_A$ and are separated from the dump tank ($V_B$) by a ball valve, which is at a lower pressure $P_B$. When the ball valve is opened the pressures equalize to $P_1$. At this point the expansion is sufficient for the gas from the mixing tank to fill the test section.](image)

The colors represent the boundaries of the respective volumes. The dump tank volume is denoted $V_B$ and has a low initial pressure $P_B$. The test section volume is labeled $V_{TS}$ and is at a higher initial pressure $P_A$. These volumes are separated by a ball valve. The aerosol mixing tank volume is $V_{MT}$ and also has an initial pressure $P_A$. The volume $V'$ is the displaced volume, which is the sum of $V_{TS}$ and the partial volume of the dump tank that is filled with the test gas. This displaced volume is an independent parameter, which can be varied depending on how far into the shock tube the aerosol needs to fill. We can then define $X$ as the non-dimensional expansion parameter.

$$X = V' / V_{TS} \quad \text{Equation. 3.1}$$
To fill only the entire test section, X would equal one. In practice, we employ a larger fill parameter X=1.5 to ensure complete filling.

Our goal is to specify the initial pressures $P_A$ and $P_B$ based on a desired $P_1$ and a fixed X=1.5. The expansion process can be assumed to occur isothermally, which allows us to write Boyle’s Law for the test gas.

$$P_A V_{MT} = P_1 (V_{MT} + V')$$  \hspace{1cm} \text{Equation 3.2a}

By dividing Equation 3.2a by $V_{MT}$ we can solve for $P_A$. We can also substitute Equation 3.1 for $V'$ to put Equation 3.2a in terms of X.

$$P_A = P_1 (V_{MT} + V_{TS}X) / V_{MT}$$  \hspace{1cm} \text{Equation 3.2b}

Now, given a desired final pressure $P_1$ and expansion parameter X, Equation 3.2b specifies the initial pressure in the test section and the mixing tank ($P_A$).

To find the initial pressure in the dump tank ($P_B$) we can write Boyle’s Law for the entire system.

$$P_A (V_{TS} + V_{MT}) + P_B V_B = P_1 (V_{TS} + V_{MT} + V_B)$$  \hspace{1cm} \text{Equation 3.3a}

Since we know $P_A$ from Equation 3.2b, we can rearrange Equation 3.3a to solve for $P_B$ in terms of known quantities.

$$P_B = (P_1 (V_{TS} + V_{MT} + V_B) - P_A (V_{TS} + V_{MT})) / V_B$$  \hspace{1cm} \text{Equation 3.3b}

Using this model, we can generate curves for $P_A$ and $P_B$ based on our desired $P_1$. In Figure 3.3, X = 1.5 and the volumes used were $V_{TS} = 0.012 \text{ m}^3$, $V_{MT} = 0.025 \text{ m}^3$, and $V_B = 0.083 \text{ m}^3$. 

44
Figure 3.3: Calculation of initial pressures (\(P_A\) and \(P_B\)) based on desired final pressure (\(P_f\)) using an isothermal assumption.

Equation 3.2b and Equation 3.3c do a reasonable job of predicting the expansion behavior during the fill procedure of aerosol shock tube; however, in practice a more accurate model is used to set the initial pressures based on a hybrid isothermal expansion and isentropic compression model, which is detailed in Appendix D. Based on this simple analysis it becomes apparent that to avoid high mixing tank pressures (\(P_A\)) it is necessary to make the dump tank large. The volumes used in this work allow for \(P_f\)’s up to \(~442\) torr while limiting \(P_A\) to atmospheric pressure (a limit that is imposed by the dump tank design). If higher pressure experiments are desired, one may use dump tank that can withstand higher pressures or increase the dump tank volume (\(V_B\)).

3.3 RESULTS

Three aspects of the AST II aerosol loading scheme performance are discussed: first, the behavior of the nebulizers; second, the spatial uniformity achieved in the aerosol mixing plenum; and third, the spatial uniformity in the filled shock tube volume.

3.3.1 NEBULIZER PERFORMANCE

The effectiveness of the AST II method of loading the shock tube with aerosol in a spatially uniform manner over a wide range of volumetric concentrations depends
strongly on the size of the liquid droplets that are used. A high liquid-volume fraction can be achieved by increasing the number of droplets or the size of droplets. Because volume is strongly dependent on diameter, it is advantageous to use larger diameter droplets. However, larger droplets settle faster and lag in gas flows. So a balance must be struck while considering the limitations of the aerosol generators. The ultrasonic ceramic-disk nebulizers are ideal for this purpose because they work even with viscous fuels such as diesel (DF-2) and bio-diesel surrogates such as methyl decanoate, and they are capable of producing high liquid volume fractions with sufficiently small diameters that track the gas flows that occur with this filling method. In order to ensure consistent results the droplet size distributions of nebulized aerosols were measured for various liquids.

The nebulizer was operated in a tube with an inner diameter of 12 cm (in liquid depths above the ceramic-disk of 2.5-4.0 cm) and the droplets were entrained in a flow that went from the sidewall of the tube and out of the top (see Figure 2.3). Aerosol size distributions were measured using a Malvern Spraytec™ (Model RTS5214). Figure 2.4 shows a plot of the droplet size distribution for several liquids: water, n-dodecane, and diesel (DF-2) fuel. The flow rates were low to keep with the low velocities encountered when filling of the shock tube. The size distributions were found to be nearly the same for all three liquids. The mass-averaged size was between 4-5 µm. The Stokes settling time for this droplet size is approximately 1 minute.

3.3.2 MIXING TANK LOADING UNIFORMITY

Spatial uniformity and knowledge of loading levels in the mixing tank is of crucial importance. This can be quantified using laser extinction if we take advantage of our measured droplet size distribution. The concentration of the aerosol can be related to the attenuation of a monochromatic laser beam using Mie theory. The theory provides that the extinction ( -ln(I/I₀) ) is given by this equation [37]
\[-\ln (I/I_0)_\lambda = C_V \left\{ \int_0^{\infty} Q_{\text{ext}}(d, n(\lambda)) \frac{\pi}{4} D^2 L \, dD \right\} / \left\{ \int_0^{\infty} f(D) \frac{\pi}{4} D^3 \, dD \right\} \]

\[= 0.31 \pm 0.01 \, [\text{m}^{-1}] \, L \, [\text{m}] \, C_V \, [\text{ppmv}] \quad \text{Equation 3.4} \]

where the $I$ is the intensity of the light that is transmitted, $I_0$ is the incident intensity, $L$ is the path length, $C_V$ is the liquid volume concentration, $Q_{\text{ext}}$ is the Mie coefficient which depends on the droplet diameter ($D$) and the index of refraction which is dependent on the wavelength of light ($\lambda$), and $f(D)$ is the fractional size distribution. These integrals can be computed for the measured $f(D)$ shown in Chapter 2 (Figure 2.4) and theoretical values for $Q_{\text{ext}}$. Because the size distributions are similar and the indices of refraction are nearly the same ($n=1.33$-$1.42$) for the liquids used in this study, the integrals can be simplified as shown in Equation 3.4.

The laser setup (shown in Figure 3.4) on the mixing plenum consisted of two lasers 30 cm apart which were sent across the center of the plenum in a horizontal plane ($L=24.2$ cm). The windows were heated (~40°C) to avoid condensation. Figure 3.5 below shows a typical test result.

Figure 3.4: The optical setup on the mixing plenum to measure the uniformity and the loading.
Figure 3.5: Uniformity in tank: water aerosol. Two lasers at 10 and 40 cm from the endwall. The discrepancy between the two measurements indicate the magnitude of the non-uniformities present in the mixture at a particular time. The coefficient of variation (COV=StDev/Ave) is plotted as a function of time.

Large variations are seen in the concentration signal while the nebulizer is on as the jets above the nebulizer disk steer the laser beams away from the detectors. The concentration rises quickly while the nebulizer is on, and then once the nebulizer is turned off (at 4s) these variations are reduced. When the fan is turned off (at 6 s) the variations are reduced further, and we see a very slow drop in the concentration (around 1%/s). This is due to the larger droplets settling. This effect is less evident in actual experiments because the fill happens directly after the fan turns off. The coefficient of variation (COV) for these measurements shows that the non-uniformity in the tank is around 1%. No strong dependence on fan speed (near the nominal value of 100 rpm) was seen.

48
Figure 3.6: Filling the tank to different concentrations: water aerosol. Various curves represent different lengths of time that the nebulizer and mixing fan was turned on. This shows the effects of leaving the nebulizer running for different amounts of time and the range of achievable concentrations (1-100 ppmv).

Figure 3.6 shows the effects of leaving the nebulizer running for different amounts of time and the range of achievable concentrations (1-100 ppmv). The AST II configuration significantly extends the concentration range beyond that which was previously achieved with the AST I method of filling the shock tube (5-20 ppmv).

3.3.3 SHOCK TUBE LOADING UNIFORMITY

Studies of shock tube loading uniformity were performed using a Plexiglass mock tube to aid in visualization. Loading in the mock tube was studied using three lasers stationed at different distances away from the endwall (10 cm, 60 cm, 110 cm) crossing the tube at its mid section. The windows were heated (~40°C) to avoid condensation. See Figure 3.7 for the experimental setup and Figure 3.8 for the results of a typical filling experiment using the AST II method.
Figure 3.7: Optical setup for measuring non-uniformities in AST II method of filling.

Figure 3.8: Plot of laser extinction measurements at three locations along the tube and the resulting coefficient of variation: water aerosol. AST II generates non-uniformities much smaller than AST I, in this case 2%.
This filling experiment (Figure 3.8) was conducted with a water aerosol using loading pressures of $P_A=759$ torr, $P_B=326$ torr, $P_f=460$ torr, and $X=1.5$. The mixing plenum filling time sequence was as follows: gas flow and fan in the mixing plenum turned on at -10 s, nebulizer is turned on at -8 s and turned off at -5 s, fan turned off at -3 s. This filling sequence achieved an aerosol liquid loading of 44 ppmv (see solid black curve). The mock tube filling sequence was as follows (same time scale): ball valve to the dump tank and gate valve to mixing plenum opened at 0 s, the aerosol contact surface crosses the first laser almost immediately, the second laser registers an increase in the aerosol concentration at 1 s, and the third laser registers an increase at 2.5 s. The liquid volume concentrations decrease between 0 s and 4 s due to the expansion of the mixture; once the pressures equalize at 4 s the concentrations at all three laser measurement locations are very similar in magnitude and decrease at a slow rate due to settling. The COV time-history indicates that the non-uniformities remain less than 2% after filling. An identical set of measurements were made using the AST I “flow-through” method of filling and non-uniformities were significantly higher in all cases and typically around 16%.

In order to minimize the non-uniformity using the AST II, one very important parameter, the plug flow rate, must also be optimized. The next set of plots in Figure 3.9-c and Figure 3.10 show the effect of varying the fill rate.
Figure 3.9a-c: These plots show measurements of aerosol concentration at three locations while filling the shock tube using the AST II filling method (a) 50 slpm fill rate (b) 4.0 slpm fill rate (c) 1.0 slpm fill rate. The flow rate was varied by using various diameter orifices.

In Figure 3.9a the flow rate is high (50 slpm) and the aerosol takes only 0.2 s to fill the test section; large differences in the aerosol concentration are seen at the three laser measurement locations. This variation is likely due to the separation of the liquid droplets from the bulk gas at high flow velocities. In Figure 3.9b the test section is filled in 2.7 s (4.0 slpm) and the aerosol is much more uniform. At significantly slower flow
rates (1.0 slpm), as in Figure 3.9c, the aerosol again becomes less uniform; droplets near the aerosol contact surface evaporatively cool and settle, beginning a “river-like” flow. At these filling rates, the aerosol flow is not an ideal plug flow and occupies only the bottom half of the tube’s cross-section. The region of uniformity occurs when the flow rate is between 2 and 5 slpm or at velocities between 30-60 cm/s. The optimal flow rate is obtained by venting the shock tube test section (or mock tube in the visualization studies) through a throat or orifice just before the ball valve to the dump tank. The throat that was chosen to produce a velocity in the test section of 45 cm/s has an orifice diameter of 5.5 mm. Figure 3.10 shows many filling experiments where the flow rate was varied by opening the ball valve to different angles.

Figure 3.10: The relationship between the resulting non-uniformity to the flow rate with which the tube was filled. The flow rate was varied by using various diameter orifices. The optimal flow rate range is between 2 and 5 slpm (gas velocity ~45 cm/s).

3.4 SHOCK WAVE EXPERIMENTS

3.4.1 FUEL LOADING UNIFORMITY

After the shock tube filling is complete, a shock wave is initiated. The incident shock wave propagates through the driven section of the shock tube into the aerosol filled test section. For these experiments a fuel aerosol (e.g. dodecane, diesel fuel, etc.) is used in order to study the chemical kinetics of that particular fuel. When the shock passes through the aerosol it quickly accelerates and evaporates the fuel. The evaporated fuel mixture then flows toward the endwall behind the incident shock.
Post-evaporation gas-phase uniformity in the test gas mixture using the new aerosol loading strategy was measured using laser absorption in region 2. In region 2 the fluid is flowing toward the endwall and a time-resolved laser measurement at a single location gives information about all of the fluid elements that pass the laser. Figure 3.11 below shows the optical setup used in these measurements.

Figure 3.11: Top View: Diagnostics used in aerosol tube experiments. Pressure measurements are used to measure shock speed and ignition delay time. Laser light at 650 nm can be used to measure liquid aerosol concentration. Laser light at 3.39 μm is used to measure gas phase concentration after the fuel has evaporated. Side View: Incident shock propagates into aerosol evaporating and mixing fuel and oxidizer. This region is called region 2.
Shown in Figure 3.12a-c, are extinction measurements \((-\ln(I/I_0)\) where \(I_0\) is the incident laser light intensity and \(I\) is the intensity after being attenuated through the shock tube) for experiments in the shock tube. At this measurement location (10 cm) two laser beams with different wavelengths were pitched through the shock tube. The visible, 650 nm laser beam was attenuated solely by Mie scattering when there are liquid droplets present. The mid-infrared 3.39 µm laser beam was also attenuated by Mie scattering, but in addition is resonant with the C-H stretch vibrational mode found in gaseous hydrocarbons in the mixture. The visible beam provides information on the aerosol loading and confirms when the aerosol is fully evaporated (i.e. no attenuation of 650 nm at ~100 µs). The mid-infrared beam provides purely gas-phase fuel concentration after the aerosol is fully evaporated. This is done using a method described in Davidson et al. [21].
Figure 3.12a-c: Three shock experiments highlighting region 2 post-evaporation uniformity for a range of fuel loadings all with n-dodecane in 21%O2/Ar. (a) Conditions: $X_f$ (n-dodecane mole fraction) = 0.00680, $T_2 = 617 \text{ K}$, $P_2 = 1.11 \text{ atm}$, $T_4 = 993 \text{ K}$, $P_5 = 4.23 \text{ atm}$ (b) Conditions: $X_f = 0.0100$, $T_2 = 584 \text{ K}$, $P_2 = 1.64 \text{ atm}$, $T_3 = 921 \text{ K}$, $P_3 = 6.25 \text{ atm}$ (c) Conditions: $X_f = 0.0150$, $T_2 = 534 \text{ K}$, $P_2 = 1.62 \text{ atm}$, $T_3 = 838 \text{ K}$, $P_3 = 6.26 \text{ atm}$.
Figure 3.12a-c shows these laser extinction measurements in regions 1, 2, and 5. Before the arrival of the shock wave, in region 1, there is no change in the extinction (-\ln(I/I_0)) of both wavelengths because the aerosol is stagnant. After the incident shock arrives, the mixture is compressed and the extinction rises. In the 650 nm measurement the signal quickly reaches a peak and falls to zero due to the rapid evaporation behind the incident shock. The 3.39 µm measurement falls due to evaporation as well, but then asymptotes to a steady plateau value. This plateau value of the gas phase absorption is used to calculate the fuel concentration. This measurement also indicates that the test gas mixture passing the measurement location had a very uniform fuel loading for all three tests shown here (<1% variation). This is a significant improvement over the results obtained using the AST I filling method where the non-uniformities were typically >5% and never better than 1.7% [21].

At the arrival of the reflected shock the mixture is further compressed. As a result the attenuation increases as seen in Figure 3.12a. A schlieren spike is also seen in the laser measurements, where the beam is temporarily steered off the detector because of the passage of the reflected shock. In Figure 3.12b the increased attenuation is not seen after the reflected shock (owing to a decrease in fuel concentration that occurs during the schlieren spike), and in Figure 3.12c the attenuation falls prior to the arrival of the reflected shock. In both cases (Figure 3.12b and Figure 3.12c), the arrival of the aerosol contact surface prior to the arrival of the reflected shock at the measurement location caused a decrease in the absorption. In order to avoid the influence of the aerosol contact surface on the measurement, either the measurement location should be moved closer to the endwall or the test section (which is initially filled with aerosol) should be made longer. Cases like Figure 3.12b and Figure 3.12c are important in characterizing the facility to understand the effects of the aerosol contact surface. Then when making combustion measurements behind the reflected shock wave, the measurement location can be selected nearer the endwall to avoid any non-uniformities in concentration associated with the aerosol contact surface.
3.4.2 Ignition Delay Time Measurements

As an example application and demonstration of this new facility to study combustion chemistry phenomena, ignition delay times in n-dodecane/O₂/argon mixtures were measured. Ignition delay time measurements are used to describe the global combustion performance of fuel/oxidizer mixtures. The ignition delay time is the length of time that a mixture, at a given initial pressure and temperature (typically under constant volume and energy constraints) will take to ignite; measurements can be made directly from real-time pressure profiles. These AST II measurements are compared with previous measurements using AST I [21] in Figure 3.13.

![Graph showing Ignition Delay Time Measurements](image)

Figure 3.13: Ignition delay times for AST I [21] and AST II. AST II data produces significantly reduced scatter and slightly lower mean values than AST I data. Pressure and Φ (equivalence ratio) were normalized to 5.0 atm and Φ=0.5 using $P^{0.86}$ and $Φ^{-1.51}$ dependences, respectively.

The new aerosol filling method produces reduced scatter. The AST II points are slightly shifted to shorter ignition times. A comparison analysis of the AST I data shows evidence of larger non-uniformity of fuel loading, suggesting that a significant portion of
the measurement difference was due to non-uniformities in the initial aerosol mixture. The new filling method produces a more uniform initial aerosol mixture and significantly reduces the scatter in the combustion measurements that were made.

3.5 CONCLUSIONS

A second-generation aerosol shock tube has been developed. Three improvements over the previous design were demonstrated. The new method now constrains the amount of shock tube that is filled with aerosol, produces a much more uniform aerosol, and allows filling the shock tube with much higher concentrations of fuel. These improvements will enable more accurate measurements of combustion chemistry processes, particularly as are needed for practical low-vapor-pressure fuels.
Gas-phase ignition delay times were measured behind reflected shock waves for a wide variety of low-vapor-pressure fuels. These purely gas-phase measurements of ignition delay times, without the added convolution with evaporation times, were made possible by using the aerosol shock tube methodology. The fuels studied include three large normal alkanes, n-decane, n-dodecane and n-hexadecane; one large methyl ester, methyl decanoate; and several diesel fuels, DF-2, with a range of cetane indices from 42 to 55. The reflected shock conditions of the experiments covered temperatures from 838 to 1381 K, pressures from 1.71 to 8.63 atm, oxygen concentrations from 1 to 21%, and equivalence ratios from 0.05 to 1.89. Ignition delay times were measured using sidewall pressure, IR laser absorption by fuel at 3.39 µm, and CH* (at 431 nm) and OH* (at 306 nm) emission. Measurements are compared to previous studies using heated shock tubes, where available, and current models. Model simulations show similar trends to the current measurements except in the case of n-dodecane/21% O₂/argon experiments. At higher temperatures, e.g. 1250 K, the measured ignition delay times for these mixtures
are significantly longer in lean mixtures than in rich mixtures; current models predict the opposite trend. As well, the current measurements show significantly shorter ignition delay times for rich mixtures than the model predictions.

4.1 INTRODUCTION

The aerosol shock tube has been shown to provide a unique method of experimentation for low-vapor-pressure fuels that effectively separates the evaporation process from the combustion. The AST II method of filling provides a homogeneous initial aerosol distribution in the shock tube. This along with a well-validated method of determining the conditions behind the incident and reflected shock waves make it ideal for measuring ignition delay times for low-vapor-pressure fuels.

Ignition delay times are good indicators of the overall behavior of combustion reactions and are regularly used as performance benchmarks for detailed chemical mechanisms. Validation of the detailed chemical mechanisms is very important, because these mechanisms are obliged to use many reactions and rate constants that are only estimated or theoretically predicted and are not derived from experiment. For large fuel molecules (which typically have low vapor pressures), the number of species that are formed during decomposition and oxidation can be very large. For example, a Lawrence Livermore National Labs (LLNL) chemical mechanism for alkanes up to n-hexadecane (C$_{16}$H$_{34}$) contains over 2,000 species and over 8,000 reactions [43]. Ignition delay times provide useful targets and some constraint on the modeling of these complex systems.

Much work is still needed to fully understand the combustion of these large fuel molecules because of the increased complexity of these mechanisms, and the added difficulty in performing experiments with these fuels [54]. This is unfortunate, because most of the devices that utilize combustion are powered by low-vapor-pressure fuels including diesel and bio-diesel fuels, and rocket and jet fuels. Many new mechanisms have been developed recently [43-46, 61, 64], but more experimental validation targets are required for these fuels and their surrogates [62]. To help address this need, we have studied a variety of low-vapor-pressure fuels using the aerosol shock tube methodology,
providing, in many cases, the first purely gas-phase shock tube ignition delay time measurements for these fuels.

4.2 **LOW-VAPOR-PRESSURE FUELS**

Fuels used in combustion devices are rarely composed of a pure single component, and in order to model a real, multi-component fuel, single- or multi-component surrogate mixtures are often employed [47, 62]. This motivates the study of various types of pure fuels that display characteristics similar to real fuels, in addition to the study of the real fuels themselves. Because fuels such as jet fuel, diesel, and bio-diesel are mostly made up of large molecules, the surrogate components which best represent these fuels have low-vapor-pressures; the aerosol shock tube is thus well-suited for the study of these fuels. Here we focus on n-alkanes, which can make up a significant fraction of distillate fuels, diesel fuels themselves, and methyl decanoate, a large methyl ester that is structurally related to bio-diesel.

4.2.1 **N-DECANE**

There are many ignition delay time studies of n-decane [48-51, 60, 12]. This is in part because its vapor pressure at room temperature is near 1.4 torr and this is sufficient to make a purely gas-phase mixture at relevant mixture fractions. n-decane (C_{10}H_{22}) has been commonly used as the alkane representation for jet fuel-relevant surrogates, but has also been used for diesel [59] and bio-diesel [45] comparisons.

4.2.2 **N-DODECANE**

Less abundant are ignition delay time studies focused on n-dodecane [48, 52]. The vapor-pressure at room temperature of n-dodecane is lower at 0.13 torr. This limits the fuel loadings that can be achieved, and heating is usually necessary to perform shock tube experiments. n-dodecane (C_{12}H_{26}) has also been used as the alkane component in jet fuel surrogates.
4.2.3 N-HEXADECANE

There are very few studies on the purely gas-phase oxidation of n-hexadecane [13, 53, 14] because its vapor pressure at room temperature is only 1.4 mtorr. n-hexadecane (cetane) is a major alkane constituent of diesel fuel, and appears to be very important in influencing its behavior upon oxidation. n-hexadecane (C_{16}H_{34}) is one of the species that is used in the definition of the cetane index scale to characterize the combustion characteristics of diesel fuel. By definition n-hexadecane has a cetane index of 100.

4.2.4 DIESSEL (DF-2)

Diesel fuel is a low-volatility distillate fuel most widely used in combustion devices. Heated shock tubes have been used in the past to study diesel ignition [55, 56], but with a distillation curve that extends up to 350°C, it can be a very difficult task to get all of the heavier components of the fuel mixture into the shock tube. Here we examine several different diesel fuel samples to show how variability in composition and cetane index affect ignition delay times.

4.2.5 METHYL DECANOATE

The author is unaware of any purely gas-phase shock tube studies of methyl decanoate, despite the fact that it is an important surrogate fuel for the study of methyl ester-based bio-diesels. A detailed mechanism has been developed at LLNL that predicts the behavior of methyl decanoate oxidation [45].

4.3 EXPERIMENTAL SETUP

For these ignition delay time measurements, the aerosol shock tube setup and supporting diagnostics are shown in Figure 4.1. As in all experiments a series of fast-response pressure sensors are used for measuring the incident shock speed. A mid-IR (3.39 μm) and a visible (650-670 nm) laser is used for measuring fuel loading. A Kistler™ 601B piezoelectric transducer located near the endwall (3 cm) is used to
measure the ignition delay time. CH\(^*\) (at 431 nm) and OH\(^*\) (at 306 nm) are both detected through sidewall windows located near the endwall.

![TOP VIEW](image)

**Figure 4.1**: Schematic of the aerosol shock tube with pressure and laser diagnostics. The pressure sensors are used for shock speed measurement and ignition delay time determination, the mid-IR HeNe laser is used for absorption-based fuel measurements, the visible laser diode is used for droplet scattering measurements, and the emission measurement is used to measure ignition delay time.

The ignition delay time can be defined by the time between the arrival of the reflected shock wave at the pressure sensor (located 3 cm from the endwall) and the time at which the pressure begins its rapid rise associated with ignition. This definition of ignition delay time exhibited the most consistency and proved to be the most reliable for these experiments. Ignition delay times determined from laser absorption measurements (at 3.39 \(\mu\)m) of fuel consumption and emission measurements of CH\(^*\) and OH\(^*\), while consistent with the pressure measurements, exhibited larger scatter and were used only to confirm the values derived from the pressure measurements.
4.4 Results

An example of a typical experiment is shown below in Figure 4.2. The top frame (a) shows 670 nm laser extinction (1), pressure (2), and CH* emission (3) all located 3 cm from the endwall. The bottom frame (b) shows 3.39 µm laser absorption (combined with Mie scattering from droplets when droplets are present) by fuel (4), and 660 nm laser extinction (5), both located 5 cm for the end wall.

![Figure 4.2](image)

Figure 4.2: Example of an ignition delay time measurement. This example was done with a DF-2 (CI 43) / 21% O₂ / argon mixture with $\Phi = 0.48$, $T_1 = 1197 K$, and $P_2 = 7.21$ atm. The diagnostics in the upper frame (a) are located 3cm from the endwall, and in the lower frame (b) are 5cm from the end wall: (1) Mie scattering extinction, (2) pressure, (3) CH* emission, (4) fuel absorption, and (5) Mie scattering extinction.

Complete evaporation of the aerosol droplets behind the incident shock wave is evident from the 660 and 670 nm laser extinction traces, which show zero extinction (at -20 µs in the upper frame (a) and at -60 µs in the lower frame (b)) before the arrival of the
reflected shock wave. This wavelength range was selected as it does not overlap with any absorption feature of the fuel (DF-2 in this case), and responds only to Mie scattering by droplets. Spikes in the laser signals at 0 µs (a) and 100 µs (b) are a result of beam steering off the detectors from the transiting shock wave.

The 3.39 µm laser absorption measurement of fuel (4) in the lower frame (b) verifies that the fuel concentration that passes the window at 5cm is uniform. This is evident from the constant absorbance by fuel-vapor seen from -60 to 100 µs after the complete evaporation of the aerosol droplets. The test gas mixture that passes the 5 cm observation station will stagnate behind the reflected shock wave at the 3 cm observation station. Thus, the fuel concentration of the fluid element that stagnates at 3 cm from the end wall behind the reflected shock wave will also be uniform. This uniformity is very important to making quality measurements using an aerosol shock tube [42].

The pressure profile (2) in the upper frame (a) shows classic shock tube behavior. At times before -80 µs, the pressure is given by the pre-shock fill pressure; from -80 to 0 µs, the pressure behind the incident shock wave is recorded; after 0 µs, the reflected shock region pressure is recorded. At 280 µs the rapid rise in pressure signifies ignition. This is coincident with the rise in CH* emission (3) and slightly delayed (at 300 µs at the 5 cm location in the lower frame (b)) by complete consumption of fuel. At 5 cm the ignition delay time that is indicated by the fuel concentration going to zero (around 200 µs) is shorter than that given by pressure and CH* emission at 2 cm. This is likely due to an acceleration of the reaction rate upstream due to the strong energy release near the endwall.

This ignition delay time has an uncertainty associated with many aspects of the measurement. The most significant contributor to the uncertainty of ignition delay measurements are the uncertainties associated with the temperature. Because ignition is so sensitive to temperature any change in temperature results in a large change in ignition delay time. The temperature is calculated through AEROFROSH as shown in Chapter 2, and the measurement which contributes most substantially to the error in the conditions is the typically the shock speed. We can measure the shock speed with an error of <0.5%.
This translates to an error in $T_5$ of <1%. An error of 1% in temperature corresponds to an error in ignition delay of about 10-15%. There are many other sources of error like pressure measurement, fuel cross section, and non-uniformity; however, the uncertainty due to the velocity measurement is typically the most severe. In some cases at the longer ignition delays >1 ms, the non-ideal facility effects cause a temperature error that exceeds 1%, so in these cases the most significant error is due to these non ideal facility effects. (See Appendix C for a more detailed discussion on the facility effect, namely a +dP/dt)

### 4.4.1 N-DECANE

Because n-decane has a higher vapor pressure at room temperature only a sparse aerosol is needed to create a stoichiometric mixture. The fraction of fuel in the final evaporated mixture that comes from the liquid droplets as compared to the amount in the saturated bath gas is small; n-decane represents one of the most volatile fuels that can be used with the aerosol shock tube methodology. Figure 4.3 shows representative data taken with the aerosol shock tube at 5 atm.

![Figure 4.3: n-decane/Air ignition delay times. Data conditions ranging over $P=4.6$-5.2 atm and $\Phi=1.0$-1.9 are scaled to $P=5$ atm, phi=1.0 using the Olchanski and Burcat correlation [61] (blue diamonds: data; blue line: correlation; black lines: best fit to Shen et al. [48]).](image)
Also shown are the Olchanski and Burcat measurements of [61] high-temperature ignition delay times for n-decane in 23% O₂ in argon, obtained in a heated shock tube. Their ignition delay time correlation can be rearranged to represent the dependence on the variables \( P \) and \( \Phi \) for constant O₂ mole fraction as

\[
\tau \sim P^{-0.625 \pm 0.06} \Phi^{0.60 \pm 0.06}
\]

Also shown in Figure 4.3 are the recent data at higher pressures (nominal values of 11 and 40 atm) published by Shen et al. in 2009 [48]. The expected trend with pressure is apparent, and these data exhibit negative temperature coefficient behavior at high pressures and low temperatures.

Both of the previous studies utilized a heated shock tube (100°C in [61]; up to 160°C in [48]). Because n-decane has a relatively high vapor pressure, only moderate shock tube temperatures are required to generate sufficient fuel loading for equivalence ratios of unity. As a result, pre-test decomposition or oxidation is likely not a problem and thus the agreement between the previous n-decane data and the aerosol shock tube data at 5 atm provides additional confidence in the aerosol shock tube methodology. As less volatile fuels are used, the heated shock tube must operate at higher temperatures and becomes more susceptible to pre-test decomposition, whereas the aerosol shock tube does not suffer from this uncertainty.

4.4.2 N-DODECANE

Because of the importance of n-dodecane as a jet fuel surrogate, several ignition delay time studies in heated shock tubes exist. Figure 4.4a presents a comparison of the current study with the heated-tube measurements of Shen et al. 2009 [48] and Vasu et al. 2009 [52].
Figure 4.4: n-Dodecane/air and n-dodecane/21% O₂/Ar ignition delay times for fuel-lean mixtures (Φ=0.5) at various pressures.

This comparison of the n-dodecane ignition delay times measured in heated shock tubes and the aerosol shock tube also shows excellent agreement. A pressure scaling of $P^{-0.89\pm0.09}$ is found for the air experiments (for all data except the Shen et al. 40 atm and Vasu et al. 20 atm data at the lowest temperatures), and a scaling of $P^{-0.86\pm0.20}$ is found for the 21%O₂/Ar experiments. The error in the fit coefficient is the standard deviation of a least squares regression. Figure 4.4b shows experiments ($\Phi=0.31-1.31$) scaled to $\Phi=0.5$ as $\Phi^{-1.51\pm0.14}$. The Westbrook et al. (LLNL) [43] and the Wang et al. (JetSurF 2.0) [63] models predict ignition delay time differences of less than a few percent when N₂ and Ar are interchanged as diluents, which is consistent with experiments. The long test times (>10 ms) in Figure 4.4b are no longer than 8 ms, but are scaled by equivalence ratio to appear longer. See Appendix C for a discussion on facility limited test times.
Figure 4.5: Variation of n-dodecane/21% O\textsubscript{2}/Ar ignition delay time with equivalence ratio scaled to 6.0 atm (4.01-8.63 atm).

In the case of 21% O\textsubscript{2} / argon, the current data shown in Figure 4.5 cover equivalence ratios (Φ) of 0.05 to 1.88. The data vary with a scaling which is not a simple power law; however, between 0.31 and 1.31 the data roughly follow a scaling of Φ\textsuperscript{-1.51±0.14}, which was used to scale all the data in Figure 4.4b to Φ = 0.5. The dependence of ignition delay time on equivalence ratio can be seen in Figure 4.6. At high temperatures there are major differences between the data and the predictions of the detailed mechanisms of Westbrook et al. (LLNL) [43] and that of Wang et al. (JetSurF 2.0) [63]. At low temperatures the data and predictions give the same trend, but deviate at high equivalence ratio.
Figure 4.6: Equivalence ratio dependence of the ignition delay times for n-dodecane at a) 1250K and b) 1000K, both at P=6.0 atm.

The dependence of ignition delay time on equivalence ratio when the oxygen mole fraction is fixed is a direct result of changing the fuel mole fraction. At all temperatures studied, the measured ignition delay times are reduced for higher equivalence ratios. The models capture this trend at lower temperatures (i.e. 1000K), however, at higher temperatures (i.e. 1250K), the models predict that higher fuel concentrations result in a longer ignition delay time. This behavior has also been observed in experiments with smaller fuels (e.g. n-butane) [58]. This behavior may be a result of excessive radical scavenging by fuel decomposition product molecules in the
model (e.g. OH+alkenes) or reduced production of radicals at higher temperatures (e.g. slower decomposition pathways that generate H-atoms).

4.4.3 N-HEXADECANE

n-Hexadecane has a very low vapor pressure and experiments by Penyazkov et al. [14] using this fuel represent the current limit for existing heated shock tube data. The vapor pressure at room temperature is only 1.4 mtorr, while a 100 torr initial pressure and a stoichiometric mixture in air would require a fuel partial pressure of 0.8 torr ($P_{\text{sat}} = 109\text{C}$). In effect, this requires that heated shock tube experiments be made at very high initial temperature. Figure 4.7a-c shows a comparison between the current data and that of Penyazkov et al. 2009 [14] (heated shock tube 100C).

Figure 4.7a presents the trend of ignition delay time with varying oxygen concentration (for the 1% and 4% O$_2$ in argon data, $\tau \sim X_{O_2}^{-0.54\pm0.08}$). However, one would expect that the variation would be larger between the aerosol shock tube data (1% and 4% O$_2$ in argon) and the heated shock tube data (21% O$_2$ in N$_2$) given the 5-fold increase in oxygen concentration. Simulations of these experiments using the LLNL C16 mechanism [43] (which demonstrates a $X_{O_2}^{-0.74}$ scaling) suggest that the ignition delay times for the 21% O$_2$ in N$_2$ experiments would be expected to be approximately one third of the 4% O$_2$ in argon experiments, whereas a reduction of only $\sim$33% is seen in the data. Fuel decomposition or oxidation to more stable components is a possible explanation of this difference as the heated shock tube in the study was kept at 100C and the mixing tank kept at 200C, with mixtures kept in the mixing tank for between 3 and 4 hours.

Figure 4.7b and c show the variation of n-hexadecane ignition delay times with pressure and equivalence ratio. For fixed oxygen concentration, the measured ignition delay times scale as $P^{-0.73\pm0.09}$, and at 4 atm, scale as $\Phi^{0.82\pm0.13d}$. Both of these are consistent with the LLNL C16 mechanism predictions of $P^{-0.70}$ and $\Phi^{0.55}$, though the model scaling with equivalence ratio is less satisfactory.
Figure 4.7: (a) Comparison of n-hexadecane ignition delay times at 4 atm and equivalence ratio of 1.0 for various oxygen concentrations. (b) Ignition delay time variation with pressure for stoichiometric n-hexadecane / 4% O₂ / Ar mixtures. (c) Ignition delay time variation with equivalence ratio at 4 atm for stoichiometric n-hexadecane / 4% O₂ / Ar mixtures.
4.4.4 **Methyl Decanoate**

Methyl decanoate also has a low vapor pressure (37 mtorr) at room temperature, making it an ideal candidate for measurements in the aerosol shock tube. Figure 4.8 presents measured ignition delay times for methyl decanoate and simulations using the Herbinet et al. model [46]. These initial experiments were performed at a low equivalence ratio.

The experiments have longer ignition delay times than the LLNL model simulations [46], by a factor of 2.5, however, the measured activation energy (44.3±5 kcal/mole) is in close agreement with the LLNL model value (43.6 kcal/mole). The small pressure range of the experiments (7.8 – 8.0 atm) precluded determining a pressure dependence and so we were unable to confirm the strong variation with pressure (τ ~ P^{1.32}) predicted by the model. Over the range of lean equivalence ratios studied, Φ = 0.08-0.17, the ignition delay times scaled as Φ^{-1.2±0.1}. This is in contrast to the model’s predicted scaling of Φ^{-4} at these extreme equivalence ratios.

![Graph showing ignition delay times for methyl decanoate / 21% O₂ / Ar mixtures at Φ = 0.1 and P=8atm and the ignition delay times from the LLNL mechanism by Herbinet et al. [46].](image)

Figure 4.8: Ignition delay times of methyl decanoate / 21% O₂ / Ar mixtures at Φ = 0.1 and P=8atm and the ignition delay times from the LLNL mechanism by Herbinet et al. [46].
4.4.5 **DIESEL**

Diesel fuel contains very heavy components and is thus an ideal fuel to be tested in the aerosol shock tube. We have tested a variety of diesel fuels with varying cetane indices and oxygen concentrations. Representative ignition delay times are shown in Figure 4.9

![Diesel Ignition Delay Times](image)

**Figure 4.9:** Diesel ignition delay times for three different diesel fuels compared with simulations using the LLNL mechanisms for various surrogate mixtures. Mixtures have an oxygen concentration of 21% with P=6atm and Φ=0.5. Colored, square symbols indicate data taken with aerosol shock tube; black circles represent data taken in a heated shock tube by Penyaakov et al. [55].

This figure shows data from 3 different diesel fuel mixtures. The red data points are from a diesel with a cetane index of 43 calculated (ASTM D976) using its density of 0.86 g/cc (at 15°C) and a distillation D86 at 50% of 265.9°C, and was provided to our laboratory from the US Army Research Office. The blue data points are from a European commercial diesel sample, which had a higher estimated cetane index of 55.
These data exhibit the shortest ignition delay times as generally expected. These measurements were both made in the aerosol shock tube. The black data points are from measurements by Penyazkov et al. [55] using a heated shock tube (heated to between 100 - 110°C).

Also shown on this plot are simulations by Westbrook et al. (LLNL) [personal communication 2010] using three different surrogate blends. The surrogate represented by a dotted line, a three-component mixture, is based on smaller fuel components, x mole % decane, y mole % toluene, and z mole % iso-octane. The theoretical cetane index of this surrogate is 55, it overpredicts the ignition delay times of the Cl=55 European diesel fuel. The other two surrogates (solid red and blue lines) considered employed larger molecules that more closely match the molecular weight of diesel fuel, and are based on primary reference fuel, PRF, components. These are mixtures of x mole % hexadecane (cetane) and y mole % iso-cetane for Cl=43, and x mole % hexadecane (cetane) and y mole % iso-cetane for Cl=55. Differences are seen in the experimental results at high temperatures, but not in the simulations using the two different cetane indexes. Also see Appendix C Figure C.0.3 for a discussion about the facility effects caused by a slight increase in temperature and pressure.

The US diesel was also tested over a range of pressures and equivalence ratios. Figure 4.10a and b show how these variations effect the ignition delay time.
Figure 4.10: Variation of ignition delay time with pressure (Φ=0.5) and equivalence ratio (P=6atm) for mixtures consisting of DF-2 (CI 43) / 21% O₂ / Ar.

As pressure increases the ignition delay time decreases following a scaling of $P^{-0.82±0.15}$. A decrease in ignition delay is also apparent if we increase the equivalence ratio (while holding oxygen concentration constant) following a scaling of $\Phi^{-0.70±0.16}$. An overall correlation for this fuel with 21% O₂ in argon is given by:

$$\tau [s] = 2.64\times10^{-8} P [atm]^{-0.82±0.15} \Phi^{-0.70±0.16} e^{25.0±1.6 [kcal/mole]/RT}$$
To show variation with the fuel blend, ignition delay times for two other diesel fuels were measured at lower oxygen concentration. The results are shown below in Figure 4.11.

![Figure 4.11: Variation in ignition delay time with aromatic content of diesel fuel. Oxygen concentrations of 4% were used with Ar as the diluent. P=6 atm and \( \Phi = 0.5 \). The two diesel fuel blend measurements were compared to simulations of mixtures of n-hexadecane and iso-cetane (CN 42, 46) using LLNL mechanisms [43, 44].](image)

The data in Figure 11 have increased ignition delay times due to the lower oxygen concentration (4% in argon). The two diesel blends were chosen to bracket the large variation in aromatic content allowed by the US EPA. The higher aromatic diesel has a general composition of: saturates 44.2%, aromatics 38.8%, and olefins 17%; whereas the lower aromatic diesel has a composition: saturates 81%, aromatics 16.2%, and olefins 2.7%. No significant difference was seen in the PRF surrogate (using only cetane and iso-cetane as components) model for the two cetane index cases. The simulations approximately capture the lower aromatic fraction fuel ignition delay times, but the higher aromatic fuel shows a larger discrepancy, implying that this simple mixture is not sufficient to capture the ignition behavior. The agreement may improve by using a mixture which sufficiently captures the aromatic chemistry that is affecting the ignition behavior.
delay times. In order to better characterize this difference, we have measured several species time-histories for many of the low oxygen concentration experiments and these results (still in preparation for later publication) may help to elucidate the discrepancy.

4.5 CONCLUSIONS

This chapter demonstrates the capabilities of aerosol shock tubes to investigate ignition delay times for many low-vapor-pressure fuels. The data obtained provide useful kinetic targets for testing the overall behavior of detailed mechanisms for pure and practical fuels.

Several important conclusions can be derived from these new data. Perhaps the most important is that n-dodecane ignition delay times for mixtures with 21% O2 exhibit a negative power law dependence with equivalence ratio at high temperatures, whereas the LLNL [43] and JetSurF [45] models both predict a positive exponent. We believe that current dodecane mechanisms may require more than just minor modification to capture this behavior accurately.

To our knowledge, this study provides the first shock tube ignition delay time data for methyl decanoate and the first aerosol shock tube measurements for n-hexadecane. The n-hexadecane data provide oxygen concentration dependence, pressure dependence and equivalence ratio dependence. The methyl decanoate data provide temperature and equivalence ratio dependences, and provide targets for the validation of large n-alkane and methyl ester (i.e. bio-diesel) reaction mechanisms.

This study also provides gas-phase ignition delay times for several types of diesel fuel and the variation of ignition delay time with cetane index, pressure, equivalence ratio, and aromatic content. These data provide a fundamental database for the testing and refinement of diesel surrogate mechanisms. The data and conditions are summarized in a table in Appendix E.
Chapter 5: APPLICATION 2 - SPECIES TIME-HISTORIES

The first simultaneous multi-species laser-absorption time-history measurements for OH and C$_2$H$_4$ during the oxidation of n-hexadecane and commercial diesel fuel (DF-2) were acquired. The experiments were performed behind reflected shock waves in the second-generation aerosol shock tube over a temperature range of 1120K to 1373K and a pressure range of 4 to 7 atm. Initial fuel concentrations varied between 150 and 1800 ppm with equivalence ratios between 0.4 and 2, and were determined using 3.39 µm He-Ne laser absorption. OH concentration time-histories were measured using absorption of frequency-doubled ring-dye laser radiation near 306.7 nm. Ethylene time-histories were measured using absorption of CO$_2$ gas-laser radiation near 10.5 µm. Comparisons are given of these species concentration time-histories with two current large n-alkane mechanisms: the LLNL-C-16 mechanism of Westbrook et al. (2008) and the JetSurf C-12 mechanism of Sirjean et al. (2009). Fair agreement between model and experiment is seen in the peak ethylene yields for both fuels; however, modeled early time-histories of
OH, an important chain-branching species, differ significantly from current measurements.

5.1 INTRODUCTION

Detailed species time-history measurements during reaction of gas-phase diesel fuel and diesel fuel surrogates are needed to test and refine the large reaction mechanisms used to model the ignition of these fuels. The aerosol shock tube is well-suited to fill this need; all that is required is to equip the shock tube with the relevant laser diagnostics. In our laboratory, we have developed sensitive, species-specific, and quantitative UV and visible laser absorption diagnostics for an array of important combustion species including OH, CH₃, CH, NH₂, and NO [64]. Recently, we have extended our suite of laser absorption diagnostics into the infrared. Using commercially available IR gas and diode lasers we have developed quantitative measurement capabilities for C₂H₄, H₂O, CO₂, CH₄ and selected n-alkanes [65-67]. Use of these laser absorption diagnostics in shock tubes has allowed the generation of multi-species time-histories under near-constant-volume conditions intended as targets for chemical kinetic modeling.

To elucidate the inner workings of the large reaction mechanisms describing diesel and diesel-surrogate ignition chemistry, we have applied this multi-species strategy to two important transient species that appear during diesel and n-hexadecane oxidation: OH, and C₂H₄. Time-history measurements of OH are extremely useful in quantifying ignition processes, as they provide critical information about the radical-pool population. OH profiles in these systems typically show an immediate rapid rise (that is dependent on fuel decomposition kinetics) to a relatively long-lived pre-ignition plateau (that is dependent on the slower oxidation kinetics of the stable alkene intermediate species), and a final strong exponential rise during ignition. Time-history measurements of ethylene, C₂H₄, provide quantitative information on the main high-temperature decomposition product and pathways of alkanes. Other groups have examined multiple species during hexadecane and diesel combustion in a jet-stirred reactor (JSR) [68-70], but these studies
do not provide the detailed information on the short, transient time scales available in shock tubes.

Here we present measurements of OH and C₂H₄ during the oxidation of diesel fuel (DF-2) and a single-component large-alkane surrogate for diesel fuel, n-hexadecane. Comparisons are given of these species concentration time-histories with two current large n-alkane mechanisms: the LLNL-C-16 mechanism of Westbrook et al. (2008) [43] and the JetSurF C-12 mechanism of Sirjean et al. (2009) [71].

5.2 EXPERIMENTAL SETUP

5.2.1 AEROSOL SHOCK TUBE

The experiments were performed in the second-generation aerosol shock tube (AST II). This facility is shown schematically in Figure 5.1. Species concentration time-history measurements are then made using laser absorption behind the reflected shock wave through sidewall windows located at 4 cm from the endwall. In Figure 5.1, the reflected shock has propagated nearly all the way through the aerosol mixture (labeled C).

![Figure 5.1: Schematic of aerosol shock tube (AST II) setup. The different regions in the tube are (from left to right): A - driver gas, B - incident-shock heated driven gas with no fuel, C - incident-shock heated test mixture with fuel, and D - reflected-shock heated test mixture.](image)

82
5.2.2 LASER ABSORPTION

Three CW laser systems are used in these experiments: an IR He-Ne laser to measure initial fuel concentration; an IR CO$_2$ gas laser to measure ethylene; and a UV ring dye laser to measure OH concentration.

Initial fuel concentration measurements were by laser absorption at 3.391 µm using a low-noise IR Helium-Neon laser (Jodon$^\text{TM}$ model HN-10G-IR). Significant interference absorption by fuel decomposition products that are formed during high-temperature oxidation prevents this single-wavelength absorption signal from being used to monitor the full time-histories of the parent fuel.

Ethylene was measured at two wavelengths using tunable CO$_2$ laser absorption. The wavelengths that were used for this experiment were 10.532 µm for “on-line” C$_2$H$_4$ measurements (strongest absorption by C$_2$H$_4$) and 10.675 µm for “off-line” C$_2$H$_4$ measurements (weak absorption by C$_2$H$_4$). The laser was tuned to the specific CO$_2$ transition (P(14) for on-line and P(28) for off-line) Potential close-lying transitions of the CO$_2$ laser were suppressed by first passing the laser beam through a monochromator.

A common-mode rejection scheme was used to reduce laser noise (for all three laser systems), employing both reference (I$_0$) and transmitted (I) beams. The transmitted CO$_2$ laser beam passed through the shock tube, through a narrow band-pass filter, and was focused onto a liquid nitrogen cooled MCT detector (Fermionics$^\text{TM}$ PV-12-100). The detection scheme is similar to that used by Pilla et al. [65]. Species concentration for ethylene (and for fuel and OH) were determined using the Beer-Lambert relation (in a slightly different form than in Equation 2.2): $-\ln(I/I_0) = -k_P X L$, where $k_P$ is the absorption coefficient [atm$^{-1}$cm$^{-1}$], P is the total pressure [atm], X is the absorbing species mole fraction, and L is the pathlength, 10 cm in the current experiments. Separate reflected shock tube and FTIR experiments, to determine the absorption coefficients for ethylene [65] and fuel, were also performed. Absorption coefficients for OH are well-established [72].

Two wavelengths were used to separate the C$_2$H$_4$ absorption from the interfering absorption of other alkene species formed during ignition. Near 10.5 µm, the secondary
(interfering) absorbers are primarily larger olefins, such as C\textsubscript{3}H\textsubscript{6}, C\textsubscript{4}H\textsubscript{8}, and the combustion products H\textsubscript{2}O and CO\textsubscript{2}. (Significant absorption from the combustion products occurs only after ignition, when ethylene concentrations are negligible, and is not included in the following analysis.) The wavelengths of the absorption peaks of these olefins are significantly removed from, and do not overlap with, the C\textsubscript{2}H\textsubscript{4} features at 10.532 \( \mu \text{m} \) and 10.675 \( \mu \text{m} \), the wavelengths of the P(14) and P(28) transitions, respectively. At these two wavelengths, absorption from the far wings of these olefins bands is assumed to be approximately constant with wavelength. With this assumption and accurate measurements of the absorption coefficient of C\textsubscript{2}H\textsubscript{4} at the two wavelengths, we are able to separate the absorption contributions of the ethylene and interfering absorbers, and uniquely determine the C\textsubscript{2}H\textsubscript{4} concentration time history.

OH concentration time-history was measured using laser absorption of the R\textsubscript{1}(5) transition in the OH A\textsuperscript{3}\Sigma\textsuperscript{+} -X\textsuperscript{2}\Pi(0,0) band at 306.7 nm. This UV wavelength was generated using a 532 nm laser (Coherent Verdi) to pump a ring-dye laser (Spectra Physics 380) that was intra-cavity frequency-doubled using a temperature-tuned AD* crystal. The laser set up was similar to that used by Herbon et al. [72] and others in our laboratory.

A similar two-wavelength technique was used to separate the OH absorption from interference absorption seen near 306 nm. In this wavelength region there is broadband absorption, likely from conjugated olefins (e.g. 1,3-butadiene). Off-line measurements (32610.4 cm\textsuperscript{-1}) between the R\textsubscript{1}(5) and the R\textsubscript{1}(7) transitions have effectively no absorption by OH, and any interference absorption (assumed to be constant with small wavelength change) can be directly subtracted from the on-line measurements to give a direct measure of the OH concentration time-history. As in the case of ethylene, two shock wave experiments are required at near-identical conditions to acquire the measurements at two wavelengths and effect the subtraction. Representative data using this method are shown in Figure 2. High SNR using the UV OH laser absorption diagnostic enables accurate subtraction of the two signals and results in minimum detection limits for OH of 1-10 ppm.
Strong interference absorption in the UV near 306 nm was seen in all of the diesel experiments as indicated in Figure 5.2. However, the hexadecane experiments showed no significant UV interference absorption. Related behavior was seen by Davidson et al. [73], where interference absorption was observed during iso-octane oxidation, but not in measurements during oxidation of normal alkanes [74].

![Figure 5.2: Diesel OH on-line and off-line laser absorption near 306.7 nm and the difference absorbance signal attributable solely to OH during diesel oxidation. The pre-ignition plateau corresponds to around 10 ppm of OH. Initial reflected shock conditions: ONLINE: 1198 K, 6.69 atm, 1228 ppm diesel; OFFLINE: 1193 K, 6.60 atm, 1197 ppm diesel both in 4% O₂ / argon.](image)

**5.3 RESULTS AND DISCUSSION**

Presented here are laser absorption measurements of OH and C₂H₄ concentration time-histories during the high temperature oxidation of n-hexadecane and diesel fuel. These measurements are also compared with model simulations of n-hexadecane oxidation using the LLNL C-16/Westbrook et al. (2008) mechanism [43], and model simulations of n-dodecane and n-heptane oxidation using the JetSurF 1.0/Sirjean et al.
(2009) mechanism [71]. All calculations were performed using the Reaction Design Aurora suite of CHEMKIN-based codes and implemented with a constant U-V (constant internal energy - constant volume) constraint.

n-Hexadecane was procured from Sigma-Aldrich (99+%) and degassed only before use. The diesel sample (DF-2) was procured locally and degassed only before use. Analysis by IAC Laboratories San Francisco indicate that for the DF-2 fuel, the C/H mass ratio is 6.26, the volume ratio of aromatic:olefin:saturated is 16.2:2.7:81.0, and the cetane index is 45.7. The chemical formula used for equivalence ratio determinations for the diesel fuel was C_{12}H_{23}.

5.3.1 N-Hexadecane Oxidation

Figure 5.3 shows OH and C\textsubscript{2}H\textsubscript{4} time-histories during n-hexadecane oxidation at 1267 K, 6.54 atm, in 1% O\textsubscript{2}/argon with an equivalence ratio \(\Phi=1.21\). Excellent signal to noise ratio (SNR) is seen at all times in the C\textsubscript{2}H\textsubscript{4} data; however, the low levels of OH measured (~2 ppm) before ignition result in a smaller SNR. The simulations shown using the Westbrook et al. [43] C-16 mechanism (labeled LLNL model) effectively capture the formation rate and nearly capture the pre-ignition C\textsubscript{2}H\textsubscript{4} plateau value. Similarly, the modeled time of ignition, indicated by the rapid rise in OH concentration matches the measurement, though the measured OH pre-ignition plateau (at times of 0 to 1000 \(\mu\)s) is approximately twice the modeled value.
Figure 5.3: OH and C₂H₄ species time-histories during n-hexadecane oxidation. Initial reflected shock wave conditions: \( \Phi = 1.2, 1267 \text{ K}, 6.54 \text{ atm} \); initial test gas mixture: 497 ppm C₁₆H₃₄, 1% O₂/argon. The constant UV simulation is based on a LLNL hexadecane mechanism by Westbrook et al. [43].

Figure 5.4 and Figure 5.5 show how the C₂H₄ and OH time-histories and the Westbrook et al. C-16 mechanism simulations vary with temperature. The simulations for the lowest and highest temperature examples overpredict the ethylene yields, while the middle temperature (1170 K) simulation is only slightly overpredicted. From the overpredictions of the ethylene yields, it can be inferred that fuel decomposition product yields of other larger olefins (e.g. propene and butene) are likely underpredicted. As well, at these high temperatures, formation times of C₂H₄ are directly related to fuel decomposition rates and pathways, and future efforts to match these profiles should result in improved rates for the decomposition and oxidation pathways for this large n-alkane.

Also plotted are C-16 mechanism simulations with facility effects incorporated into the simulation. In these experiments, there was a slight pressure increase behind the reflected shock (dP/dt-0.2 atm/ms) see Appendix C and Figure C.0.2 for an explanation and a characteristic pressure trace. This pressure rise only significantly affected the lowest temperature case by shortening the ignition delay. The ethylene yield stayed the same, so the discrepancy in ethylene yield is most likely not due to facility effects at the lowest temperature and is an indication of a problem with the chemical mechanism.
Figure 5.4: \( \text{C}_2\text{H}_4 \) species time-histories during n-hexadecane oxidation. Initial reflected shock wave conditions: \( \Phi = 0.8, 1170 \text{ K}, 4.60 \text{ atm}, 326 \text{ ppm C}_{16}\text{H}_{34}, 1\% \text{ O}_2/\text{argon}; \Phi = 1.2, 1267 \text{ K}, 6.54 \text{ atm}, 497 \text{ ppm C}_{16}\text{H}_{34}, 1\% \text{ O}_2/\text{argon}; \) and \( \Phi = 1.2, 1333 \text{ K}, 6.77 \text{ atm}; 493 \text{ ppm C}_{16}\text{H}_{34}, 1\% \text{ O}_2/\text{argon}. \) Modeled using the LLNL model by Westbrook et al. [43] with constant UV and accounting for facility dP/dt.

Figure 5.5: \( \text{OH} \) species time-histories during n-hexadecane oxidation. Initial reflected shock wave conditions: \( \Phi = 0.8, 1170 \text{ K}, 4.60 \text{ atm}, 326 \text{ ppm C}_{16}\text{H}_{34}, 1\% \text{ O}_2/\text{argon}; \Phi = 1.2, 1267 \text{ K}, 6.54 \text{ atm}, 497 \text{ ppm C}_{16}\text{H}_{34}, 1\% \text{ O}_2/\text{argon}; \) and \( \Phi = 1.2, 1333 \text{ K}, 6.77 \text{ atm}; 493 \text{ ppm C}_{16}\text{H}_{34}, 1\% \text{ O}_2/\text{argon}. \) Modeled using the LLNL model by Westbrook et al. [43] with constant UV and accounting for facility dP/dt.
Peak OH concentrations are accurately modeled at the two lower temperatures (1170 and 1267K) simulations, but not for the highest temperature case. Given that OH concentrations are closely related to the other important small radical species (H-atoms, O-atoms and HO2 radicals) that contribute to chain branching, efforts to refine rates and pathways in the mechanism that improve predictions of OH should improve predictions of all the small radicals contributing to ignition progress. A detailed review of all chain-branching reactions would be required to understand the cause of the discrepancy between the model and the measurements.

5.3.2 DIESEL OXIDATION

Figure 5.6 shows OH and C2H4 time-histories during diesel oxidation at 1198 K, 6.69 atm, in 4% O2/argon with an equivalence ratio Φ=0.54. As in the case of n-hexadecane, good SNR is seen in the ethylene trace. Interestingly, improved SNR is seen at early times in the OH trace. Simulations using three single-component diesel fuel surrogates, C7H16, C12H26 and C16H34, (using mixtures with identical oxygen mole fraction and equivalence ratios) are also shown. While all three of the diesel fuel surrogate simulations give similar ethylene peak yields (and similar OH peak values), none of the simulations closely matches the ignition delay time (derived from the time to half peak OH concentration). As well, none of the three single-component surrogate models accurately predicts early time OH concentrations and all three models underestimate the start of the OH plateau by an order of magnitude. Given that this diesel sample is 81% saturated paraffins, it might have been expected to be modeled relatively well by a single large n-alkane. The approximately ±30% variation between the modeled (JetSurf and LLNL models) and experimental ignition delay times is a measure of the goodness-of-fit one can expect using any of the current single-component diesel surrogates. Post-ignition values of ethylene are expected to be near zero; however absorption by the combustion products H2O and CO2 begins to appear at ignition, and thus the absorption-based C2H4 profile is not shown beyond 1200 µs.
Figure 5.6: OH and C$_2$H$_4$ species time-histories during diesel oxidation. Initial reflected shock wave conditions: $\Phi=0.54$, 1198 K, 6.69 atm; initial test gas mixture: 1228 ppm diesel, 4% O$_2$/argon. Constant UV simulations for single-component surrogate models shown are: n-heptane and n-dodecane which use the JetSurf mechanism and n-hexadecane which uses the LLNL mechanism.

Figure 5.7 and Figure 5.8 present variations in the OH and C$_2$H$_4$ time-history measurements as a function of temperature for diesel oxidation. In both the OH and the C$_2$H$_4$ time-histories, modeled values of peak yields (using the n-hexadecane single-component surrogate) are relatively close to (but consistently exceed) the measured values at all temperatures. Time scales in the simulations for formation of OH and C$_2$H$_4$ typically vary by a factor of two from the experiment. Given the current relatively confident state of knowledge about large n-alkane pyrolysis and oxidation chemistry (albeit tempered by the comparisons shown earlier for n-hexadecane), the differences seen between the single-component surrogate modeling and the diesel experiments indicates that a multi-component surrogate for diesel will be needed to capture the finer details of these experiments. In particular, interfering absorption near 306.7 nm that indicates the presence of UV absorbing species (i.e. conjugated olefins) during diesel oxidation chemistry, but not during n-hexadecane oxidation, point to a need to include these larger, more chemically complex, intermediate species in diesel modeling.
Figure 5.7: C$_2$H$_4$ species time-histories during diesel oxidation. Initial reflected shock wave conditions: $\Phi=0.8$, 1119 K, 4.63 atm, 1761 ppm diesel, 4% O$_2$/argon; $\Phi=0.5$, 1198 K, 6.69 atm, 1228 ppm diesel, 4% O$_2$/argon; and $\Phi=0.6$, 1373 K, 6.33 atm, 1380 ppm diesel, 4% O$_2$/argon. Modeled using the LLNL model by Westbrook et al. [43] for n-hexadecane as the fuel with constant UV and accounting for facility dP/dt.

Figure 5.8: OH species time-histories during diesel oxidation. Initial reflected shock wave conditions: $\Phi=0.8$, 1119 K, 4.63 atm, 1761 ppm diesel, 4% O$_2$/argon; $\Phi=0.5$, 1198 K, 6.69 atm, 1228 ppm diesel, 4% O$_2$/argon; and $\Phi=0.6$, 1373 K, 6.33 atm, 1380 ppm diesel, 4% O$_2$/argon. Modeled using the LLNL model by Westbrook et al. [43] for n-hexadecane as the fuel with constant UV and accounting for facility dP/dt.
The increased noise in the C$_2$H$_4$ and OH profiles in Figure 5.7 and Figure 5.8 respectively is also a result of a reduction in SNR due to subtraction of absorption from interfering species. Also the inclusion of the facility dP/dt shortened the ignition delay in the coldest experiment.

5.4 CONCLUSIONS

The first multi-species time-history measurements for high-temperature n-hexadecane and diesel oxidation are presented. Measured time-histories for OH and C$_2$H$_4$ are compared with single-component diesel surrogate models. Agreement in ignition delay times and species concentrations typically are within a factor of two at all temperatures. However, early-time predictions of OH mole fraction, indicative of the ability of these mechanisms to capture the important chain-branching species concentrations, vary widely from the experiments.

These measurements provide quantitative kinetic targets for the testing and refinement of n-hexadecane and diesel surrogate models. Further work is planned to extend species time-history measurements for these fuels to include simple alkanes (i.e., methane and ethane), larger alkenes particularly propene and butene, and conjugated alkenes (e.g., 1,3-butadiene).
Chapter 6: CONCLUSIONS

6.1 FACILITY AND METHOD

A new facility and method of studying the chemical kinetics of low-vapor-pressure fuels has been developed. The aerosol shock tube was modified to a second-generation aerosol shock tube, which displayed significant improvement in aerosol spatial uniformity. Previously the aerosol shock tube relied on a continuous flow with turbulent mixing to fill the shock tube. The improved facility uses a non-continuous, laminar plug flow. This required the construction of a mixing tank, which is connected directly to the endwall, a specially designed endwall gate valve, driven gate valve, and a dump tank. The aerosol is created in the mixing tank, which is capable of aerosol loadings up to 5 times higher than those possible with the first-generation aerosol shock tube. The aerosol then flows into the test section of the driven section of the tube between the gate valves. This is done by gently pulling the aerosol through expansion into the dump tank. This method of filling produced significant improvements in the spatial uniformity of the aerosol. This uniformity was shown to impact the reproducibility of the chemical kinetic measurements that were made.
6.2 **Ignition Delay Times**

Using this new facility and technique, measurements of ignition delay times for several low-vapor-pressure fuels were made including n-decane. n-Decane has been studied quite extensively in the past using the heated shock tube method, which for this fuel we do not worry about premature decomposition. We see good agreement between the heated shock tube and aerosol shock tube measurements. We then measured even lower vapor pressure fuels including n-dodecane, n-hexadecane, and methyl decanoate and produced some of the first measurements of ignition delay time for these fuels.

We also applied the aerosol shock tube method to the measurement of ignition delay times for real multi-component fuels. ignition delay times for a low volatility jet fuel known as JP-7 were determined using this method [42]. We also measured the ignition delay time of several different batches of diesel fuel from around the world. We found that cetane number affects the ignition delay at high temperatures. Also, that aromatic content affects the ignition delay as well. This work has also brought attention to the fact that there needs to be better surrogate mixtures and mechanisms to simulate the combustion of diesel fuel. These high quality ignition delay times, which are unaffected by partial distillation and evaporation, provide accurate benchmark validation targets for the development of such surrogate mechanisms.

6.3 **Species Time-Histories**

To improve these validation targets we drew upon our laboratory’s ability to measure concentrations of important combustion species, and applied unique laser absorption diagnostics to the study of low-vapor-pressure fuels in the aerosol shock tube. We measured OH and C$_2$H$_4$ during the oxidation of n-hexadecane and diesel fuel.

To measure OH we used a ppm-sensitive UV absorption diagnostic. For C$_2$H$_4$ we used a mid-IR CO$_2$ laser. We measured the OH and C$_2$H$_4$ time-histories for a range of temperatures for both fuels. The results for n-hexadecane showed agreement with a mechanism developed at LLNL by Westbrook and coworkers in some cases. For diesel
fuel we compared the measurements to a primary reference fuel surrogate mechanism also developed at LLNL, and the agreement was not as good. This is understandable because the primary reference fuel is not meant to capture the details of the oxidation, only the ignition delay.

6.4 Future Work

The aerosol shock tube can be applied to many engineering and science problems and through this work we have found many alternative applications for this unique facility. For example, others in our laboratory have used it to study low-vapor-pressure pyrolysis, bio-aerosol-shock interactions, and nano-aluminum-slurry combustion. These successful applications demonstrate the wide versatility of this facility and beg the question of what else can be done with this facility.

6.4.1 Negative Temperature Coefficient

Many recent studies for smaller fuel molecules have been focused on the negative temperature coefficient (NTC) behavior. This is where a link in the fuel decomposition slows the overall reaction with increasing temperature for certain conditions. This occurs typically at lower temperatures and higher pressures. Coincidentally this occurs at the same conditions where most diesel engines operate. Because this behavior is highly dependent on the fuel decomposition pathways it is very important that as we extend the experimental database to large fuel molecules with the aerosol shock tube that we include the behavior of these fuels in the NTC regime.

Much of this work on the aerosol shock tube was focused on making sure that this new method and facility worked at extending the range of fuels that can be studied using shock tubes. The future of this facility should include the measurement of NTC behavior and that will require applying new shock tube techniques such as driver extensions and driver inserts pioneered in our laboratory.
6.4.2 BIOFUELS

As shown in Figure 1.1 bio-diesel has one of the highest distillation curves of these practical fuels. This makes it an ideal candidate for the aerosol shock tube. Also because of pressure to reduce dependence on foreign sources of fuel and to limit the carbon footprint that petroleum fuels cause, biofuels are a promising future source of energy. In this work, I presented measurements of methyl decanoate ignition delay time. This fuel however is only a smaller version of the molecules that are prevalent in bio-diesel blends. The second-generation aerosol shock tube is fully capable of being used for the large chain methyl esters that are found in bio-diesel (e.g. methyl palmitate, methyl stearate, methyl oleate, methyl linoleate, and methyl linolenate).
APPENDIX A

A.1 LIQUID FILMS

Any laser measurement in the aerosol shock tube is confounded by the fact that we have droplets and highly condensable fuels. The fuel is slightly elevated in temperature (a degree or two above room temperature) due to the energy involved in nebulization. Then it flows into the shock tube. Because the aerosol has a large surface area, the gas surrounding the droplets can be reasonably assumed to have the saturation vapor pressure of the fuel at the temperature of the droplets. Every surface that this mixture comes in contact with including the windows, which are a few degrees cooler than the gas, will condense fuel. As I referred to earlier heating the windows is needed to avoid window fouling. To avoid this condensation, a few degrees of heating would suffice.

The problem worsens though as we perform a shock experiment. After the passage of the incident shock the temperature is instantly raised to somewhere around 600K. At this temperature the saturation vapor pressure is several orders of magnitude above the value at room temperature, and so the aerosol evaporates until there is no liquid fuel left. The fuel vapor partial pressure never reaches the saturation value for the temperature of the bulk gas. However, near the edges of the shock tube there is a boundary layer where the temperature rapidly decreases to room temperature at the shock tube wall, so there exist large gradients in both temperature and fuel concentration. These gradients produce large diffusive fluxes of heat and fuel. The temperature of the wall only rises slightly due to the fact that the shock experiment is so short and the heat conduction of the metal is very high so the rise in temperature is spread quickly into the bulk of the material. The fuel that makes it through the boundary layer is met by, relatively speaking, a very cold wall, and so the molecules stick and condense. This is
very short so not much fuel is built up, but the measurements can be affected by even micron thicknesses of a liquid fuel film.

Figure A.0.1: Examples of shock velocity attenuation for various window heating configurations. Note that the old heater raised the temperature in region 1 accelerating the shock near the endwall.

The solution to this problem is to heat the windows to temperatures such that the fuel molecules will not stick to the window, but stay in the gas phase. The temperature where this becomes an effective method is around 70°C. This also becomes a problem however, because it creates a naturally convective flow inside the shock tube as well as a longitudinally non-uniform temperature field in the region near the endwall. The non-uniform temperature field has been seen to affect the shock speed (Figure A.0.1). As the shock propagates into regions with higher temperatures the shock accelerates. This is a problem because our method of measuring shock speeds with pressure transducers has a limited spatial resolution and relies on extrapolation of a shock speed versus distance curve, so it is very sensitive to changes in the behavior of the attenuation. Because heating creates these complications, it was necessary to minimize the area which was heated to minimize the disturbance to the initial conditions of the shock tube. This is facilitated by a heating and cooling scheme built into the mount that holds the windows (Figure A.0.2). The results are windows that are capable of being heated to around 100°C, while the wall all around the window is maintained at room temperature.
A.2 Window Design

The mount is made of brass inside of which there is a water-cooled cavity surrounding the copper window plugs that are isolated thermally with a ceramic that would minimize heat transfer, but withstand the high forces involved in a shock and/or detonation wave. There are band heaters around the copper plugs, which transfer the heat to the windows and then a flow of cold water around the plugs immediately removes the heat. The window mount is shown below in Figure A.0.2.

![Window Mount](image)

Figure A.0.2: New heated window mount prior to installing on shock tube. Copper tubes are wrapped with ring heaters which conduct heat to windows. The mount is cooled by flowing cool water through inside of mount.

A.3 Operational Conditions

The temperature of the window is usually held at the lowest temperature that does not allow window condensation. Recognizing the presence of condensation elucidates two distinct ways that condensation occurs. The extinction of the visible laser normally indicates the presence of droplets and after evaporation the extinction will typically go to zero and stay at zero. If the extinction raises again slowly in region 2 and faster in region 5, then condensation is happening at distinct nucleation sites on the window. The condensation creates bumps of liquid on the surface and scatters the beam as these bumps...
grow, the scattering increases. The increase is faster in region 5 because the partial pressure of fuel is higher in this region.

The other less common method of condensation is where nucleation sites are not apparent and the only indication of a liquid on the surface comes from a negative extinction of the non-resonant beam. The extinction decreases monotonically during evaporation, but asymptotes to a value below zero. The only way for this to happen is if the I is larger than the I_o (in the formula \(-\ln(I/I_o)\)). So in this case we first need to rule out emission, which is not usually a problem in region 2. We find that this is the same effect as an anti-reflection coating on a window. What is happening is that the fuel is condensing in a smooth film over the window. Because we are required to use specialized windows like sapphire to transmit the mid-IR light there is a large difference in the index of refraction of sapphire (1.7) as compared to that of the gas mixture (1.0) in the shock tube. Therefore a thin film of fuel (1.4) will effectively reduce the net effect of Fresnel reflections, which initially caused attenuation in the signal.
B.1 SHOCK AEROSOL INTERACTIONS

When the shock wave hits an aerosol the liquid droplets contained in that aerosol rapidly exchange mass, momentum, and energy with their surroundings. This state of non-equilibrium lasts longer than in a typical purely gas-phase shock, and so it is informative to understand what is happening in this transient process behind the shock wave.

Figure B.0.1: X-t diagram for shock aerosol interaction. Particle breakup occurs fastest with particle acceleration occurring more slowly. Evaporation and diffusion occur most slowly after which the flow is in equilibrium. The measurement location is selected such that all these processes have occurred to a sufficient extent upon arrival of the reflected shock.
The process is shown on an X-t diagram (Figure B.0.1). This details the position of the shocks in the shock tube. We start at the bottom of the graph where the incident shock is on the left travelling right toward the endwall.

Behind the incident shock the quickest transfer happens with momentum. As the shock wave passes the droplet it leaves behind a small bow shock which reflects off the surface of the droplet. The droplet then begins to accelerate from the momentum transfer of the subsonic gas which is decelerated by the bow shock. As the droplet moves toward the endwall it is surrounded by the higher velocity gas and is eventually travelling at the speed of the gas surrounding it. This typically takes less than 10 µs for aerosol used in this study (d ~ 4µm).

A somewhat slower process which happens at the same time as the momentum transfer is the transfer of mass and energy. This process takes longer to complete, with evaporation happening in about 100 µs for our 4 µm aerosol. The transfer of energy occurs at the surface of the droplet. The gas surrounding the droplet is flowing and convectively transferring heat to the droplet for the first 10 µs. When the droplet accelerates to the same speed of the gas the heat is being transferred to the droplet purely conductively. A gradient in temperature in the gas at the surface sustains a heat flux, which is matched by a smaller gradient in the liquid droplet. As such the temperature of the droplet is ever increasing with the coldest point at the center of the droplet. The hottest point of the droplet is the surface which is evaporating fuel to match the local vapor pressure surrounding it. And as a result the fuel vapor concentration is higher near the surface of the droplet creating a diffusive flux of fuel away from the droplet. This evaporation process consumes the fuel and the droplet diameter shrinks until it is completely evaporated.

**B.2 Gas Phase Diffusion**

After evaporation we have a purely gas phase mixture of a very low-vapor-pressure fuel. This is not the end of the non-equilibrium state though. Once the mixture is completely gas phase, we are left with localized cold spots due to the localized
consumption of the heat of vaporization, as well as localized fuel rich pockets. These localized pockets could be detrimental to a combustion experiment resulting in temperature and equivalency averaged behavior. So we must be sure that these gradients are effectively smoothed out prior to the arrival of the reflected shock.

This fuel diffusion problem can be approximated as a spherically symmetric diffusion problem. We will over-estimate the diffusion time if we approximate the fuel as initially concentrated in a small sphere of mole fraction equal to unity surrounded by pure bath gas out to a radius equal to half the inter-droplet spacing. At this shell we can assume that a no flux or symmetry boundary condition is appropriate. This problem is very similar to the free diffusion problem with a self-similar solution. The important result is that the time it takes the fuel to diffuse to a radius R is proportional to $R^2/D$ where D is the diffusion coefficient for the fuel molecules diffusing into the bath gas. This result tells us that the diffusion time is strongly related to the distance between the droplets.

This gives us insight into how we should design our experiment to minimize any small scale non-uniformities. The amount of time these bumps take to smooth out depends on the radius of the symmetry boundary condition very strongly. This means that we would like to have as small of an inter-droplet spacing as possible. In setting up an experiment the inter-droplet spacing is set by the equivalence ratio and fuel loading that we want to achieve for our experiment. But we do have control over the droplet diameter, which for reasons mentioned earlier (section 2.2), we noted that it would be advantageous to make the droplet diameter small to track the flow. As for diffusion times, this is also the case. If we make the droplet smaller, while keeping the fuel concentration constant, we need more droplets per volume and hence a smaller inter-droplet spacing. We can insert estimates for the values and conditions we are hoping to achieve and find that the diffusion time is around 100 µs using this rudimentary analysis. If we model this numerically we get similar answers. Below is a plot of the fuel vapor concentration evolving with time for an example case (Figure B.0.2). Note that the inter-droplet spacing for a $C_V = 15$ ppmv and $d = 4.5$ µm is about 400 µm.
Figure B.0.2: Evolution of gas phase fuel concentration. Assuming spherical symmetry and that the droplet instantaneously evaporates. In this case, it takes only 15 µs for the fuel concentration to be 95% uniform.

If we perform these calculations over a range of liquid volume concentrations (Figure B.0.3) we see that the diffusion time decreases with increasing loading. This is because the inter-droplet spacing decreases. The same thing happens if droplet size decreases, because there are more droplets present for a specific loading.
Figure B.0.3: Time to achieve 95% uniformity with varying volume fraction of liquid for monodisperse size distribution of various diameters.

This analysis presumes a spherically symmetric scenario, which is a simplification. When the momentum transfer first occurs, the stagnation point on the surface of the droplet is going to have higher transfer rates breaking the symmetry. Also depending on the shock strength, droplet breakup has been known to occur for Webber Numbers above 12. All of this will only serve to enhance mixing and speed up these processes, so in the purely diffusive spherically symmetric case we are considering is a worst-case scenario.

This analysis is very important, because it also tells us where to place our measurement diagnostics in the shock tube. As noted before, the laser measurements are made longitudinally across the shock tube through two windows in the sidewalls near the endwall of the shock tube. It is advantageous to have this diagnostic as close to the endwall as possible especially for high energy release conditions. However due to practical constraints the measurement is typically made no less than 2 cm from the endwall. The distance the measurement location is from the endwall directly determines the time between the arrival of the incident shock and the arrival of the reflected shock.
This however is the referred to as the laboratory time, and is not the same as the fluid time. The difference is explained in the next section.

## B.3 Lab Time and Particle Time

The difference between lab time and fluid time is due to the fact that the fluid is passing by the measurement location continuously between the incident shock arrival and the reflected shock arrival. The situation is best understood when looking at the X-t diagram in Figure B.4.

![Figure B.4: X-t diagram showing the reflection of the incident shock wave at the endwall. Also shown is a particle path for the fluid element that is at the measurement location in region 5. This particle experience region 2 conditions for longer than the measurement location views region 2 resulting in a difference between lab time and particle time.](image)

This is a plot of distance on the vertical axis and time on the horizontal axis. The shocks are shown as well as the path of a fluid element. The incident shock starts in the lower left hand corner and travels toward the endwall and along the way intersects the fluid
element and accelerates it toward the endwall. This begins the fluid time. Then the shock passes the measurement location and the lab time is started. The incident shock then hits the endwall and a reflected shock is created and travels back upstream. The fluid element was chosen as the fluid element that intersects the reflected shock at the moment it passes the measurement location. This ends the fluid time and the lab time simultaneously. This tells us that the time that the fluid element is exposed to region 2 conditions is longer than the time that the measurement location experiences region 2 conditions. The relationship between the lab time (LT) and fluid time (FT) is

\[ FT = \frac{\rho_2}{\rho_1} LT \]  
Equation B.1
APPENDIX C

C.1 BEHIND THE REFLECTED SHOCK

When the reflected shock arrives at the measurement location it stagnates the flow. At this point the calculation of the shock jump is much easier because there is no phase change. The shock wave is initiated such that the conditions at this point are sufficient to begin to decompose the fuel. This process can be observed at the measurement location optically and typically we have a pressure sensor measuring the pressure. For high energy release conditions pressure rise is a good indication of ignition. Other things such as fuel decomposition species time-histories and emission can be measured as well.

C.2 TEST TIME

These measurements of concentration and emission are easily modeled if the conditions are not affected by facility-induced perturbations, the most striking of which would be the arrival of the expansion fan to the measurement location. This expansion fan has to travel from the diaphragm to the end of the driver then reflect and travel the entire length of the shock tube before reaching the measurement location. The effect that this will have is a rapid expansion and cooling of the fluid element along with an acceleration of the fluid away from the endwall. In terms of the combustion event it will slow and stop any significant reactions.

The arrival of the expansion fan can be delayed by several methods. The composition of the driver can be altered by lowering the ratio of specific heat. This will effectively slow the speed of sound of the mixture and slow the expansion wave in the driver mixture. Another method is to make the driver longer. This has been employed in previous studies and a similar shock extension was added to the aerosol shock tube as seen in Figure C.0.1.
C.3 CONTACT SURFACE REFLECTION

There is also another effect that can limit the test time even before the arrival of the expansion fan. This occurs because of the existence of a contact surface that exists between the driver gas and the driven gas. This interface travels toward the endwall at the same speed as the gas behind the incident shock wave. The incident shock will arrive at the endwall long before the contact surface. As a result the reflected shock as it is travelling back toward the driver will intersect the contact surface. Because this surface marks a change in gas mixtures the speed of sound in each mixture is different. This difference will cause a slight reflection of the reflected shock wave, which will travel back toward the endwall. At the measurement location a slight pressure increase is the result. Along with this increase is also an increase in temperature, thus ending our test time.

In order to minimize the impact of this effect and extending the test time, we tailor the driver gas mixture. Typically the driver is helium, if we add nitrogen the mixtures speed of sound is reduced. We can create a mixture in the driver that will have a gamma exactly matched to the gamma of the driver gas at the temperatures of region 2,
and in essence we can avoid reflecting the reflected shock (Figure C.0.2). This only works to a point. The contact surface is not a step function but is a region of mixed gases so the end result is very small pressure oscillation.

![Aerosol Shock Tube Tailored Driver Test](image)

Figure C.0.2: Pressure trace from pressure transducer located at 2 cm from the endwall on a test using a tailored driver mixture. At 0 ms the incident shock arrives followed closely by the reflected shock. In region 5 the pressure slowly increases by some non-ideal facility effects. At 6 ms the reflection off the contact surface arrives but with no significant pressure jump. The pressure trace is reasonably level until the arrival of the expansion wave at 11 ms.

**C.4 CONSTANT U, V OPERATION**

Another facility-dependent effect that becomes important at long test-time conditions is a slightly positive dP/dt (this effect can be seen in the first 6 ms of Figure C.5) accompanied by a dT/dt, which after enough time effects the chemistry. This effect occurs because the boundary layer’s viscous dissipation slows the incident shock, and as a result region 2 (and consequently region 5) has a pressure profile that decreases
closer to the endwall. As the pressure profile equalizes near the endwall the pressure increases. This challenges the constant UV assumptions that are very useful for modeling. This will artificially make the measured ignition delay times occur sooner than would be predicted by a constant UV assumption. See Figure C.0.3.

Some attempts have been made to capture this non ideal effect in the model and thus predicting the roll off. But these are complicated when there is significant heat release upon ignition. A more elegant solution involves removing the rise in pressure by partially reflecting the expansion wave prematurely using specially designed driver inserts to keep the pressure profile constant.

Another method of accounting for this pressure rise is to include it in the modeling as below in Figure C.0.3. The model was modified by specifying a pressure that matches the measured pressure. This is not completely accurate because during ignition when a large amount of energy is released the pressure will rise, but it gives us some insight as to what conditions this effect becomes significant.

![Image](image)

**Figure C.0.3:** Figure 4.9 of ignition delay time plot vs. inverse of temperature showing the effect of modeling as constant UV or with a 0.2 atm/ms dP/dt. The effect becomes apparent at test times above 10 ms.
APPENDIX D

D.1 DETAILED CALCULATION OF INITIAL PRESSURES

In practice, a more complex model than the isothermal model presented in Section 3.2.2 is used for setting the initial pressures for the second generation aerosol shock tube. To help understand this more complex model a very simplified representation of the expansion process is shown in Figure D.0.1. Initially $P_A$ is larger than $P_B$ and a sliding piston, which separates the volumes $V_A$ and $V_B$, is held in place. The piston is then allowed to move, (this is analogous to opening the ball valve) and the gas on the left is compressed as the gas on the right expands until the pressures equalize to $P_1$.

![Diagram](image)

Figure D.0.1: Simplified schematic of the expansion process showing (a) the initial state and (b) the final state.

The volume $V_A$ represents the test section and mixing tank ($V_A = V_{TS} + V_{MT}$) and $V_B$ represents the dump tank from Figure 3.2. $V_T'$ is the total displaced volume and is related to $V'$ (See Figure 3.2) by $V_T' = (V_{TS}/V_{MT} - 1)V'$. This definition makes the equations simpler.
Expansion experiments were performed in the shock tube with a water aerosol. In these experiments, we kept the initial pressure in the aerosol mixing tank and test section constant \((P_A = 700\, \text{torr})\) and we varied the initial pressure in the dump tank \((P_B)\). We then measured the resultant equilibrium pressure \((P_1)\). The data are shown in Figure D.0.2. To model these results we first assumed the process proceeded as in Figure D.0.1 isothermally. The isothermal model underpredicts the pressure as seen in Figure D.0.2.

![Graph showing measurements of final pressure (P₁) after expansion of gas/aerosol mixture into dump tank.](image)

Figure D.0.2: Measurements of final pressure \((P_1)\) after expansion of gas/aerosol mixture into dump tank. Initial pressure in the aerosol mixing tank and test section \((P_A)\) was around 700 torr and the initial pressure in the dump tank \((P_B)\) was varied. Also shown are various models used to predict the expansion behavior. The hybrid model that assumes isothermal expansion and isentropic compression seems to predict the final pressure quite well.

We then tried an isentropic model, which does a much better job of predicting the final pressure. To better understand what happened in our experiment, we made a temperature measurement in the core of the dump tank and the core of the test section near the endwall. We saw a slight increase in temperature in the dump tank, which would be expected in an isentropic compression, but no noticeable change in the temperature in the test section during expansion. This is most likely due to the fact that the droplets regulate the temperature by acting as condensation sites. Because of this
result, a hybrid process would be more appropriate. More specifically, we used the isothermal assumption in the aerosol mixing tank and test section for the expansion, and an isentropic assumption in the dump tank for the compression. The final pressures predicted using this hybrid model match most closely with the experimental data.

Now that we know which model is most accurate, we can use this hybrid model to find the initial pressures given a desired final pressure using the equations below.

\[
\begin{align*}
P_B &= ((V_B - V_T^+)/V_B)^\gamma P_1 \quad \text{Equation. 3.1a} \\
P_A &= P_1(V_A + V_T^+)/V_A \quad \text{Equation. 3.1b}
\end{align*}
\]

The pressures and volumes are defined in Figure 3.1 and Figure D.0.1. \(\gamma\) is the ratio of specific heats for the bathgas.

An example of this calculation is shown in Figure D.0.3. The initial pressures \(P_A\) and \(P_B\) are plotted on the left axis versus the desired \(P_1\). If a 100 torr pre-shock pressure \((P_1)\) is required, the aerosol mixing tank and test section should be set to 185 torr and the dump tank should be set to 62 torr for a non-dimensional expansion of \(X = 2\).

![Figure D.0.3: Plot indicating how to set initial pressures in the mixing tank/test section and the dump tank.](image)

For example, to achieve an equilibrium pressure \((P_1)\) of 100 torr and expansion factor of 2, the mixing plenum and test section should be set initially to 185 torr \((P_A)\) and the dump tank should be set initially to 62 torr \((P_B)\).
### E.1 Ignition Delay Time Data

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Table E.1: Table shows ignition delay time data with associated conditions. See chapter 4 for analysis.

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APPENDIX F

F.1 AEROFROSH CODE

c**********************************************************************
c**********************************************************************
c     AeroFrosh Program
  One-Dimensional Two-Phase Shock Code
  Adapted from David Davidson's Code
  Dan Haylett dhaylett@stanford.edu
  Uses C:\Sandia\Sandia.dat for Thermodynamic Data
  Writes to C:\Sandia\Output.dat
  November 1, 2004
  **********************************************************************
  **********************************************************************
c

    Initialization and Setup

Implicit Double Precision (A-H,O-Z), Integer(I-N)
Character*20 Species, MIXTURE
Character*10 Xcn
Character*2  Ele, Tempele
Dimension Species(20),Xmolefraction1(20),Xmolefraction2(20)
Dimension Xmolefraction5(20)
Dimension TDat(7,2,20), TempDat(7,2)
Dimension Ele(4,20),TempEle(4),NumEle(4,20),NumeleTemp(4)
Dimension HoverRT(20),CpoverR(20)
OPEN(11, FILE='c:\sandia\output.dat', STATUS= 'UNKNOWN')

Write(*,*) ' *****************************************************'
Write(*,*) ' AeroFrosh Program                                 '
Write(*,*) ' One-Dimensional Two-Phase Shock Code              '
Write(*,*) ' Adapted from David Davidson's Code               '
Write(*,*) ' Dan Haylett dhaylett@stanford.edu               '
Write(*,*) ' Uses C:\Sandia\Sandia.dat for Thermodynamic Data '
Write(*,*) ' Writes to C:\Sandia\Output.dat                 '
Write(*,*) ' November 1, 2004                                  '
Write(*,*) ' *****************************************************'
Write(11,*) ' *****************************************************'
Write(11,*) ' AeroFrosh Program                                 '

Set initial conditions $P_1$, $T_1$, LSF position, ppmv

Write current conditions, ask for changes

$P_1 = 150.$
$T_1 = 293.$
$\text{endwall} = 1877.8$
$n\text{endwall} = 2$
$\text{abso} = 0.632$
$\text{ppmv} = 0$
$\text{readflag} = -1$
$\text{MIXTURE} = \text{Dodecane/Air}$
$n\text{mixture} = 1$

500 call $\text{condx}(P_1, T_1, \text{endwall}, \text{abso}, \text{ans}, \text{MIXTURE})$
if (ans.eq.1) then
Write('*, *) 'New $P_1$ [torr]?'
read('*, *) $P_1$
GOTO 500
endif (ans.eq.2) then
Write('*, *) 'New $T_1$ [K]?'
read('*, *) $T_1$
GOTO 500
endif (ans.eq.3) then
Write('*, *) 'New Abs [3.39]?'
read('*, *) $\text{abso}$
476 GOTO 500
endif (ans.eq.4) then
Write('*, *) 'New LSF Position?, 1=endwall, 2=2nd last port'
read('*, *) $n\text{endwall}$
if(nendwall.eq.2) endwall=1877.8
if(nendwall.eq.1) endwall=1997.8
GOTO 500
endif (ans.eq.5) then
Write('*, *) 'New Mixture?'
Write('*, *) '1=Dodecane/Air'
Write(*,*) '2=Dodecane/Argon'
Write(*,*) '3=Water/Air'
Write(*,*) '4=Water/Argon'
Write(*,*) '5=JET-A/Argon/O2'
Write(*,*) '6=Dodecane/Argon/O2'
Write(*,*) '7=JET-A/Argon/4%O2'
Write(*,*) '8=JET-A/Argon/1%O2'
Write(*,*) '9=Hexadecane/Argon/4%O2'
Write(*,*) '10=Hexadecane/Argon/1%O2'
read(*,*) nmixture
if(nmixture.eq.1) mixture='Dodecane/Air'
if(nmixture.eq.2) mixture='Dodecane/Argon'
if(nmixture.eq.3) mixture='Water/Air'
if(nmixture.eq.4) mixture='Water/Argon'
if(nmixture.eq.5) mixture='JET-A/Argon/O2'
if(nmixture.eq.6) mixture='Dodecane/Argon/O2'
if(nmixture.eq.7) mixture='JET-A/Argon/4%O2'
if(nmixture.eq.8) mixture='JET-A/Argon/1%O2'
if(nmixture.eq.9) mixture='Hexadecane/Argon/4%O2'
if(nmixture.eq.10) mixture='Hexadecane/Argon/1%O2'
GOTO 500
  elseif (ans.eq.6) then
go to 7777
endif

goto 7778

c  Get the Incident shock speed
c
7777  Write(11,*) 'Current Mixture: ',Mixture
Write(11,*) ' P1      T1      Cv      LSF Position'
Write(11,*) ' [torr]  [K]     [ppmv]  [mm]        '
Write(11,7713) P1, T1, ppmv, endwall
7713  Format(F7.1,F8.1,F6.1,F11.1)

c  call velcalc(U1,atten,ENDWALL)
write(*,*) 'Please enter shock velocity at endwall'
read(*,*) u1

c  Enter species and mole fractions
c
if(nmixture.eq.1) nchoice=2
if(nmixture.eq.2) nchoice=2
if(nmixture.eq.3) nchoice=1

122
if(nmixture.eq.4) nchoice=1
if(nmixture.eq.5) nchoice=3
if(nmixture.eq.6) nchoice=2
if(nmixture.eq.7) nchoice=3
if(nmixture.eq.8) nchoice=3
if(nmixture.eq.9) nchoice=4
if(nmixture.eq.10) nchoice=4

c    assume DROPLETS at 20C  Densities from CRC 56th ed. pgs. F-5, C-274
    If(nchoice.EQ.1) density=0.998234
    If(nchoice.EQ.2) density=0.7487

c    http://www.chevron.com/products/prodserv/fuels/bulletin/aviationfuel/2_at_fuel_perf.shtm#energycontent
      If(nchoice.EQ.3) density=0.810
      If(nchoice.EQ.4) density=0.773
      If(nchoice.EQ.5) density=0.730
      If(nchoice.EQ.1) DropMW=18.015
      If(nchoice.EQ.2) DropMW=170.34
      If(nchoice.EQ.3) DropMW=167.311
      If(nchoice.EQ.4) DropMW=226.441
      If(nchoice.EQ.1) cros=9999.
      If(nchoice.EQ.2) cros=65.5
      If(nchoice.EQ.3) cros=58.54
      If(nchoice.EQ.4) cros=80.00

c    here are the four mixtures

c    The mole fractions are based on a background 22C vapor pressure of aerosol

105    if(nmixture.eq.1) then
          NumberSpecies=3
          SPECIES(1)='N2'
          SPECIES(2)='O2'
          SPECIES(3)='C12H26'
          XMolefraction1(1)=0.79*(P1-0.1040)/(P1)
          XMolefraction1(2)=0.21*(P1-0.1040)/(P1)
          XMolefraction1(3)=0.1040/(P1)
          JDROP=3
    elseif(nmixture.eq.2) then
          NumberSpecies=2
          SPECIES(1)='AR'
          SPECIES(2)='C12H26'
          XMolefraction1(1)=(P1-0.1040)/(P1)
          XMolefraction1(2)=0.1040/(P1)
JDROP = 2
elseif(nmixture.eq.3) then
   NumberSpecies = 3
   SPECIES(1) = 'N2'
   SPECIES(2) = 'O2'
   SPECIES(3) = 'H2O'
   XMolefraction1(1) = 0.79*(P1-19.8)/(P1)
   XMolefraction1(2) = 0.21*(P1-19.8)/(P1)
   XMolefraction1(3) = 19.8/(P1)
   JDROP = 3
endif(nmixture.eq.4) then
   NumberSpecies = 2
   SPECIES(1) = 'AR'
   SPECIES(2) = 'H2O'
   XMolefraction1(1) = (P1-19.8)/(P1)
   XMolefraction1(2) = 19.8/(P1)
   JDROP = 2
endif(nmixture.eq.5) then
   NumberSpecies = 3
   SPECIES(1) = 'AR'
   SPECIES(2) = 'O2'
   SPECIES(3) = 'JET-A'
   this value is for dodecane should be updated for JET-A
   XMolefraction1(1) = 0.79*(P1-0.1040)/(P1)
   XMolefraction1(2) = 0.21*(P1-0.1040)/(P1)
   XMolefraction1(3) = 0.1040/(P1)
   JDROP = 3
endif(nmixture.eq.6) then
   NumberSpecies = 3
   SPECIES(1) = 'AR'
   SPECIES(2) = 'O2'
   SPECIES(3) = 'C12H26'
   XMolefraction1(1) = 0.79*(P1-0.1040)/(P1)
   XMolefraction1(2) = 0.21*(P1-0.1040)/(P1)
   XMolefraction1(3) = 0.1040/(P1)
   JDROP = 3
endif(nmixture.eq.7) then
   NumberSpecies = 3
   SPECIES(1) = 'AR'
   SPECIES(2) = 'O2'
   SPECIES(3) = 'JET-A'
   this value is for dodecane should be updated for JET-A
   XMolefraction1(1) = 0.96*(P1-0.1040)/(P1)
XMolefraction1(2)=0.04*(P1-0.1040)/(P1)
XMolefraction1(3)=0.1040/(P1)
JDROP=3
elseif(nmixture.eq.8) then
NumberSpecies=3
SPECIES(1)=\textquoteleft AR\textquotefr"
\[ X_{dcc} = \text{ppmv} \times 1e^{-6} \times \text{density}/\text{DropMW} \]
\[ X_{dtorr} = X_{dcc} \times 82.06 \times T_1 \times 760 \]
\[ T_T = P_1 + X_{dtorr} \]
\[ X_{Molefraction2}(j_{drop}) = X_{Molefraction2}(j_{drop}) + X_{dtorr}/T_T \]
\[ X_{Molfrac2} = 0 \]
Do 112 \( j = 1 \), NumberSpecies
112 \( X_{Molfrac2} = X_{Molfrac2} + X_{Molefraction2}(j) \)
Do 113 \( j = 1 \), NumberSpecies
113 \( X_{Molefraction2}(j) = X_{molefraction2}(j)/X_{Molfrac2} \)

Here we assume Mole Fractions are same in (2) and (5)
Do 114 \( j = 1 \), NumberSpecies
114 \( x_{molefrac5}(j) = x_{molefrac2}(j) \)
Write(*,*) 'Species                X(1)   X(2)'
Write(11,*) 'Species                X(1)   X(2)'
Do 119 \( j = 1 \), NumberSpecies
119 Write(11,129) Species(j), Xmolefraction1(j), Xmolefraction2(j)
129 Format(1x,A20,2F7.4)

***********************************************************************
***********************************************************************

Enter the Sandia Thermodynamic Data

Write(*,*)
Write(*,*) 'Thermodynamic data file is C:\SANDIA\SANDIA.DAT'
Write(*,*)
OPEN(10, FILE='c:\sandia\sandia.dat', STATUS= 'OLD')
READ(10,*)
READ(10,*)

Read compound name, atoms and number of atoms, put in temporary file

READ(10,93)
XCN,TempELE(1),NUMELETemp(1),TempELE(2),NUMELETemp(2),
1                          TempELE(3),NUMELETemp(3),TempELE(4),NUMELETemp(4)
If(XCN.EQ.'END') goto 225
READ(10,41) (TempDAT(II,1),II=1,5)
READ(10,43) (TempDAT(II,1),II=6,7),(TempDAT(JJ,2),JJ=1,3)
READ(10,45) (TempDAT(KK,2),KK=4,7)
93  FORMAT(A10,T25,4(A2,I3))
41  FORMAT(5(E15.8))
126
If Species read in needed, write to Tdat, Ele and NumEle files

Do 222 Mc=1, NumberSpecies
  IF(XCN.EQ.Species(Mc)) Then
    Do 223 IJK=1,7
      Tdat(ijk,1,mc)=Tempdat(ijk,1)
      Tdat(ijk,2,mc)=Tempdat(ijk,2)
    End If
  End If
  GOTO 201
  Continue
  Close(10)

Check to see everything worked

Do 226 i=1,NumberSpecies
  IF(TDAT(1,1,i).EQ.0.0) Write(*,*) 'PROBLEMS WITH THERMODATA.'

Get everything in the right units

We already have P1 [Torr], T1 [C], Vs [mm/us]
We need P1 [Pascal], T1 [K], Vs [m/s]
We need rho1 [kg/m3], v1 [m3/kg], U1 [m/s], h1 [J/kg]

P1=P1/760*101325

To get rho1 and v1 we need Mixture Molecular Weight and PV=NRT

XMolwt1=0.
XMolwt2=0.
DO 100 j=1,4
  DO 100 k=1,Numberspecies
    IF(ELE(J,k).EQ.'AR') THEN
      XMOLWT1=XMOLWT1+NUMELE(J,k)*39.948*xmolefraction1(k)
      XMOLWT2=XMOLWT2+NUMELE(J,k)*39.948*xmolefraction2(k)
    ELSEIF(ELE(J,k).EQ.'C ') THEN
      ...
XMOLWT1 = XMOLWT1 + NUMELE(J,k) * 12.011 * x mole fraction 1(k)  
XMOLWT2 = XMOLWT2 + NUMELE(J,k) * 12.011 * x mole fraction 2(k)  
GOTO 100
ELSEIF(ELE(J,k).EQ.'H') THEN
XMOLWT1 = XMOLWT1 + NUMELE(J,k) * 1.008 * x mole fraction 1(k)  
XMOLWT2 = XMOLWT2 + NUMELE(J,k) * 1.008 * x mole fraction 2(k)  
GOTO 100
ELSEIF(ELE(J,k).EQ.'HE') THEN
XMOLWT1 = XMOLWT1 + NUMELE(J,k) * 4.003 * x mole fraction 1(k)  
XMOLWT2 = XMOLWT2 + NUMELE(J,k) * 4.003 * x mole fraction 2(k)  
GOTO 100
ELSEIF(ELE(J,k).EQ.'N') THEN
XMOLWT1 = XMOLWT1 + NUMELE(J,k) * 14.007 * x mole fraction 1(k)  
XMOLWT2 = XMOLWT2 + NUMELE(J,k) * 14.007 * x mole fraction 2(k)  
GOTO 100
ELSEIF(ELE(J,k).EQ.'O') THEN
XMOLWT1 = XMOLWT1 + NUMELE(J,k) * 15.999 * x mole fraction 1(k)  
XMOLWT2 = XMOLWT2 + NUMELE(J,k) * 15.999 * x mole fraction 2(k)  
100 ENDIF
XMolwt5 = Xmolwt2

Add mole fraction of droplets * droplet molecular weight to Xmolwt1
Xdroplets = ppmv*(1e-6)/(piD^3/6)/Na  /(P1/RT1)  r=82.06 P1=atm D=cm
| number of drops/cc |#/mole| moles/cc at P1,T1

MWdroplets= density (pi/6)D^3 Na

XdMwd=ppmv*1e-6*82.08*T1*density/(P1/101325.)
Xmolwt1=Xmolwt1+XdMwd
Rgas1=8.314/Xmolwt1*1000
Rgas2=8.314/Xmolwt2*1000
Rgas5=Rgas2

here Universal Gas Constant Rbar = 8.314 [J/mol/K]
and molecular weight is in gms/mole so multiply by 1000
but make sure that we add the droplets to the initial density
so we add droplets to rho1 and the recalculate v1
v1=Rgas1*T1/P1
v1nodrops=v1
we will need v1nodrops later on during enthalpy calculation
rho1=1./v1
 rho1=rho1+ppmv*1e-6*density*1e6*0.001

check units kg/m3 = (n.d.)*gm/cc*cc/m3*kg/gm
v1=1./rho1

128
Here we calculate \( \frac{C_p}{R} \) and \( \frac{h}{RT} \) from Sandia for each Species

\[
K = 1
\]
\[
\text{If}(T1 \leq 1000) \; K = 2
\]
\[
\text{Cp} = 0
\]
\[
\text{htemp} = 0
\]
\[
\text{Do} \; 200 \; \text{i} = 1, \text{NumberSpecies}
\]
\[
A1 = \text{TDAT}(1,K,I)
\]
\[
A2 = \text{TDAT}(2,K,I)
\]
\[
A3 = \text{TDAT}(3,K,I)
\]
\[
A4 = \text{TDAT}(4,K,I)
\]
\[
A5 = \text{TDAT}(5,K,I)
\]
\[
A6 = \text{TDAT}(6,K,I)
\]
\[
\text{HoverRT}(I) = A1 + A2 \times T1 /2 + A3 \times T1 \times T1 /3 + A4 \times T1 **3/4 + A5 \times T1 **4/5 + A6 / T1
\]
\[
\text{CpoverR}(I) = A1 + A2 \times T1 + A3 \times T1 \times T1 + A4 \times T1 \times T1 \times T1 + A5 \times T1 **4
\]
200 Continue

determine the mixture properties

do 203 \; \text{i} = 1, \text{Numberspecies}
\[
\text{Cp} = \text{Cp} + \text{xmolefraction1(i)} \times \text{CpoverR(i)}
\]
203 \[
\text{htemp} = \text{htemp} + \text{xmolefraction1(i)} \times \text{HoverRT(i)}
\]
\[
\text{Cp} = \text{Cp} \times 8.31434 \times (1000 / \text{Xmolwt1})
\]
\[
\text{htemp} = \text{htemp} \times 8.31434 \times T1 \times (1000 / \text{Xmolwt1})
\]
\[
\text{h1noevap} = \text{h1}
\]
these were unitless, then in Joule/mole, but now are in Joule/kg

determine the enthalpy of the droplets using the same standard conditions

determine the enthalpy of the droplets using the same standard conditions

at 20\(^\circ\)C

- **WATER**
  - Based on Sandia: Water Vapor \( h = -13433.7 \) kJ/kg
  - Based on Sandia: Water Liquid \( h = -15887.7 \) kJ/kg
  - Thus based on Sandia: Heat Evap \( h = 2454.0 \) kJ/Kg
  - In agreement with VanWylen+Sonntag pg645

- **DODECANE**
  - Based on Sandia: Dodecane vapor \( h = -1715.676 \) kJ/kg
  - Based {CRC 56th:pg.C-738}: Heat Evap \( h = 291.3 \) kJ/kg
  - Converting CRC to Sandia: Dodecane Liq \( h = -2007.00 \) kJ/kg

**JET-A**
Based on Sandia
JET-A vapor \( h = -1269.09 \) kJ/kg
Converting CRC to Sandia
JET-A Liqd \( h = -1819.63 \) kJ/kg
Based \{CRC 56th:pg.C-738\}
Heat Evap \( h = 550.54 \) kJ/kg
HEXADECANE
Based on Sandia
Hexadecane vapor \( h = -1661.9 \) kJ/kg
Based on DDBST
Heat Evap \( h = 361.234 \) kJ/kg
Converting to Sandia
Hexadecane liquid \( h = -2023.13 \) kJ/kg

Here \( h_1 \) is Joules per kilogram of mixture
so we need to add the liquid enthalpy
for the amount of water droplets in a kilogram of mixture
1 kg of mixture is what volume? \( v_{\text{nodrops}} \) [m\(^3\)/kg]
If(nchoice.EQ.1) \( h_{\text{add}} = -15887.7*1000 \).
If(nchoice.EQ.2) \( h_{\text{add}} = -2007.00*1000 \).
If(nchoice.EQ.2) \( h_{\text{add}} = -2036.10*1000 \).
If(nchoice.EQ.3) \( h_{\text{add}} = -1819.63*1000 \).
If(nchoice.EQ.4) \( h_{\text{add}} = -2023.13*1000 \).
\( y_1 = v_{\text{nodrops}} * \text{ppmv} * 1e-6 * \text{density} * (0.001) * 1.6 \)
write(\#\#) \'y_1 = ',y_1
\( h_1 = (1-y_1)*h_1 + h_{\text{add}}*y_1 \)

\( h_1 = h_1 + h_{\text{add}}*v_{\text{nodrops}} * \text{ppmv} * 1e-6 * \text{density} * (0.001) * 1.6 \)
check units J/kg = J/kg * m\(^3\)/kg *(n.d.) * gm/cc * kg/gm * cc/m\(^3\)

***********************************************************************
Solve the Incident Shock Equations
\( \rho_1*U_1 = \rho_1*U_2 \)
\( P_1+\rho_1*U_1^2 = P_2+\rho_2*U_2^2 \)
\( h_1+(1/2)*U_1^2 = h_2+(1/2)*U_2^2 \)
by solving the following pair of equations
\( f_1 = (P_1/P_2-1)+\rho_1*U_1^2/P_1/{\{v_2/v_1-1\}} \)
\( f_2 = (h_2-h_1)/((1/2)*U_1^2)+{v_2^2/v_1^2-1} \)
start by guessing using ideal shock relations
\( P_2/P_1 = 1+(2*\text{gamma}/(\text{gamma}+1))*(M^2-1) \)
\( T_2/T_1 = (P_2/P_1) \{1-((2/(\text{gamma}+1))(1-1/M^2) \}
\text{gamma} = c_p_1/(c_p_1-1) \)
\( M = U_1/V_{\text{sound}} \)
and then using the Newton-Raphson method

***********************************************************************
First solve with droplets not evaporated
***********************************************************************
130
\[
gamma_1 = \frac{(C_p1/R_{gas1})}{(C_p1/R_{gas1}-1)}\\
V_{sound 1} = \sqrt{\gamma_1*P_1/\rho_1}\\
x_{M1} = \frac{U_1}{V_{sound 1}}\\
\text{IF}(x_{M1} \leq 1.0) \text{ WRITE}(*,*) 'SUBSONIC SPEED: NO SHOCK'\\
P_2 = P_1*(1+(2*\gamma_1/(\gamma_1+1))*(x_{M1}^2-1))\\
T_2 = T_1*(P_2/P_1)^*(1-(2/(\gamma_1+1))*(1.0-x_{M1}/x_{M1}))
\]

\[
\text{we need} \quad h_2, v_2
\]
\[
\text{and here is where the N-R loop starts}
\]
\[
\text{Note here that we are using Xmolwt1 everywhere as mixture has not changed}
\]
\[
count = 0\\
R_{gas 2} = 8.31434/Xmolwt1*1000\\
t_{2old} = T_2\\
p_{2old} = P_2\\
COUNT = COUNT + 1\\
v_2 = R_{gas 2}*T_2/P_2\\
K = 1\\
\text{IF}(T_2 \leq 1000) K = 2\\
\text{Cptemp = 0}\\
\text{htemp = 0}
\]
\[
\text{Do 1207 I} = 1,\text{NumberSpecies}\\
A1 = TDAT(1,K,I)\\
A2 = TDAT(2,K,I)\\
A3 = TDAT(3,K,I)\\
A4 = TDAT(4,K,I)\\
A5 = TDAT(5,K,I)\\
A6 = TDAT(6,K,I)\\
HoverRT(I) = A1+A2*T_2/2+A3*T_2*T_2/3+A4*T_2**3/4+A5*T_2**4/5+A6/T_2\\
CpoverR(I) = A1+A2*T_2+A3*T_2*T_2+A4*T_2**3/4+A5*T_2**4/5\\
1207 \text{ Continue}
\]
\[
\text{Do 1208 i} = 1,\text{Numberspecies}\\
\text{Cptemp = Cptemp+xmolefraction1(i)*CpoverR(i)}\\
1208 \text{ htemp = htemp+xmolefraction1(i)*HoverRT(i)}\\
P_2 = Cptemp *8.31434*(1000/Xmolwt1)\\
h_2 = htemp*T_2*8.31434*(1000/Xmolwt1)
\]
\[
\text{Now on with the business of solving the equations}
\]
\[
\text{The order f1 is calculated could cause errors if not done in double precision}
\]
\[
\text{As we are subtracting two nearly identical large numbers}
\]
const1 = 1./P1  
const2 = U1**2./P1/v1**2.  
const3 = 2./U1**2.  
const4 = 2.*v2/v1**2.  

vdv = v2/v1  
f1 = p2*const1 -1. + const2*v1*(vdv-1.)  
f2 = (h2-h1noevap)*const3 + vdv**2.-1.  

dvdt2 = v2/T2  
dvdp2 = -v2/P2  
dhdt2 = Cp2  
dhdp2 = 0.  

dpdt2 = Rgas2/v2  

df1dp = const1 + const2*dvdp2  
df1dt = const1*dvdt2 + const2*vdvdt2  
df2dp = const3*dhdp2 + const4*dvdp2  
df2dt = const3*dhdt2 + const4*dvdt2  

c  
c  Solve using newton-raphson method  
c  
det = df1dp*df2dt - df1dt*df2dp  
p2 = p2-(f1*df2dt-f2*df1dt)/det  
t2 = t2-(f2*df1dp-f1*df2dp)/det  
PX2 = P2/101325.  

c  Conditional, and return to do again, goto 1888  
c  
crit1 = abs((T2-t2old)/T2)  
crit2 = abs((P2-p2old)/P2)  
if(crit1.LT.1.E-6.and.crit2.LT.1.E-6) goto 1889  
if(count.GT.20.) GOTO 389  
goto 1888  
1889  Write(*,*).  
WRITE(*,*) 'INCIDENT SHOCK CONDITIONS WITH NO EVAPORATION'  
WRITE(*,*)  
Write(*,*)' T2 P2 rho2/rho1 Ms'  
ATMP2 = P2/101325.  
densratio = v1/v2  
Write(*,1667) T2, ATMP2, densratio, XM1  
WRITE(*,*)  
Write(11,*)  
WRITE(11,*) 'INCIDENT SHOCK CONDITIONS WITH NO EVAPORATION'  
WRITE(11,*)
Write(11,*)' T2  P2  rho2/rho1  Ms'
Write(11,1667) T2, ATMP2, densratio, XM1
WRITE(11,*)

1667  Format(F10.1, 3F10.3)
c

c***********************************************************************
c      Now solve with droplets fully evaporated

c***********************************************************************
c
gamma1=(Cp1/Rgas1)/(Cp1/Rgas1-1)
Vsound1=sqrt(gamma1*P1/rho1)
xM1=U1/Vsound1
P2=P1*(1+(2*gamma1/(gamma1+1))*(xM1**2-1))
T2=T1*(P2/P1)*(1- (2/(gamma1+1))*(1./xM1/xM1))
c
c    we need  h2, v2
c    and here is where the N-R loop starts

c
Rgas2=8.31434/Xmolwt2*1000
Count=0
888  t2old=T2
     p2old=P2
     v2=Rgas2*T2/P2
     COUNT=COUNT+1.
K=1
IF(T2.LE.1000) K=2
     Cptemp=0
     htemp=0
     Do 207  I=1,NumberSpecies
         A 1  =  T D A T ( 1 , K , I )
         A 2  =  T D A T ( 2 , K , I )
         A 3  =  T D A T ( 3 , K , I )
         A 4  =  T D A T ( 4 , K , I )
         A 5  =  T D A T ( 5 , K , I )
         A6 = TDAT(6,K,I)
         HoverRT(I) = A1+A2*T2 /2+A3*T2 *T2 /3+A4*T2 **3/4+A5*T2 **4/5+
                      1A6/T2
         CpoverR(I) = A1+A2*T2+A3*T2*T2+A4*T2**3/4+A5*T2**4
 207  Continue
     Do 208 i=1,Numberspecies
         Cptemp=Cptemp+xmolefraction2(i)*CpoverR(i)
 208         htemp= htemp+xmolefraction2(i)*HoverRT(i)
     Cp2=Cptemp  *8.31434*(1000/Xmolwt2)
\[
h_2 = h_{\text{temp}} T_2 \times 8.31434 \times (1000/X_{\text{molwt2}})
\]

```
c Now on with the business of solving the equations
c The order f1 is calculated could cause errors if not done in double precision
c As we are subtracting two nearly identical large numbers

c
const1=1./P1
cconst2=U1**2./P1/v1**2.
cconst3=2./U1**2.
cconst4=2.*v2/v1**2.
cvdv=v2/v1
cf1=p2*const1 -1. + const2*v1*(vdv-1.)
cf2=(h2-h1)*const3 + vdv**2.-1.

c dvdt2=v2/T2
c dvp2=-v2/P2
c dhdt2=Cp2
c dhdp2=0.
c dpdt2=Rgas2/v2
cdf1dp=const1+const2*dvdp2
cdf1dt=const1*dpdt2+const2*dvdt2
cdf2dp=const3*dhdp2+const4*dvdp2
cdf2dt=const3*dhdt2+const4*dvdt2

c Solve using newton-raphson method

c
det=df1dp*df2dt-df1dt*df2dp
cp2=p2-(f1*df2dt-f2*df1dt)/det
cT2=t2-(f2*df1dp-f1*df2dp)/det
PX2=P2/101325.
c
Conditional, and return to do again, goto 888

c
crit1=abs((T2-t2old)/T2)
crit2=abs((P2-p2old)/P2)
cif(crit1.LT.1.E-6.and.crit2.LT.1.E-6) goto 889
cif(count.GT.20.) GOTO 389
go to 888

889 U2=v2*U1/v1
Write(*,*)
WRITE(*,*) 'INCIDENT SHOCK CONDITIONS WITH COMPLETE EVAPORATION'
WRITE(*,*)
```

134
Write(*,*)' T2  P2  rho2/rho1  Ms  U2'  
ATMP2=P2/101325.  
densratio=v1/v2  
Write(*,667) T2, ATMP2, densratio, XM1, U2  
WRITE(*,*)  
Write(11,*')  
WRITE(11,*) 'INCIDENT SHOCK CONDITIONS WITH COMPLETE EVAPORATION'  
WRITE(11,*)  
Write(11,*)' T2  P2  rho2/rho1  Ms  U2'  
ATMP2=P2/101325.  
densratio=v1/v2  
Write(11,667) T2, ATMP2, densratio, XM1, U2  
WRITE(11,*)  
667 Format(F10.1, 3F10.3, F10.1)  

If(nchoice.EQ.2) then  
c cros=39.451+0.11859*T2-1.5169e-4*T2**2+4.7163e-8*T2**3  
cros=-215.615+1.82209*T2-0.00430507*T2**2+4.44253e-06*T2**3  
c-1.7023e-09*T2**4  
Write(*,*) T2,cros  
endif  
If(nchoice.EQ.4) then  
c cros=39.451+0.11859*T2-1.5169e-4*T2**2+4.7163e-8*T2**3  
cros=cros*1.32335  
c cros=-2.6797+0.18573*T2-0.00011356*T2**2  
c cros=cros*1.32335  
WRITE(*,*) T2,cros  
endif  

If(nchoice.EQ.5) then  
c cros=39.451+0.11859*T2-1.5169e-4*T2**2+4.7163e-8*T2**3  
cros=cros*1.32335  
c cros=-2.6797+0.18573*T2-0.00011356*T2**2  
c cros=cros*1.32335  
WRITE(*,*) T2,cros  
endif  

error=Xmolefraction2(JDROP)-(abso*8.314*T2)/  
1 (cros*atmP2*101325.*0.1)  
write(*,*) (abso*8.314*T2)/(cros*atmP2*101325.*0.1),  
1 Xmolefraction2(JDROP),ppmv  
write(11,*') (abso*8.314*T2)/(cros*atmP2*101325.*0.1),
If(ABS(error).gt.0.0000001) then
    ppmv=ppmv-error*100
if (ppmv.lt.0.0) then
    write(*,*) 'ERROR: The code assumes there is at least the
    saturation vapor pressure of fuel. Abs must be wrong'
    write(11,*) 'ERROR: The code assumes there is at least the
    saturation vapor pressure of fuel. Abs must be wrong'
end if
P1=P1*760/101325
GOTO 105
end if

Now we solve reflected conditions

Solve the Reflected Shock Equations

\[ \rho_2 U_{2\text{dash}} = \rho_5 U_5 \]
\[ P_2 + \rho_2 U_{2\text{dash}}^2 = P_5 + \rho_5 U_5^2 \]
\[ h_2 + (1/2) U_{2\text{dash}}^2 = h_5 + (1/2) U_5^2 \]
\[ U_{2\text{dash}} = U_5 + U_1 - U_2 \]
\[ U_5^2 = (P_5 - P_2)/\rho_5/((\rho_5/\rho_2 - 1) \]
by solving the following pair of equations
\[ f_1 = (P_5/P_2 - 1) + (U_1 - U_2)^2/P_2/(v_5 - v_2) \]
\[ f_2 = (h_5 - h_2)/((1/2)*(U_1 - U_2)^2)/(v_5 + v_2)/(v_5 - v_2) \]
start by guessing using ideal shock relations
\[ \alpha = (\gamma + 1)/(\gamma - 1) \]
\[ P_5/P_2 = (\alpha + 2 - P_1/P_2)/(1 + \alpha P_1/P_2) \]
\[ T_2/T_1 = (P_5/P_2)(\alpha + P_5/P_2)/(1 + \alpha P_5/P_2) \]
\[ \gamma = c_p_1/(c_p_1 - 1) \]
and then using the Newton-Raphson method

Guess ideal t_5, p_5 conditions

\[ \alpha_1 = (\gamma_1 + 1)/(\gamma_1 - 1) \]
\[ p_{12} = p_1/p_2 \]
\[ p_{52} = (\alpha_1 + 2 - p_{12})/(1 + \alpha_1 P_{12}) \]
\[ t_{52} = p_{52}^2/(\alpha_1 + p_{52})/(1 + \alpha_1 P_{52}) \]
\[ p_5 = p_{52}^2/p_2 \]
\[ t_5 = t_{52}^2 \]
c
now start to iterate
c
count=0
875    p5old=p5
t5old=t5
v5=Rgas5*T5/P5
COUNT=COUNT+1
c
I need U2
U2=v2*U1/v1
c
K=1
IF(T5.LE.1000) K=2
Cptemp=0
htemp=0
Do 707 I=1,NumberSpecies
A1 = TDAT(1,K,I)
A2 = TDAT(2,K,I)
A3 = TDAT(3,K,I)
A4 = TDAT(4,K,I)
A5 = TDAT(5,K,I)
A6 = TDAT(6,K,I)
HoverRT(I) = A1+A2*T5 /2+A3*T5 *T5 /3+A4*T5 **3/4+A5*T5 **4/5+1A6/T5
CpoverR(I) = A1+A2*T5+A3*T5*T5+A4*T5*T5*T5+A5*T5**4
707 Continue
Do 408 i=1,Numberspecies
Cptemp=Cptemp+xmolefraction5(i)*CpoverR(i)
408 htemp= htemp+xmolefraction5(i)*HoverRT(i)
Cp5=Cptemp *8.31434*(1000/Xmolwt5)
h5 =htemp*T5*8.31434*(1000/Xmolwt5)
c
construct the two equations f1 and f2 from
conservation of mass/momentum and energy
c
du122=0.5*(U1-U2)**2
dv52=v5-v2
dv522=(v5-v2)**2
f1=p5/p2-1+2.*du122/p2/dv52
\[ f_2 = \frac{(h_5-h_2)}{du_{122}} + \frac{(v_5+v_2)}{dv_{52}} \]

c solve using newton-raphson method

dv_{dt5} = v_5/T_5

dv_{dp5} = -v_5/P_5

dh_{dt5} = C_{p5}

dh_{dp5} = 0.

dp_{dt5} = R_{\text{gas}5}/v_5

const1 = 1/p_2
const2 = -2*du_{122}/p_2/dv_{522}
const3 = 1/du_{122}
const4 = -2*v_2/dv_{522}
df_{1dp} = const1 + const2*dv_{dp5}
df_{1dt} = const2*dv_{dt5}
df_{2dp} = const3*dh_{dp5} + const4*dv_{dp5}
df_{2dt} = const3*dh_{dt5} + const4*dv_{dt5}
det = df_{1dp}*df_{2dt} - df_{1dt}*df_{2dp}
p_5 = p_5 - (f_1*df_{2dt} - df_{1dt}*f_2)/det

t_5 = t_5 - (df_{1dp}*f_2 - f_1*df_{2dp})/det

c determine if we have convergence

crit1 = abs((T_5-T_5old)/T_5)
crit2 = abs((P_5-P_5old)/P_5)
if(crit1.lt.1.d-6.and.crit2.lt.1.d-6) goto 765
if(count.GT.20.) GOTO 389
goto 875

765 U_5 = v_5*(U_1-U_2)/(v_2-v_5)
WRITE(*,*) 'REFLECTED SHOCK CONDITIONS WITH COMPLETE INCIDENT EVAP IORATION'
WRITE(*,*) T_5, P_5, U_5'
ATMP_5 = P_5/101325.
WRITE(*,668) T_5, ATMP_5, U_5
668 Format(F10.1, F10.3, F10.1)
WRITE(11,*) REFLECTED SHOCK CONDITIONS WITH COMPLETE INCIDENT EVAP IORATION
WRITE(11,*)

138
SUBROUTINE VELCALC(u1,atten, ENDWALL)
implicit DOUBLE PRECISION (a-h,o-z), integer (i-n)
dimension xpos(4),dpos(4),tpos(4),ptsmem(4),vpos(4)

Read in geometric data for Stanford Aerosol Shock Tube

xpos(1)=0
xpos(2)=460.8
xpos(1)=869.3
xpos(2)=1186.4
xpos(3)=1491.1
xpos(4)=1760.6

1877.8 is the second last port window location (for incident work)
1997.8 is the shock tube end wall
dpos(2)=304.8
dpos(3)=304.6
dpos(4)=234.4

User inputs 4 time intervals from keyboard and we record which intervals are zero

110   Write(*,*
     write(*,*
Write(*,*) 'input the last 4 counter times in us'
Write(*,*) 'if no time available, enter 0'
Write(*,*)
zpts=0.0
xpts=0.0
do 45 n=1,4
vpos(n)=0.0
45    ptsmem(n)=0.
read(*,*) tpos
do 166 i2=1,4
if(tpos(i2).eq.0.0) then
zpts=zpts+1.
ptsmem(i2)=zpts
else
xpts=xpts-1.
ptsmem(i2)=xpts
vpos(i2)=dpos(i2)/tpos(i2)
endif
166   continue
write(*,* 'got to here'
c
First do simple cases
c
IF(zpts.EQ.3.)THEN
   do 200 i=1,4
      if(ptsmem(i).eq.-1.) then
         u1=1000.*dpos(i)/tpos(i)
         atten=0.0
         goto 500
      endif
   200        continue
ELSEIF(zpts.EQ.2.)THEN
   do 201 i=1,4
      if(ptsmem(i).eq.-1.) then

140
va=dpos(i)/tpos(i)
xa=xpos(i)
elif(ptsmem(i).eq.-2.) then
vb=dpos(i)/tpos(i)
xb=xpos(i)
endif
201 continue
const2=(va-vb)/(xa-xb)
const1=va-const2*xa
u1=const1+const2*endwall
ATTEN=-const2*100000./u1
u1=1000.*u1
goto 500
ENDIF

c
Calculate the linear least-squares-fit of the data.
c using formulae from CRC Math Tables 23rd ed. pg. 576
c
VSUM=0.
XSUM=0.
x2sum=0.
xvsum=0.
xpts=-xpts
DO 150 I=1,4
  if(ptsmem(i).lt.0.0)then
    VSUM=VSUM+Vpos(I)
    XSUM=XSUM+Xpos(I)
    x2sum=x2sum+xpos(i)**2
    xvsum=xvsum+xpos(i)*vpos(i)
  endif
150 CONTINUE
coef1=(xpts*xvsum-xsum*vsum)/(xpts*x2sum-xsum*xsum)
coef0=vsum/xpts-coef1*xsum/xpts
u1=coef1*endwall+coef0
ATTEN=-(COEF1)*100000./u1
u1=u1*1000.
c output information
500 WRITE(*,*)
  Write(*,80) u1
  Write(*,81) ATTEN
  Write(*,*)
  Write(11,*)
  Write(11,80) u1
SUBROUTINE CONDX(P1,T1,endwall,abso,ans,MIXTURE)
  implicit DOUBLE PRECISION (a-h,o-z), integer (i-n)
  character*20 MIXTURE
  Write(*,*)
  Write(*,*) 'Current Mixture: ',Mixture
  Write(*,*) ' P1      T1      Abs      LSF Position'
  Write(*,*) ' [torr]  [K]     [3.39]  [mm]        '
  Write(*,7712) P1, T1, abso, endwall
  7712 Format(F7.1,F8.1,F8.3,F11.1)
  Write(*,*)
  Write(*,*) 'Make changes:'
  Write(*,*) '1...P1'
  Write(*,*) '2...T1'
  Write(*,*) '3...Abs'
  Write(*,*) '4...LSF Position'
  Write(*,*) '5...Mixture'
  Write(*,*)
  Write(*,*) '6...Run current conditions'
  Write(*,*) '7...Exit AeroFrosh'
  Read(*,*) ans
  Write(*,*)
  Write(*,*)
  Write(*,*)
  end
REFERENCES

8. R.W. Hurn, K.J. Hughes, Combustion characteristics of diesel fuels as measured in a constant-volume bomb, SAE Q. Trans. 6 (1952) 24-35.


