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A new experimental chamber has been created to directly observe combustion events under ambient temperatures and at constant pressures up to 300 MPa. Several supporting systems were designed and built to operate this chamber including high-pressure gas systems and redundant control systems. To test the data gathering and analysis techniques, the JA2 modified double-base gun propellant was tested at pressures between 14.1 – 207.7 MPa. Experimental burning rates were similar to previously published rates and correlated to:

$$r_b (mm/s) = 1.659[P(MPa)]^{0.91} \text{ (for } 14.1 < P < 207.7 \text{ MPa)}$$

By utilizing a windowed chamber, the first direct observations of the quality of JA2 combustion at elevated pressures were obtained.

The burning rates of nitromethane, when burned as a monopropellant, were obtained for pressures between 3.6 – 101.7 MPa. Three distinct burning regimes were observed for nitromethane when burned in a 10.6 mm ID glass tube:

1. For pressures between 3.6 – 18.2 MPa, burning rates correlated to:

   $$r_b(mm/s) = 0.1829[P(MPa)]^{1.15}$$

2. For pressures between 18.2 – 40.8 MPa, burning rates followed a near-linear transition, as a function of pressure, between a burning rate described by a liquid-gas phase interface to a supercritical burning rate that could be described by a freely-propagating flame speed.

3. For pressures between 40.8 – 102 MPa, burning rates correlated to:

   $$r_b(mm/s) = 11.04[P(MPa)]^{0.679}$$

Nitromethane was also tested using tubes of varying sizes from 1 – 14 mm ID. The size of the tube was found to affect burning rates in the 2nd and 3rd burning regimes with an increasing tube diameter.
correlating to an increasing burning rate for a given pressure. A set of equations was developed to predict burning rates in the third burning regime for tube sizes within this range.

To support the experimental analysis, numerical and analytical predictions for several nitromethane physical properties were developed. These predictions were not experimentally verified during the study.
TABLE OF CONTENTS

List of Figures ........................................................................................................ viii
List of Tables ........................................................................................................... xii
Nomenclature .......................................................................................................... xiii
Acknowledgements .................................................................................................. xvi

Chapter 1 Introduction ............................................................................................ 1
  1.1 Research Motivations ....................................................................................... 1
    1.1.1 Propellant Burning Behaviors ................................................................. 1
    1.1.2 Unexplained Burning Behaviors ............................................................. 3
  1.2 Research Objectives ......................................................................................... 4
  1.3 Method of Approach ....................................................................................... 5

Chapter 2 Background and Review ......................................................................... 7
  2.1 Burning Rate Measurement Techniques ....................................................... 7
  2.2 JA2 Solid Propellant ....................................................................................... 8
  2.3 Nitromethane Liquid Monopropellant .......................................................... 10
  2.4 Supercritical Combustion ............................................................................. 13

Chapter 3 Ultra-High Pressure Optical Chamber .................................................. 16
  3.1 Chamber Overview ....................................................................................... 16
  3.2 Test Stand ...................................................................................................... 19
    3.2.1 CAD ........................................................................................................ 19
    3.2.2 Installation ............................................................................................... 20
  3.3 Plumbing ......................................................................................................... 21
  3.4 Lifting Mechanism ......................................................................................... 24
  3.5 Modular Inserts ............................................................................................. 28
  3.6 Windows .......................................................................................................... 29
    3.6.1 Analytical analysis of window loads ...................................................... 30
    3.6.2 Pre-Experiment FEA simulations ....................................................... 31
    3.6.3 Material behavior during experiments ............................................... 33
    3.6.4 Post-Experiment FEA simulations ...................................................... 39

Chapter 4 Control and Data Collection ................................................................... 44
  4.1 Control and Data Collection Systems ............................................................ 44
    4.1.1 Hardware Control ................................................................................... 44
    4.1.2 Software Control ................................................................................... 46
    4.1.3 Data Collection ...................................................................................... 47
  4.2 Data Post-Processing ...................................................................................... 48
Appendix D UHPOC Standard Operating Procedures .................................................. 118

D.1 General Safety Procedures .................................................................................. 118
D.2 Bottom end-closure installation ......................................................................... 118
D.3 Compressor Startup and Chamber Filling .......................................................... 119
D.4 Test Execution procedures .................................................................................. 122
D.5 End of test procedures ....................................................................................... 123
D.6 Bottom end-closure removal .............................................................................. 124
D.7 Compressor Maintenance .................................................................................. 125
D.8 Loss of System Control ........................................................................................ 126

References.................................................................................................................. 129
List of Figures

Figure 1. Certain propellant components exhibit well-behaved burning rates that can be described by a single pressure exponent within this pressure range. [2] ..........................2

Figure 2. Ammonium perchlorate burning rates over a wider pressure range show an unstable burning region and multiple pressure exponents. [2], [4], [5] ..........................2

Figure 3. Experimental nitromethane results from Boyer and Kuo [6] were difficult to explain without direct observation of the combustion process. ................................4

Figure 4. Experimental JA2 burning rates reported by Gazonas et al. [14], Reaugh et al. [15], and Kuo and Zhang [16] show consistent behavior between 10 – 600 MPa........9

Figure 5. Experimental nitromethane burning rates reported by Boyer and Kuo [6], Sabourin et al. [24], and Rice and Cole [20] show large variations in behavior between 3 – 170 MPa..........................12

Figure 6. The Ultra-High Pressure Optical Chamber (UHPOC). .......................................17

Figure 7. Cross-sectional view of the Ultra-High Pressure Optical Chamber. ..................17

Figure 8. UHPOC pressurization times starting with different bottle pressures..............18

Figure 9. The chamber's pressure slowly decreases for several minutes after pressurization .............................................................................................................19

Figure 10. FEA analysis of test stand showed max stress ~4% of yield......................20

Figure 11. (left) assembled mounting stand; (center) mounting of the chamber and stand; (right) chamber installed into test cell.........................................................21

Figure 12. Project PID. ..................................................................................................23

Figure 13. (left) chamber plumbing installation; (right) valve installation.................24

Figure 14. Scissor lift design for lifting mechanism.......................................................25

Figure 15. Pneumatic platform design for lifter mechanism.......................................26

Figure 16. Design of final lifting mechanism that uses a cable-supported platform. ....27

Figure 17. Lifting mechanism without (left) and with (right) sealing plug and strand burner. ..................................................................................................................28

Figure 18. Strand burner insert with 1/4-in strand insert installed............................29

Figure 19. The von Mises stress for stacked polycarbonate windows....................32
Figure 20. The von Mises stress for a single polycarbonate window ........................................ 33
Figure 21. Fused quartz windows failed at approximately 15,000 psi ........................................ 34
Figure 22. Inner window of the three-window stack of polycarbonate windows .................. 34
Figure 23. A stack of two polycarbonate windows without (left) and with (right) an
intermediate mineral oil layer .................................................................................................. 35
Figure 24. Polycarbonate window distortion progresses as a function of pressure .............. 37
Figure 25. Plot of transient window deflection during a single pressurization cycle .......... 38
Figure 26. Permanent window deformation after being pressurized to given pressure........ 39
Figure 27. FEA window failure simulation. The pink color represents stress above tensile
strength of quartz ................................................................................................................. 40
Figure 28. Close-up of failed windows with initial fracture point highlighted in red ............ 40
Figure 29. Material stress analysis when the supporting gasket thickness was doubled 41
Figure 30. Material stress analysis when window opening was non-circular ..................... 42
Figure 31. Material stress analysis when window support was at a 45 degree angle rather
than perpendicular to the viewing direction ........................................................................ 42
Figure 32. Hardware control panel ...................................................................................... 45
Figure 33. Software control panel ........................................................................................ 46
Figure 34. High-speed camera setup ..................................................................................... 48
Figure 35. The video analysis process included marking the location of the millimeter
marks from the internal scale (left) and using the marked locations to determine the
time the burning surface reached each location (right) ......................................................... 49
Figure 36. Time-location data for JA2 burning rate at 34.8 MPa (left) and 172 MPa
(right) ................................................................................................................................. 50
Figure 37. Measurement of the average (left) and true (right) burning surface for
a nitromethane sample. Reflections make the flame appear larger than tube diameter ... 51
Figure 38. JA2 sample with yellow paint on surface and nichrome wire ignitor on top .... 54
Figure 39. Nitromethane sample with solid propellant ignition booster suspended on
the tube opening tube using nichrome wire .......................................................................... 55
Figure 40. JA2 burning at 172 MPa ..................................................................................... 56
Figure 41. Measured burning rates of JA2 shows good agreement with published closed-bomb data.

Figure 42. Nitromethane burning at 3.6 MPa produced a clear plume.

Figure 43. Nitromethane burning at 18.2 MPa over three different time steps shows a flat burning surface and laminar flame.

Figure 44. Nitromethane burning at 20.6 MPa over three different time steps shows a turbulent burning surface.

Figure 45. Nitromethane burning at 25.7 MPa over three different time steps shows exaggerated turbulence compared to the 20.6 MPa test.

Figure 46. Time-location data for nitromethane burning rate at 25.7 MPa.

Figure 47. Nitromethane burning surfaces at 35.5 MPa (top), and 60.4 MPa (bottom).

Figure 48. Average cell diameters in the high-pressure burning regime of nitromethane did not vary significantly over the pressure range.

Figure 49. Experimental nitromethane burning rate results shown with examples of burning behavior.

Figure 50. Correlation between a pure burning rate model and a pure flame speed model using a transition power of 0.79.

Figure 51. Experimental data fell within the wrinkled laminar flame regime.

Figure 52. Estimated fractional burning surface varied across experiments but had a correlation of a constant 1.4x.

Figure 53. Final transition region correlation with a transition power of $h = 0.95$.

Figure 54. Thermal conductivity of water.

Figure 55. UHPOC experimental data and final correlations.

Figure 56. Mole fractions of major components near propellant surface.

Figure 57. Estimated critical temperatures of numerically simulated conditions.

Figure 58. Estimated critical pressures of numerically simulated conditions.

Figure 59. Burning rates of nitromethane are affected by tube diameter.

Figure 60. At pressures above 40 MPa, all tube sizes behave similarly.

Figure 61. Burning rates for a fixed pressure vary predictable across tube sizes.
Figure 62. Saturated liquid density of nitromethane at 298 K .............................................86
Figure 63. Dynamic viscosity of nitromethane at 298 K .........................................................87
Figure 64. Estimations for supercritical viscosity of nitromethane ...........................................90
Figure 65. Comparison of low temperature and supercritical nitromethane estimations ..........91
Figure 66. Kinematic viscosity for nitromethane at 298 K .......................................................92
Figure 67. Updated nitromethane burning-rate model differs slightly from the previous version .................................................................................................................96
Figure 68. Estimated flame speeds of nitromethane by Dobbins and Smooke. [55] ............98
Figure 69. Estimated flame thicknesses of nitromethane by Dobbins and Smooke. [55] .......98
Figure 70. Overall schematic for hardware control panel .........................................................114
Figure 71. Schematic for Hand Valve Actuator (HVA) control system ..................................115
Figure 72. Pinouts for HVA control boxes ...............................................................................116
Figure 73. Schematic for isolation valve LED circuits ...............................................................117
List of Tables

Table 3-1. Transmission ranges of window materials. ..........................................................30
Table 5-1. Second region curve-fits for various tube sizes.................................................78
Table 5-2. Third region curve-fits for various tube sizes......................................................78
Table 5-3. Predictions of unified burning rate equations compared with experimental results. ..................................................................................................................80
Table 6-1. Equation variables for Thompson et al. method.................................................85
Table 6-2. Variable values for Equation 24. ........................................................................89
Table 6-3. Lennard-Jones PVT coordinates..........................................................................89
Table 6-4. Values of $b_j$ for supercritical viscosity calculations........................................89
Table 6-5. Pure Component properties used to calculate critical temperature and pressure....93
Nomenclature

\( a \)  
Temperature-related constant for burning rate equation

\( a_p \)  
Pressure-dependent burning rate constant for unified equations

\( c_{pg} \)  
Specific heat of the gas phase

\( c_{pc} \)  
Specific heat of the condensed phase

\( F_o \)  
Adjustable parameter for supercritical viscosity calculation

\( h \)  
Transition power exponent

\( k_g \)  
Reaction rate constant

\( k_b \)  
Boltzmann constant

\( l_k \)  
Kolmogorov scale thickness

\( l_o \)  
Integral scale thickness

\( L \)  
Turbulent length scale

\( m \)  
Mass of one molecule

\( M \)  
Molecular weight

\( n \)  
Pressure exponent for burning rate equation

\( n_p \)  
Pressure-dependent burning rate exponent for unified equations

\( N_A \)  
Avogadro’s number

\( P \)  
Pressure

\( P_c \)  
Critical pressure

\( P_{cm} \)  
Mixture critical pressure

\( P_L \)  
Lower pressure bounds for burning rate correlation

\( P_r \)  
Reduced Pressure

\( P_U \)  
Upper pressure bounds for burning rate correlation
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{vp}$</td>
<td>Vapor pressure</td>
</tr>
<tr>
<td>$P^+$</td>
<td>LJ reduced pressure</td>
</tr>
<tr>
<td>$Q_g$</td>
<td>Heat of reaction in gas phase</td>
</tr>
<tr>
<td>$Q_s$</td>
<td>Surface heat transfer</td>
</tr>
<tr>
<td>$r_b$</td>
<td>Burning rate</td>
</tr>
<tr>
<td>$r_{b,c}$</td>
<td>Correlated burning rate</td>
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<tr>
<td>$S_L$</td>
<td>Laminar flame speed</td>
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<tr>
<td>$S_\sigma$</td>
<td>Slope for $\sigma$ as a function of $T_r$</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
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<tr>
<td>$T_c$</td>
<td>Critical temperature</td>
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<td>$T_{cm}$</td>
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<tr>
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<tr>
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<td>$U$</td>
<td>Turbulent flame speed</td>
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<td>$v$</td>
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<tr>
<td>$v_s$</td>
<td>Saturated liquid specific volume at vapor pressure</td>
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<tr>
<td>$\alpha_u$</td>
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<td>$\varepsilon$</td>
<td>Energy dissipation rate</td>
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<tr>
<td>$\epsilon$</td>
<td>Depth of LJ potential well</td>
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<td>$\eta_L$</td>
<td>Low temperature viscosity</td>
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<tr>
<td>$\eta_{SL}$</td>
<td>Saturated liquid viscosity</td>
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<td>Dynamic viscosity of saturated liquid at vapor pressure</td>
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<td>$\nu$</td>
<td>Kinematic viscosity</td>
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<tr>
<td>$\rho$</td>
<td>Density</td>
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<td>$\rho_p$</td>
<td>Propellant density</td>
</tr>
<tr>
<td>$\rho_g$</td>
<td>Propellant density (gas phase)</td>
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<td>$\dot{\omega}$</td>
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<td>Mixture acentric factor</td>
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<td>Modified acentric factor</td>
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<tr>
<td>$\xi$</td>
<td>Reduced inverse viscosity</td>
</tr>
<tr>
<td>$\Omega_v$</td>
<td>Collision integral</td>
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</table>
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Chapter 1

Introduction

1.1 Research Motivations

1.1.1 Propellant Burning Behaviors

The burning rates of propellants are of fundamental interest to engineers and scientists, not only for their use in propulsion calculations [1], but also for their ability to shed light on the underlying chemical and physical processes of the propellant. Burning rates are usually described using St. Robert’s law over a specific pressure range by the empirical equation: \( r_b = aP^n \). In this equation, the constant \( a \) is typically a function of temperature and the pressure exponent \( n \) shows the exponential pressure dependence. Because the influence of temperature and pressure are separated in this matter, the two parameters are able to be studied independently. Figure 1 shows the linear burning rates of several propellant components. Within the listed pressure ranges, these components are well-behaved and can be described by a single pressure exponent. However, if the data for aluminum perchlorate (AP) is extended to higher pressures, as shown in Figure 2, this compound shows very different behaviors. Between 13.8 and 27.6 MPa, AP has a region of unstable burning. Once the burning behavior stabilizes above 27.6 MPa, it does so with a higher pressure exponent than before it entered the unstable burning region. Propellants that are created using these components have burning rates that are influenced by, but not necessarily follow, the components’ burning rates. Studies have shown that composite propellants can exhibit slope breaks, burning rate plateaus, and even negative pressure dependencies that do not directly follow the trends of the individual components. [2] [3]
Figure 1. Certain propellant components exhibit well-behaved burning rates that can be described by a single pressure exponent within this pressure range. [2]

Figure 2. Ammonium perchlorate burning rates over a wider pressure range show an unstable burning region and multiple pressure exponents. [2], [4], [5]

These limited examples provide evidence of the impact that pressure has on the burning rate. The empirical equation $r_b = aP^n$ can be valid for only limited pressure ranges and is not necessarily determinable using the burning rates of the propellant’s components. Directly testing
the burning rate of a propellant over all desired pressures is important to both inform numerical calculations as well as to understand how the chemical and physical processes change with pressure.

1.1.2 Unexplained Burning Behaviors

There are multiple methods of measuring burning rates that involve closed and windowed chambers. If possible, directly observing the combustion process is ideal. These observations allow the scientist to quickly infer changes in the combustion process, such as levels of soot in the flame’s plume, which would not be possible in a closed vessel. Without direct observations of the burning process, the presence of non-ideal burning (e.g., burning in cracks, side burning, etc.) that impact a burning-rate measurement can only be inferred. A relevant example of this is shown in Figure 3 that plots the burning rate of nitromethane as a function of pressure from the work of Boyer and Kuo [6]. This research found two separate slope breaks of propellant behavior, the first at ~15 MPa and the second at ~70 MPa. The authors reported a correlated pressure exponent of 2.33 for the middle region, which, based on a simplified relation by Kubota [7], implies a reaction order of ~4-5. A reaction order this high is not realistic from a chemistry perspective, so some mechanism other than a change in chemistry must be the cause. Because the only tests that were directly observed were below 12 MPa, the reasons for the two slope breaks were largely unexplained. As shown later in this work, direct observation of nitromethane combustion provides significant insight into the underlying factors behind these multiple burning regions.
1.2 Research Objectives

The overall research goals were to develop an experimental facility to observe burning phenomena of solid and liquid propellants at ultra-high pressures and then use that facility to provide the first direct observations of propellant combustion at those pressures. The major milestones set to accomplish these goals were:

- Design, manufacture, and install a new experimental apparatus capable of observing burning phenomena at pressures up to 300 MPa.
- Develop the support and data collection systems needed to perform experiments with the new system.
- Validate the system and data collection techniques by performing tests with a propellant believed to have a well-understood behavior throughout the entire pressure range.
• Perform tests on a propellant that has non-understood behavior through a specific pressure range.

• Use numerical and analytical techniques to update existing propellant models to account for new experimental results.

1.3 Method of Approach

Through the evaluation of existing literature, the need for additional high-pressure experimental facilities was determined by the project’s investigators, Dr. Richard Yetter, Dr. Grant Risha, and Dr. Eric Boyer. They worked with external vendors to design and build the new device.

Review of previous publications, listed in Chapter 2, provided a state of the art for the measurement of high-pressure burning-rates and for the published results of JA2 and nitromethane burning rates. These propellants were considered candidates for further study with a high-pressure optical chamber due to their well-behaved and ill-behaved nature, respectively.

Chapter 3 describes the Ultra-High Pressure Optical Chamber (UHPOC) installation and configuration. The design and construction of several additional systems that were created to support the chamber’s operation are also described. Significant effort was spent on post-construction analysis of the chamber’s windows; this analysis is also described in Chapter 3.

Any new experimental apparatus needs corresponding control and data collection systems. Chapter 4 describes the design and creation of these systems. This chapter also details the data reduction and analysis techniques used for this research.

Once the UHPOC and supporting systems were installed and tested, experiments were performed on the JA2 and nitromethane propellants. The methods and results used for these experiments are detailed in Chapters 5.
Numerical and analytical work used to enhance existing models or support the analysis of experimental results was performed. The process and results from this effort are in Chapter 6. Additional supporting work in the form of real-gas simulations of nitromethane flames were performed by a team at Yale. The resulting findings are also included in this chapter.

Finally, the overall findings are summarized in Chapter 7. This effort produced several possible new directions of research which are also described in this chapter.
Chapter 2

Background and Review

2.1 Burning Rate Measurement Techniques

The pressure-dependent behavior of burning-rates is of fundamental importance to the characterization of propellants and explosives. Burning rates are, ideally, collected using windowed chambers where the combustion process can be directly observed. The burning surface location at a specific time is noted and a burning rate can be computed using the slope of the resulting time-location data. This process works well for lower pressures, however for pressures higher than 50 MPa, which is the operating range for gun propellants, non-windowed chambers using breakwires or closed bombs have been the only available options. Of these methods, the breakwire technique is the most straightforward. This method uses multiple fuse wires located at fixed locations in a strand sample [8], [9] which break when the burning surface passes the wire. The loss of signal through the wire indicates the position of (at least a portion of) the burning surface at the given time. More recently, ultrasonic sensors [10] or X-ray [11] techniques have been developed to measure the location of the burning surface at a specific time. The closed-bomb technique uses a sample, in the form of a strand or compressed powder, which burns in a relatively small volume without observation. This method was refined by Crawford et al. [12] and uses pressure-time data to deduce the burning rate from a model developed to describe the experiment that must account for variable chemistry, heat loss, ignition, and irregular surfaces. Because the closed bomb technique is highly dependent on a pre-existing model to deduce burning rates, developing a model in parallel with experiments can be problematic.
None of the indirect burning-rate measurement techniques allow the regression and gas-phase combustion behavior to be directly observed for a qualitative assessment. By directly observing the burning behavior, the accuracy of the data is only limited by the quality of optical recording equipment available. Additionally, any irregular burning can be taken into account at measurement time for a specific sample rather than having to infer it from many samples. Direct observation data are also beneficial for informing model development rather than requiring a fully-functional model before experiments can begin.

2.2 JA2 Solid Propellant

The JA2 gun propellant is a modified double-base propellant consisting of nitrocellulose, nitroglycerin, and diethylene glycol dinitrite (DEGDN). [13] This propellant has been studied extensively, so only a relevant subset of publications and their results will be introduced.

One of the earliest unclassified studies on JA2 burning rate was performed by Gazonas et al. [14] These experiments measured the ambient temperature burning rates of JA2 using closed-bomb techniques at pressures between 10 – 550 MPa. Results showed well-behaved burning rates that could be described by a single pressure exponent if the startup and shutdown transients were neglected.

Extending the work by Gazonas et al., Reaugh et al. [15] tested the ambient burning rates of JA2 by using a combination of closed-bomb and breakwire techniques at similar pressure ranges. The resulting burning-rate data were consistent with Gazonas et al. except at the lowest and highest pressures. The authors noted considerable scatter in the low-range data due to “start-up of a single grain”.

The work by Kuo and Zhang [16] covered several significant findings about JA2. The authors characterized how the transient burn rate of JA2 varied versus the steady-state burning rate.
This analysis found no significant dynamic burning effects for the propellant. Experimental burning-rate tests were performed at pressures between 1 – 68 MPa using an optical chamber and resulted in two separate burning rate regimes occurring above and below 13.8 MPa. A detailed analysis of temperature sensitivity was also performed.

One of the most recent efforts using JA2 was modeling work by Conner and Anderson [17]. This work produced a slightly updated chemical mechanism and the resulting predictions agreed well with existing experimental data.

Figure 4 shows the burning rates of the JA2 gun propellant at ambient temperature as reported by Reaugh et al. [15], Gazonas et al. [14], and Kuo and Zhang [16]. These published data show that the burning rate of JA2 changes in a fairly predictable way with respect to pressure. Of these four data sets, the only published curve-fitting was from Kuo and Zhang [16]:

\[
r_b (mm/s) = 5.822[P(MPa)]^{0.97} \text{ (for } 13.8 < P < 96.5 \text{ MPa)}
\]  

(1)

Figure 4. Experimental JA2 burning rates reported by Gazonas et al. [14], Reaugh et al. [15], and Kuo and Zhang [16] show consistent behavior between 10 – 600 MPa.
2.3 Nitromethane Liquid Monopropellant

Nitromethane (CH₃NO₂) is an industrial solvent that has also been explored as a fuel additive and monopropellant. This molecule is comprised of a methane molecule with one of the hydrogens replaced by a nitro group. The interest in nitromethane combustion comes not only from its use as a monopropellant but also in its potential to provide insight into the combustion behavior of nitramines and nitro group-containing materials. [6]

Investigations into nitromethane as a high-energy monopropellant for propulsion applications were active by the mid-1940s by multiple different companies. [18] During this time, nitromethane was found to have a very high working pressure (low-pressure deflagration limit) of approximately 30 atm without the inclusion of additional oxygen. [19] The first pressure-dependent burning-rate measurements were made by Rice and Cole at the Naval Ordnance Laboratory in 1953 to understand why rocket experiments using nitromethane had rough and unstable burning. [20] These experiments were conducted in a closed vessel and used fuse-wires embedded in Pyrex tubes to infer the location of the burning surface for a specific time. Their results had relatively large uncertainties due to pressure changes and showed burning rates that varied significantly between 3.5-103 MPa.

The first published attempt to model the deflagration of nitromethane was by Kelzenberg et al. in 1999. [21] This work used a simplified two-step reaction mechanism and stated good agreement with experimental data at low pressures. These low pressure experiments were conducted using 5 mm plastic tubes to hold the nitromethane. The next major work into burning rate measurement and modeling was undertaken by Boyer et al. beginning in 1999. [6], [22], [23] These experiments used multiple different apparatuses to measure burning rate: for pressures below 15 MPa, nitromethane was placed in quartz tubes and the combustion processes were directly observed using an optical strand burner; for pressures above 15 MPa, nitromethane was placed in
combustible straws that used fuse-wires to determine the burning surface location. Additional tests were also performed at low pressures using a constant flow apparatus that maintained a free burning surface during combustion. This research produced an updated chemical mechanism for nitromethane combustion as well as the first attempt at a numerical model using a complete mechanism for predicting deflagration. The model’s results aligned well with the experimental data through ~15 MPa, but diverged significantly at higher pressures.

Sabourin et al. [24] studied the effect of additives on the burning rate of nitromethane and appears to be the first published attempt at quantifying any effect on burning rate from the diameter of the propellant tube. Experiments of neat propellant reported no difference in burning rate across various tube diameters between 8 – 22 mm. These tests used quartz tubes in an optical strand burner at pressures below 10 MPa.

McCown III et al. studied ambient temperature burning rates of nitromethane using various additives up through 13 MPa. [25] The ignition process in this study was an electrically-heated nichrome wire suspended in the propellant. The current through the wire was left on until the propellant ignited, but neither the ignition delay time, nor the heat addition, was accounted for in the paper. Because of the assumed non-ambient conditions of the propellant, these data were not used as a reference.

Significant published works exist that study burning rates of nitromethane/air flames due to nitromethane’s use as a fuel additive (Examples: [26], [27], [28]), as well as catalyzed nitromethane [29], but were not directly applicable to this work.

Figure 5 shows the burning rates of nitromethane at ambient temperature as reported by Boyer and Kuo [6], Sabourin et al. [24], and Rice and Cole [20]. In this figure, only the data from 3 – 12 MPa was obtained with an optical-access chamber, with the remaining data collected using closed chambers and breakwire techniques. All displayed data were collected with the propellant held in clear tubes during testing with the exception of the Boyer and Kuo Ultra High-Pressure
Strand Burner (UHPSB) data which used combustible straws. The data show two slope breaks: one at 15 MPa and the other at 70 MPa described by separate correlations for each region by Boyer and Kuo [6]:

\[
\begin{align*}
    r_b (\text{mm/s}) &= 0.299[P(\text{MPa})]^{1.03} \quad (\text{for } 2.5 < P \leq 15 \text{ MPa}) \quad (2) \\
    r_b (\text{mm/s}) &= 0.009[P(\text{MPa})]^{2.33} \quad (\text{for } 15 < P \leq 70 \text{ MPa}) \quad (3) \\
    r_b (\text{mm/s}) &= 4.153[P(\text{MPa})]^{0.86} \quad (\text{for } 70 < P \leq 170 \text{ MPa}) \quad (4)
\end{align*}
\]

While the kinetic mechanisms of nitromethane are considered relatively well known, current numerical models based on these mechanisms do not predict the observed behaviors. [23] One hypothesis is the lower pressure burning rate is conventional burning with an interface between the liquid and gas, while the higher pressure burning rate occurs without an interface, that is, under supercritical conditions, and the higher slope in-between represents a transition region. Without direct observation of the burning behavior above 15 MPa, it has been difficult to determine if this hypothesis is one of the contributing factors to the change in burning behavior.

Figure 5. Experimental nitromethane burning rates reported by Boyer and Kuo [6], Sabourin et al. [24], and Rice and Cole [20] show large variations in behavior between 3 – 170 MPa.
2.4 Supercritical Combustion

The study of combustion under supercritical conditions has received a significant amount of focus over the past 30 - 40 years. The first notable experimental work in this area was by published by Faeth et al. in 1969. [30] Decane droplets were burned in air and oxygen environments at pressures above the critical pressure for the fuel. Results were in “reasonable agreement” with supercritical theories regarding behavior at varying pressure, oxygen concentrations, and flame-zone location.

In 1975, Canada and Faeth [31] studied the combustion of many different fuels under supercritical conditions to understand how the gasification rates, surface temperatures, and transport properties of the liquid fuels changed at elevated pressures. Their results found large errors in the gasification rates of the fuels between prediction and experiment; these errors were attributed to the complexity of the combustion model and the uncertainties for certain physical properties. Other results for surface temperatures and gas phase property models agreed well with predictions.

In 1992, Shuen et al. [32] studied supercritical combustion of a wide range of liquid fuels with various oxidizers. The most important outcome of this research was a comprehensive new model for bi-propellant supercritical combustion that was derived from first principles.

The vaporization of propellants at transcritical and supercritical conditions was studied by Delplanque and Sirignano [33] for liquid oxygen and was later expanded on by Sirignano and Delplanque [34] for fuels and other propellants. Although this research was focused on bi-propellants, some of the details do apply to monopropellants. In both instances, the authors describe the difficulties in modeling supercritical behavior due to the large variability in thermophysical properties as a compound crosses through its critical point. A publication by Bruno in 2006 [35] provides an excellent summary of why determination of these properties is so important and
difficult. Additionally, the critical point of a compound was described as having a strong non-linear dependence on chemical makeup which made it difficult to compute. [34] This computation of a mixture’s critical properties has received significant study by Li [36], Kreglewski [37], Grieves and Thodos [38], He et al. [39], and Najafi [40], among many others. Although each author has derived a unique method for identifying the critical point of a mixture, most only work for binary mixtures, and all can have significant errors with certain hydrocarbon mixtures.

In 2000, a significant review of supercritical fluid behavior from both experimental and numerical sources was published by Bellan [41]. This study attempted to identify the underlying physics, as well as common erroneous assumptions, from a diverse set of studies. Despite a very tight scope of source material, dozens of studies were analyzed. This work showed the breadth of supercritical fluid research and produced an excellent analysis of the state of the art which still holds up well nineteen years later.

One of the most recent works into supercritical combustion was published in mid-2018 by Yang et al. [42] This research studied how hydrodynamic instabilities impacted the spherical propagation of a non-premixed flame at supercritical conditions. Results showed increasing acceleration of the flame front with increasing turbulence intensity.

Many of the works on supercritical combustion described thus far were for fuels that either existed as a liquid at ambient temperature or were combusted in the phase that existed at ambient temperatures. However, many rocket engines use propellants that are only liquid at cryogenic temperatures. [1] A majority of the relevant work to cryogenic, non-premixed supercritical combustion was compiled and summarized by Mayer and Smith [43]. This work was fairly comprehensive and covered rocket-engine-specific topics ranging from spraying and mixing to flame structure and flame holding. Poblador-Ibanez and Sirignano [44] have also recently published numerical work on cool liquids being introduced to a hot environment above the liquid’s critical pressure, such as in a thrust chamber. Although these studies are not directly applicable to this work
(which involves a propellant that is liquid at room temperature), the phenomena are qualitatively similar.

Most published work into supercritical combustion thus far has focused on bi-propellants and non-premixed conditions. Work into premixed combustion at supercritical conditions has been limited. A recent work by Liang et al. [45] provided a fairly comprehensive treatment of premixed supercritical hydrogen/air and methane/air combustion. This research is more directly applicable to monopropellants than the previous non-premixed work and found substantial changes in flame speed predictions from an ideal gas baseline when incrementally adding the effects of a real gas equation-of-state, real-fluid enthalpy, thermal conductivity, and mass diffusivity.

A glaring omission in existing literature is coverage of supercritical monopropellant combustion. In fact, an extensive survey of existing literature has turned up only one relevant study. Birk et al. [46] studied spray combustion of supercritical monopropellants into a ~30 MPa and 500°C N₂ environment. This resulted in a few conclusions that were specific to spray combustion, but provided little insight into the underlying mechanisms. This study also attempted a single test with pure nitromethane, but was unable to get autoignition of the injected propellant. Additionally, no published research was found regarding the physical properties of nitromethane, such as density, viscosity, and thermal conductivity, under supercritical conditions. This work will show that several previously published experimental results were actually burning in the supercritical regime ([6], [20]), but at the time of publication, supercritical behaviors could only be hinted at and not proven.
Chapter 3

Ultra-High Pressure Optical Chamber

The Ultra-High Pressure Optical Chamber (UHPOC) was designed to study a wide range of combustion scenarios, under constant pressure, using multiple methods of ignition including conventional nichrome wire and laser-induced ignition. This chamber, designed and built by the High Pressure Equipment Co. in Erie, PA, provides optical access for direct measurement of combustion events at pressures up to 300 MPa.

3.1 Chamber Overview

The UHPOC assembly, shown in Figure 6, has a length of 1.7 m, an outer diameter of 0.53 m, and an inner diameter of 0.13 m. The total interior volume of the chamber is approximately 12 liters which allows for a wide variety of experimental apparatuses and provides near-constant pressure conditions for combustion experiments. The chamber was machined from 4340 steel and has an overall mass of approximately 2300 kg. The defining features of the chamber are the two diametrically-opposed windows placed approximately one-third of the chamber’s length from the bottom end. A diagram of the chamber can be seen in Figure 7. The chamber was designed to attain a maximum working pressure of 340 MPa (50,000 psi) with the windows replaced by steel blanks. The maximum pressure with the windows installed is dependent on the window material used, with sapphire windows predicted to achieve a working pressure of 310 MPa (45,000 psi). The combination of optical access and very high pressure capacity makes this chamber unique in the world, allowing for previously impossible combustion observations.
Figure 6. The Ultra-High Pressure Optical Chamber (UHPOC).

Figure 7. Cross-sectional view of the Ultra-High Pressure Optical Chamber.
Access to the chamber’s interior for plumbing or instrumentation is accomplished through a total of ten 9/16-in, ten 1/4-in, and two 1/8-in high-pressure fittings machined into the chamber’s body and end-closures. Conax Technologies HPPL14 sealing wire glands pass signal wires into and out of the chamber through two of the high-pressure fittings. Although these glands are only rated for 30,000 psi, they have been successfully tested through 43,000 psi.

The chamber and supporting systems are able to use nitrogen and argon pressurants without the replacement of any seals. Unfortunately, the chamber’s large interior volume and high pressure capacity can result in substantial pressurization times. These times vary not only by the target pressure, but also by the pressure of the source gas bottles. A plot of fill times for the chamber, using four parallel 304 cu. ft source cylinders, is shown in Figure 8.

![Figure 8. UHPOC pressurization times starting with different bottle pressures.](image)

After being pressurized, the chamber experiences a slow drop in pressure for several minutes (Figure 9). This drop is believed to be caused by a combination of very small leaks and pressurant entering the system at an elevated temperature from the compressor; as the temperature drops to that of the chamber, the pressure experiences a corresponding drop. During experiments,
this pressure-drop rate was significantly slower than any of the measured burn times and could be neglected.

![Pressure vs Time Graph](image)

Figure 9. The chamber's pressure slowly decreases for several minutes after pressurization

3.2 Test Stand

To provide a mounting platform and support structure for the chamber, a test stand was designed by Dr. Grant Risha, co-principal investigator of this project, and manufactured from plain-carbon steel. The stand’s upper plate is 1.5-in-thick with a 12-in circular cutout for access to the chamber’s lower end-closure. This plate was supported by vertically mounted W36x135 I-beams which were attached to a slotted base for forklift access.

3.2.1 CAD

A static structural finite element simulation using SolidWorks 2017-2018 Education Edition was performed on the stand to validate the hand calculations ran during design and to
demonstrate suitability of the stand before installing the chamber. The results of this analysis, shown in Figure 10, predicted a maximum von Mises stress of approximately 4% of the yield stress of the material. The top plate showed stress concentrations on opposing sides of the opening, but due to the low stress levels, it was determined these concentrations would not result in a failure mode.

![Figure 10. FEA analysis of test stand showed max stress ~4% of yield.](image)

3.2.2 Installation

The final chamber had a mass of approximately 2300 kg, which necessitated the use of a crane and forklift to mount the chamber to the test stand. The mounting process was performed outside of the test facility and the chamber and stand assembly was moved into the building’s test cell for final installation. After the assembly was placed in its final location, a support bracket connected to the chamber was bolted through the 18-in-thick reinforced concrete wall to anchor the chamber in the event of a sudden pressure release event. The progression of the chamber installation is shown in Figure 11.
3.3 Plumbing

After the chamber was mounted within the test cell, the high-pressure plumbing for the chamber was installed. All high-pressure plumbing used for this project was rated at 60,000 psi, giving a 16,500 psi (114 MPa) margin for the highest planned pressures of 300 MPa. A burst disc rated at 51,900 psi was also fitted to the chamber as a safety mechanism. Gas flow to and from the chamber was controlled via a series of needle (HiP-60-11HF9) and pneumatic (HiP-60-11HF9-MPO-NC and -NO) isolation valves also rated at 60,000 psi. The variable needle valves control the rate of gas flow to and from the chamber. These valves were designed by the manufacturer as hand-operated valves, but manual operation of these valves in the test cell would put personnel at risk if an unforeseen event were to occur during an experiment. To eliminate the need for an operator to be present in the test cell, the valve handle was removed and a DC motor was fitted to the stem using a fabricated adaptor. This DC motor allowed the valve to be operated from the system’s
control panel in a safe location. The pneumatic isolation valves were supplied the required 50 psi of control gas via a low-pressure air compressor. The flow between the air compressor and the valves was controlled by relay-actuated solenoids. Finally, exhaust gas from the chamber was filtered and then vented to atmosphere via low-pressure plumbing rated at 3190 psi.

The pressurant gas used for all experiments was nitrogen marked as “< 2 ppm moisture.” All system components were able to also use argon as a pressurant without replacing any seals or materials. The nitrogen was stored in low-pressure cylinders at 2500 psi and was fed to the high pressure compressor using stainless steel plumbing rated at 4300 psi. A Hydro-Pac Li’l Critter gas compressor was used to boost the pressurant gas from bottle pressure to the required working pressure for the experiment. This compressor was rated for a maximum working pressure of 45,000 psi (310 MPa). The high-pressure compressor required water cooling to reduce the temperature of the gas output, so was hooked up to the building’s water supply and drainage systems using PVC tubing rated at 200 psi. To regulate the flow of water to the required 1-2 gpm flow rate, a visible float flow meter was installed in the water tubing upstream of the compressor. Figure 12 shows the full PID for this setup, with images of the final high-pressure plumbing and valve installations shown in Figure 13.
50Ksi Combustion Testing PID

Rev. 9/07/2017

Hydro Pac

PG1
PG2

BV1
MV2

P1
P2

Test Chamber

Burst Disc

High Speed Camera

BV2
MV2

BV3

Exhaust

Valve Power

Manual switches

Gauge camera display

LabView

Experimental Gas

Control Gas

Signals/Control

BV = Ball Valve
P = Pressure Sensor
PG = Pressure Gauge
MV = Manual Valve
VA = Valve Actuator

Figure 12. Project PID.
Figure 13. (left) chamber plumbing installation; (right) valve installation.

3.4 Lifting Mechanism

To access the interior of the chamber, the lower end-closure of the chamber must be removed. This end-closure was a two-part sealing system (sealing plug and threaded collar) and had a mass of approximately 55 kg. The end-closure had to be precisely lifted 0.7 m into the chamber under the tight horizontal constraints of the test stand interior. Additionally, the collar and plug had to be lifted and rotated independently to be properly installed. Moving this sealing system by hand would be prohibitive to most operators so a mechanism was created to facilitate installation.

Several designs were attempted for this lifting mechanism. Because of the relatively small volume of the support stand’s interior, a large amount of lifting distance was required using a small
footprint. The designs that met this requirement were a scissor lift, direct pneumatic lift, and direct cable lift.

The scissor lift idea was first considered because of the small footprint of the lifting mechanism. The two main flaws for this design were 1) the amount of horizontal space needed for the pneumatic piston extended well beyond the physical constraints of the test stand, and 2) the top plate that supported the end closure did not move horizontally, so all work on a test sample would need to be completed underneath the test stand. The most recent version of the design before being abandoned is shown in Figure 14. Also visible in this figure are two design elements that were used in the final design which were a spring-loaded platform that allowed the collar to raise and lower independently of the center plug and a ball-bearing turntable that allowed the collar to be rotated freely on the platform.

![Figure 14. Scissor lift design for lifting mechanism.](image)

The next design that was attempted was a lifting platform that used pneumatics to raise and lower the platform. This design improved on scissor-lift concept because the pneumatics no longer had to be housed under the test stand and instead could be extended above the stand. Additionally, the platform could have horizontal rails for sliding the end closure assembly out from under the test stand for easy sample access. Unfortunately, the main flaw of this design continued to be the
placement of the pneumatics. Although several positions were tried, the length of the pneumatics obscured either the chamber’s windows or instrumentation ports. The most recent version of the design placed within a mockup of the test stand is shown in Figure 15.

Figure 15. Pneumatic platform design for lifter mechanism.

The final version of the lifter design was a variation on the pneumatic platform that used a cable lift instead of the pneumatics. Because of the easily-routed cable, the motor assembly could be placed both outside of the test stand and out of the way of the test chamber. The cable from the motor could then be used to support and move the platform using a series of pulleys. In addition to the design elements brought over from the previous design, linear rails were used to keep the platform in a precise location within the center of the platform and still allow smooth travel. After performing FEA simulations of the mechanism with the end closure in various positions, legs were also added to the base of the platform to support the end closure’s weight while on the ground. The final design for the cable-lifted platform is shown in Figure 16.
Figure 16. Design of final lifting mechanism that uses a cable-supported platform.

The installed lifting mechanism is shown in Figure 17 and performs, for the most part, exactly as anticipated during the design phase. One of the main deviations from the designed behavior was in the behavior of the linear rails and the linear-rail bearings. The I-beams that made up the test stand walls were not precisely parallel to each other. This meant the rails themselves were not able to be precisely aligned. To account for this deviation, the bearings were switched from the standard bearings that had a fixed alignment to ones that could vary by ± 1°. Although this variation is small, it allowed the platform to shift slightly while being raised and lowered due to the torque caused by the cable. This shift must be manually offset by an operator during the lifting process.
3.5 Modular Inserts

The relatively large interior of the chamber (12 liters) allowed for a wide variety of modular diagnostic and experimental equipment to be placed within the chamber. The apparatus used for all experiments described in Chapter 5 was a strand-burner insert designed by Dr. Grant Risha, co-principal investigator for this project. This insert is shown in Figure 18 and can be operated with and without a co-flow of inert gas around the sample. The strand holder can be replaced to accommodate various sample sizes of solid propellants and liquid propellant holders. Two electrically isolated posts support the electrodes for nichrome-wire ignition. The hollow base of the strand burner houses excess signal and ignition wires that were routed through the end closer. Two indexing pins are also fixed to the base, which align the strand burner with the window openings.
3.6 Windows

The UHPOC was designed to have modular window inserts, which can be replaced depending on the needs of the experiment. The window assemblies, visible near the center of the chamber in Figure 7, use a piston sealing system against the chamber. The window inserts are placed within these assemblies and are sealed with a proprietary series of gaskets and O-rings.

Although many criteria can be used to select one type of window material over another, the three primary criteria for the initial experiments were the ability to withstand high pressures, the ability to transmit a high percentage of light in the visible spectrum (~380 to 750 nm), and the manufacturability of the material at a reasonable cost. Of these criteria, the two that received the most focus during the design phase were the pressure criteria, which determined the operational pressure range of the chamber, and the transmission criteria, which determined what kind of data could be collected. For the experiments in this study, the only data collected through the windows
were high-speed videos of the combustion events. Light transmission outside of the visible rage, such as the ranges needed for spectroscopy, was desirable, but was not a primary consideration.

Three materials were first considered for use in the UHPOC windows – sapphire, quartz, and polycarbonate. The sapphire and quartz materials were recommended by the chamber manufacturer High Pressure Equipment Co; polycarbonate was considered as a low-cost alternative. The transmission ranges for all materials are listed in Table 3-1 showing that all three materials met the criteria of visible light transmission. The initial methods for determining the suitability of materials were FEA simulations of the windows within the chamber and analytical computations. The results and analysis of these two methods are presented in this section.

Table 3-1. Transmission ranges of window materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Transmission Range (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sapphire</td>
<td>~200 to 5000</td>
</tr>
<tr>
<td>Quartz</td>
<td>~250 to 2500</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>~400 to 1400</td>
</tr>
</tbody>
</table>

3.6.1 Analytical analysis of window loads

The chamber manufacturer, HiP, provided guidance that fused silica and quartz windows would be suitable up to 35,000 and 50,000 psi respectively at 100° F. These values were calculated using the formulas for bending and deflection of circular plates presented by Young et al. [47] and assuming a factor of safety of 1.5 on the resulting thickness. To determine safe operational limits of polycarbonate, the glass and plastic pressure vessel window design guidelines from Brookhaven National Labs (BNL) [48] were adopted. The computational procedures in this guide for polycarbonate at ambient temperature were followed using the guide’s maximum allowable design stress of 2000 psi. These calculations predicted a polycarbonate window in this chamber needed to
have a minimum thickness of 3.085 inches to withstand a uniform 45,000 psi. Because the chamber required a window thickness of 3.750 inches to be properly installed, polycarbonate was considered a viable alternative window material. Although polycarbonate windows with a 3.750-in thickness could be custom manufactured, this was found to be cost and time prohibitive for the project. As an alternative, stacking 1.25-in-thick polycarbonate windows was considered as this material was readily available. Unfortunately, no published research could be found on the impact of stacked versus single windows under this usage scenario, so any modified analytical predictions for the stacked window configuration was not possible. Instead, FEA simulations were used to help predict any possible divergence of behavior between these configurations.

3.6.2 Pre-Experiment FEA simulations

The static simulation package in SolidWorks 2017-2018 Education Edition was the primary tool used to model the polycarbonate window behavior under various pressure loads. Each window configuration was inserted into a model of the window closure and was given a uniform pressure load on the interior surface. Because the specific material manufacturer, and thus exact material properties, was not known at this point, average values of 9,200 psi, 12,500 psi, and 13,500 psi were used for shear strength, compressive strength, and flexural strength of polycarbonate, respectively. The intended process was to increase pressure until the window began to exceed its shear strength and then compare the relative behaviors of the configurations. However, the SolidWorks simulator would fail to solve at pressures above 10,000 psi for the stacked window configuration. Therefore, both single and stacked configurations were ran at 10,000 psi, which was below the failure point of the window, and the results were compared to determine the difference, if any, between the loads of single and stacked windows.
The von Mises results for the stacked and single window configurations are shown in Figure 19 and Figure 20, respectively. The maximum stress and distribution of stress are almost identical between the two configurations. The stacked window configuration does show stress concentrations at the window edges that do not appear in the single window model, however under compressive loads, these locations should not result in a failure mode. The region of interest around the window opening shows practically identical behavior between the two configurations. Note that the color scale on the chart is relative to the maximum shear stress of polycarbonate. The red/pink region in the viewport is made from steel, so this stress load is not a concern. Charting the displacements of these two configurations also showed near-identical behavior of the two configurations, having deformation to within 0.001 mm across all locations. The similarities of the stress and displacement simulations led evidence to the theory that a stack of 3 - 1.25-in windows would be a suitable replacement for the single 3.75-in window and their behavior could be predicted using similar methods.

Figure 19. The von Mises stress for stacked polycarbonate windows.
3.6.3 Material behavior during experiments

Two of the window materials – fused quartz and polycarbonate were used for initial experiments with the chamber. The first pressurization experiments were performed with two fused quartz windows measuring 3.750-in-thick and 3.500-in-dia. that were sourced from United Silica. These windows were both installed in the chamber allowing opposing views of a test sample. During testing, both quartz windows cracked at a chamber pressure of approximately 15,000 psi, well short of the maximum pressure of 35,000 psi predicted by the chamber’s manufacturer. The failed windows are shown in Figure 21 as seen directly after the test.

Because early tests with quartz windows resulted in window failures, subsequent tests switched to polycarbonate windows. At the time, the reason for the failures was unknown and polycarbonate was both a cheaper material and was less brittle which would have mitigated any failures due to stress concentrations caused by manufacturing defects. The polycarbonate selected was 1.25-in-thick Zelux® W polycarbonate was sourced from Alro Plastics. The polycarbonate...
was cut to make 3.500-in-dia discs. When these discs were stacked, the total thickness of the window was larger than the required 3.750 +/- 0.005 in tolerance. To fit the windows into the chamber, the inner surface of the inner window was machined down to the required tolerance. The remaining window fit within the assembly’s retaining ring and retained a polished surface in the center that protruded from the retaining ring. Figure 22 shows an image of the machined window.

Figure 21. Fused quartz windows failed at approximately 15,000 psi.

Figure 22. Inner window of the three-window stack of polycarbonate windows.
Early tests with the polycarbonate windows produced poor results. In order to illuminate the propellant sample, external lighting was directed through the same window that the video camera was recording through. This lighting caused significant internal reflections within the three polycarbonate window stack. The reflections obscured the view of the sample preventing pre-test setup and data collection. The internal reflection was mitigated (although not totally eliminated) by adding a very thin layer of mineral oil between each of the windows in the stack. Mineral oil has a refractive index similar to polycarbonate and has been shown to reduce optical distortion on the flat surfaces of another thermoplastic – acrylic. [49] Figure 23 compares a polycarbonate window stack without and with the mineral oil layer. After adding the mineral oil, the reflections caused by an external light source was significantly reduced. Another consideration of the mineral oil layer was how it would behave under pressure. Research by Knittle and Jeanloz used mineral oil as a pressure transmitting medium and found acceptable results. [50]

Figure 23. A stack of two polycarbonate windows without (left) and with (right) an intermediate mineral oil layer.
After adding intermediate mineral oil layers to the windows stacks, experiments using polycarbonate windows produced acceptable results below 172 MPa (25,000 psi). Because the only optical data collected was high-speed video, acceptable performance was defined as the ability to see the combustion process with minimal distortion or artifacts. Light surface scratches on the inner and outer surfaces from the machining process were visible in high-speed videos, but did not prohibit any data collection or analysis. Above ~172 MPa, the windows began showing severe optical distortion. Figure 24 shows how the view through the window changed with pressure. The cause of this distortion was the physical deformation and extrusion of the window through the opening. This deformation caused a convex surface to form on the outer window, distorting the edges of the window and magnifying sample area. An internal scale was used to mitigate some of the effects of this distortion since distances could still be calculated with acceptable error. However, once the distortion obscured the scale, the window was considered to have failed. The exact point of optical failure appeared to vary based on the number of pressurization and depressurization cycles. One set of windows that went through approximately 15 pressure cycles hit optical failure at ~221 MPa, while another set that went through a single pressure cycle failed at ~193 MPa. It should be noted that the failure calculations presented earlier in Section 3.6.1 were based on mechanical failure of the material; because the usable failure mode turned out to be optical, it is unknown whether the final mechanical failure for the material would have matched with the analytical predictions.
The polycarbonate windows experienced both transient deflection while under pressure and eventually plastic deformation at higher pressures. Figure 25 plots the transient deflection of the windows during a single pressurization cycle. The deflection behavior was smooth and slightly accelerating as pressure increased. Once pressurization was stopped, the material was already past its linear stress/strain behavior point as the window continued to deflect even though the pressure remained constant.
Figure 25. Plot of transient window deflection during a single pressurization cycle.

The permanent plastic deformation of the polycarbonate windows is plotted in Figure 26. Window sets 1 and 2 were the normal stack of thee polycarbonate windows while the “Stiff-Backed” set was a single polycarbonate layer backed by a 2.5-in stiff material that was used as a sapphire substitute. This figure shows essentially no permanent deformation of the polycarbonate until the chamber is pressurized above 138 MPa. Above that limit, increased pressure continues the plastic deformation until the window reaches optical failure. Both of the window configurations tested produced similar deflection results.
Early experiments resulted in behaviors for both quartz and polycarbonate windows that diverged significantly from the analytical results. As a result, FEA simulations were attempted to both explain experimental behaviors as well as help make better predictions for future setups.

The first set of simulations was designed to identify the root cause of the quartz window failures. Because the quartz windows had failed at ~100 MPa, this pressure was applied to all inner faces of the window and the window was constrained using the dimensions of the window assembly. This configuration was ran as a static simulation and resulted in the stress output shown in Figure 27. In this image, the pink color denotes where the von Mises stress exceeded the tensile stress of the quartz material. This simulation predicted that the quartz tensile stress would be exceeded just inside of the supporting material. Figure 28 is a close-up of the failed windows with the location of the initial break highlighted in red. The actual failure location is identical to the location predicted by the FEA software. This result provided evidence that the analytical failure
calculations used in the design phase did not apply to this physical situation. Subsequent discussions and analysis with the chamber’s manufacturer identified a limit to the stress-loading calculations used for the window design; windows with a thickness-to-unsupported-diameter ratio above ~0.5 cannot be predicted by the formulas in their reference text. As of this writing, the chamber manufacturer has re-designed the window assemblies and is working closely with us to test the new assemblies. Updated FEA models from the manufacturer indicate that the redesigned windows would allow the chamber to reach its originally intended working pressure of 300 MPa using sapphire windows.

Figure 27. FEA window failure simulation. The pink color represents stress above tensile strength of quartz.

Figure 28. Close-up of failed windows with initial fracture point highlighted in red.
Because the FEA analysis methods were predicting the quartz failures well, several alternative designs were also simulated to look for a design that would withstand higher pressures. This effort was done in parallel to the work done by the chamber manufacturer. The design changes that were investigated were: increasing the window gasket thickness, using non-circular windows, and supporting the windows on a 45° angle, rather than on a flat plane. The stress maps resulting from these simulations are shown in Figure 29, Figure 30, and Figure 31 respectively. Note that in these images, the supported portion of the window is visible as opposed to being colored black as was done in Figure 27; only the stress on the unsupported section of the window was considered in both cases. These images show that none of the attempted design changes resulted in a substantial change to the stress concentrations inside of the unsupported boundary.

Figure 29. Material stress analysis when the supporting gasket thickness was doubled.
During all of the above simulations, modeling polycarbonate using only linear-elastic material properties was found to give results that diverged significantly from experimental behavior. To improve the FEA results, attempts were made to model polycarbonate using more realistic non-linear material properties. In order to run these non-linear simulations, the software needed data curves for the non-linear portions of the stress-strain curves. An example of these data can be found from the work of Heymans [51]. Unfortunately, the FEA software did not behave well with the negative slope of the stress-strain curve and would treat the data as invalid. Attempts to manipulate the data into a form that the software would accept resulted in highly incorrect results.
at lower pressures (≤ 35 MPa) and failed solutions at higher pressures. These polycarbonate simulations were also attempted with the ANSYS Mechanical v19.1 FEA software. Setup of the material was similar in that the negative-slope curve data were disregarded and the software would only accept data once tweaked to be a positive slope. The ANSYS Mechanical software would solve the nonlinear solution over a wider range of pressures, however, the results differed significantly from the SolidWorks software. Because all completed solutions from the polycarbonate simulations were using non-realistic materials, and resulted in incorrect solutions, this effort was eventually discontinued. If a software package can be found that is able to handle the negative stress-strain cure slopes, good progress could be made in this effort. However, it is unknown if such software currently exists.
Chapter 4

Control and Data Collection

The control system for the UHPOC was built to emphasize redundancy and safety. Most of the system’s features are able to be controlled through either of two independent systems – one controlled with analog electrical hardware and the other a computerized control system through LabVIEW. The user control area is separated from the test cell by an eighteen-inch-thick reinforced concrete wall, so all data collection and system monitoring must be done remotely. Both control systems are interconnected so that valve status, valve control, power status, pressure, and video are synchronized between the two, allowing one system to take over control if the other system becomes unresponsive. Because both systems are able to operate most of the systems independently, multiple control points must fail before control of the chamber is lost. In the unlikely event that a complete loss of control occurs, the system fails to a safe state, venting any pressurized gas to atmosphere.

4.1 Control and Data Collection Systems

4.1.1 Hardware Control

The UHPOC hardware control system operates using analog electrical hardware and hardware relays. The operator panel is shown in Figure 32 and allows full remote control and monitoring of all UHPOC systems. This hardware system is considered the “master” of the two control systems because a toggle switch on this panel chooses which system is in control at any
given time. This switch, positioned in the lower left by the master power switch, controls whether a 5 V power signal is sent to either the hardware relay or the software-controlled relay.

Figure 32. Hardware control panel.

Control of the isolation valves is accomplished through toggle switches that operate a hardware relay board. The relay, in turn, operates the electronic solenoids within the test chamber that controls the flow of gas to the valve. The red and green LED status lights are a custom circuit that monitors whether or not power is flowing to the electronic relays. This method was more complicated than monitoring the switch positions directly but was necessary to allow the hardware panel to know the position of each valve regardless of which system was currently controlling the chamber. The LED status circuit is also the synchronizing mechanism for valve status between the hardware and software control panels.

The hardware panel has two redundant ways of monitoring pressure: Closed-circuit cameras allow viewing of analog gauges that are mounted on the chamber and feed system, and signal from the chamber’s pressure gauge is also sent directly to this panel.

The primary method of ignition is electrically heating a nichrome wire using a variable AC source. Controlling this ignition process is a two-step operation in which a safety key must be
armed and then a toggle switch must be flipped to allow the current to flow. Removal of the arming key prevents any ignition of the system using this panel.

The only feature not able to be redundantly operated by the software control system is the operation of the needle valves. Momentary switches on the panel send a combination of voltages to the DC motor controllers that dictate the speed and direction of the motors. The decision to make this feature non-redundant was made to simplify the design of the control system for the initial setup. Future updates to the control systems could allow these valves to be redundantly operated. The schematics for the hardware control circuits are listed in Appendix C.

4.1.2 Software Control

The software control system was designed to be independent and redundant to the hardware control system and be the primary method of data collection for experiments. The user interface was a LabVIEW program that utilizes a National Instruments 6361 USB I/O device to input and output data and a Measurement Computing USB-SSR24 relay to control valves. The user interface to the software control system is shown in Figure 33.

![Figure 33. Software control panel.](image-url)
The software panel controlled most of the UHPOC system functions if the control toggle on the hardware panel was switched. The one exception was the needle valve control, mentioned previously, that was only available on the hardware panel. The video feeds of the analog pressure gauges came directly from the camera and continue to operate if the hardware panel lost power. As in the hardware panel, energizing the ignition system was a two-step operation – the system is armed by a toggle switch and finally energized by clicking a button.

Because of the software control system’s dependence on the National Instruments (NI) device for signal input and output, additional steps had to be taken to ensure data accuracy, most notably an adjustment of the common mode ground level. The data coming in from the sensors was ~15V offset from the ground level of the NI box. This difference meant that the NI box was unable to read sensor data. To correct this issue, a unity-gain op-amp buffer was installed to shift the voltage levels and unify the grounds between the system and computer.

4.1.3 Data Collection

The data collection system integrated into the software control panel was able to collect a wide variety of data for combustion experiments. A custom LabVIEW program monitored and recorded both chamber and feed pressures generated from Omega PX91N1-50KS5T pressure sensors through a National Instruments USB-6361 data acquisition system. Visual burning-rate information was captured via a Phantom v310 high-speed camera. Figure 34 shows the high-speed camera setup, protected by a blast-proof enclosure, using a first-surface mirror setup to observe the windows. This data collection system is extensible, allowing collection of gas temperatures, sample subsurface temperatures, and supply pressure as needed by the experiment.
4.2 Data Post-Processing

Pressure and video data from each combustion experiment was combined and analyzed to determine average burning rates, average pressures, and qualitative combustion characteristics. These data were processed using a set of custom MATLAB scripts that guided the user through analyzing the video data, which included measuring the internal scale, marking the time-location data for the burning surface, and entering details about the experiment such as video framerate. These data were then automatically processed in parallel with the pressure data to determine the experimental average burning rate, average pressure, pressure change, and error range for the experiment. A sample of the time-location determination process is shown in Figure 35.
Figure 35. The video analysis process included marking the location of the millimeter marks from the internal scale (left) and using the marked locations to determine the time the burning surface reached each location (right).

Custom MATLAB codes also produced two pieces of information to help the user determine the validity of the experimental data. The first piece of information, with two examples shown in Figure 36, was a plot of the time-location points and error ranges along with the correlated slope and the slope’s error ranges. The user is prompted to ensure the error on the slope encompasses all data points and error ranges. The variation of the data about the curve fit line shown in these images was typical of all JA2 and much of the nitromethane data. The second piece of information was the timing of the burn plotted on top of the pressure data to ensure the two lined up properly.
Figure 36. Time-location data for JA2 burning rate at 34.8 MPa (left) and 172 MPa (right)

In addition to the above analyses, the videos for nitromethane experiments were analyzed using the ImageJ [52] software package to determine an estimation of the burning surface area and cell diameter. To determine the burning surface area, the length of the surface perpendicular to the camera was measured assuming it was flat oval. The actual surface was then computed by measuring the roughness of the surface above the flat baseline. The depth of the surface was assumed to be the tube diameter of the same roughness as the perpendicular surface. Using these values, the area of the surface could be estimated. The cell diameter and plume velocity were calculated in a similar manner. Figure 37 shows part of the burning surface area measurement for a nitromethane sample.
Figure 37. Measurement of the average (left) and true (right) burning surface for a nitromethane sample. Reflections make the flame appear larger than tube diameter.

For all tests, measurement uncertainty and error ranges were quantified as:

- **Pressure** – An error range of ± 0.45% was used for pressure measurements to account for calibration and measurement error ranges.

- **Time-Location Data** – An error range of ± two pixels (from a 512 x 512 pixel video) was used for the location of burning surface at a given time, and a range of ± two video frames was used for the time the burning surface reached that point.

- **Average Burning Rate** – The error for an individual burning rate was taken as a multiple of the standard deviation of the sample points. For most tests, a range of ± two standard deviations was enough to encompass all data points and their respective error ranges. For tests that had some amount of optical distortion for the pressurized windows, an error range of ± five standard deviations was used.

- **Turbulent Nitromethane Burning Rates** – Analyzing the nitromethane videos to determine burning rates of tests above 18 MPa was a source of human interpretation error because of the constantly changing burning surface geometry. Although repeated
analyses of the same test by the same person typically agreed within 1-2% of each other, variations between analyses by different researchers could vary by up to 5%. Therefore, the error ranges of the turbulent nitromethane tests were increased to ± 5% (if not already above this value) to account for the variation in human interpretation.
Chapter 5

Experiments and Results

The two propellants discussed in the introduction, JA2 and nitromethane, were tested using the UHPOC system. The JA2 propellant was chosen due to its expected well-behaved nature through the full pressure regime. This behavior allowed the chamber’s data collection and analysis systems to be developed and verified with a reasonable expectation of what the results should look like. The second propellant, nitromethane, was selected for testing because the UHPOC could provide the first direct burning-rate observations at pressures above 15 MPa, shedding light into the mechanisms responsible for the multiple burning regimes.

5.1 Experimental Setup

5.1.1 JA2

To prepare a JA2 sample, a cylindrical section of the propellant, approximately 38-mm long with a 6.3-mm diameter, was placed vertically in the UHPOC’s strand burner. The lateral surface of the propellant was covered in a thin coat of paint to inhibit the flame from spreading onto the sample’s outer surface [16]. The sample was ignited using a nichrome wire electrically heated from a variable AC source. An image of this setup is shown in Figure 38.
5.1.2 Nitromethane

The nitromethane used for these experiments was sourced from Lancaster Synthesis, Inc. and was marked as 98+% pure. For the baseline tests, a borosilicate glass tube, with an inner diameter of 10.6 mm and a height of 100 mm, was used to contain propellant. All baseline results and analysis were performed using this size tube as a previously published work into nitromethane burning rates reported that tube diameter did not affect the results [24]. The effect of tube diameter on burning rate was later re-examined and will be discussed in Section 5.3.2. For tests above 20 MPa, the glass tubes would frequently crack during testing, which would occasionally invalidate a test. To minimize this behavior, the tubes were covered in a single layer of 69 μm-thick polypropylene tape which slowed the formation of cracks in the tube during the test. Testing with tube diameters smaller than 10.6 mm did not need the tape layer as these tubes were not as prone to cracking, likely due to the lower heat release from the smaller burning surface. The tube was filled with nitromethane and was ignited from the top using a booster of NOSOL-363 solid.
propellant approximately 6 mm in diameter and 4 mm in length. The NOSOL-363 was threaded over a strand of nichrome wire and placed in contact with the nitromethane propellant surface. The nichrome wire was electrically heated from a variable AC source, which ignited the NOSOL-363, and in turn ignited the nitromethane. Once a propellant sample was secured, the strand burner assembly was inserted in the chamber and the chamber was pressurized with nitrogen (< 2 ppm moisture) to the desired pressure. The chamber was then allowed to sit for several minutes to allow the pressurant gas to become quiescent and equalize in temperature. Figure 39 shows a typical experimental setup for nitromethane.

![Nitromethane sample with solid propellant ignition booster suspended on the tube opening tube using nichrome wire.](image)

**Figure 39.** Nitromethane sample with solid propellant ignition booster suspended on the tube opening tube using nichrome wire.

### 5.2 JA2 Results

The steady-state burning behavior of JA2 propellant was tested at pressures between 14.1 - 207.7 MPa. Because the burning process was directly observed, time-location data were able to be collected at many different times and not limited to a small number of breakwires. The number of recorded data points for each test would vary if a portion of the visible burn had not yet reached
steady-state or if the window was obscured by smoke. Smoke was generally not an issue for these tests and only resulted in a small number of lost data points across all experiments. At pressures above 100 MPa, deformation of the polycarbonate windows also magnified the viewing area which limited the total distance that could be measured (an internal calibration scale was used to correct for the magnification effect).

The burning behavior of JA2 was similar across all pressures with a bright yellow flame and a relatively flat burning surface that regressed uniformly. Figure 40 shows an image of this behavior. The small dark spots just above the burning surface in the plume are flecks of the inhibitor paint coming off of the lateral surface. Also visible in this figure is optical distortion around the edge of the window, seen as a widening of the plume near the top of the image, caused by deformation of the polycarbonate windows due to pressure. The plume lengths for these tests could not be accurately measured due to their relatively long length with respect to the size of the window opening.

Figure 40. JA2 burning at 172 MPa.
A curve fit for the JA2 burning rate data was developed to both facilitate in interpolating results for arbitrary pressures as well as providing insight into the overall reaction order. These results, compiled along with previously published data, are shown in Figure 41. This figure does include error bars for all UHPOC data; however, most are small enough to be obscured by the data point. The data collected using the UHPOC aligned well with the previous publications from Reaugh et al., Gazonas et al., and Kuo and Zhang. The linear-fit correlation of the UHPOC data resulted in a burning rate expression of:

\[ r_b (\text{mm/s}) = 1.659[P(\text{MPa})]^{0.91} \text{ (for } 14.1 < P < 207.7 \text{ MPa}) \]  

The pressure exponent of 0.91 does differ slightly from the 0.97 value published by Kuo and Zhang, although it does cover over double the pressure range. The close agreement between the UHPOC data and previously published data for JA2 helped to validate UHPOC data collection and analysis methods as well as provided visual evidence to reinforce the assumptions made in the closed-bomb experiments. This validation was a critical milestone before testing the less well-behaved propellant nitromethane.
5.3 Nitromethane Results

5.3.1 Baseline Results

The steady-state burning behavior of nitromethane liquid, burned as a monopropellant, was tested at pressures between 3.6 – 101.7 MPa. Unlike the uniform behavior of JA2, nitromethane was expected to exhibit very different burning behaviors with changing pressure.

5.3.1.1 Observations

At the lowest pressure test of 3.6 MPa, nitromethane burned with a nearly invisible plume (Figure 42), while at higher pressures, it burned with a very luminous yellow plume (Figure 43). This color transition likely indicated a larger presence of soot in the plume at the higher pressures.
Figure 43 shows the burning progression at 18.2 MPa which was typical of the behavior in the 10.7 – 18.2 MPa pressure range. In this range, the liquid surface remained flat and the burning was well behaved. These results match previous direct observations within this pressure range [6], [24]. An observation not described in previous archival publications, but was noted by Boyer [22], was the presence of highly luminous gas bubbles boiling off the surface edge near the tube wall. The resulting bubbles were observed at 3.6 MPa only intermittently and quickly dissipated; they grew in frequency and luminosity as pressure increased up through 18.2 MPa. The boiling behavior was no longer observed when burning behavior changed at pressures above 18.2 MPa.

Figure 42. Nitromethane burning at 3.6 MPa produced a clear plume.
Figure 43. Nitromethane burning at 18.2 MPa over three different time steps shows a flat burning surface and laminar flame.

A small increase in pressure to 20.6 MPa resulted in a distinct change of nitromethane’s burning behavior. Figure 44 shows this new behavior with a highly turbulent burning surface. This turbulence was likely the result of hydrodynamic instability at the surface due to a loss of surface tension. Also visible in Figure 44 are small cracks forming on the side of the glass tube that were mentioned in Section 5.1.2. These cracks did not appear to affect the burning rate of the propellant and always occurred after the burning surface had passed that location. When the chamber pressure was increased to 25.7 MPa, the surface turbulence of the propellant also increased. Figure 45 shows the burning behavior at this pressure and features larger peaks and valleys compared to those in Figure 44 as well as longer tendrils of unburned propellant extending into the plume.
Figure 44. Nitromethane burning at 20.6 MPa over three different time steps shows a turbulent burning surface.

Figure 45. Nitromethane burning at 25.7 MPa over three different time steps shows exaggerated turbulence compared to the 20.6 MPa test.

One of the most likely causes of the loss of surface tension is the fluid transitioning to supercritical conditions. The critical temperature and pressure for nitromethane are 588.15 K and 6.3216 MPa respectively. [23] These values were collected from multiple, sometimes conflicting, sources by Boyer and Kuo for use in nitromethane propulsion. The transition from a smooth to turbulent
burning surface was observed at pressures greater than the critical pressure; the causes of this behavior will be discussed later in this chapter.

Because of the turbulent burning surface at pressures above 18.2 MPa, determination of time-location data were handled slightly differently than for lower pressure tests; at the higher pressures, each datum was selected at the intersection point of the liquid level and the center axis of the tube at fixed distance increments. This intersection point was used because a single level for the entire burning surface could not be obtained. The collection of points was then processed in the same manner as the lower-pressure data with experimental uncertainty increasing proportionally to the increase in the standard deviation of the data set. Figure 46 shows the time-location data collected for the 25.7 MPa nitromethane test, which shows much larger, although not unreasonable, variation in individual data points and a wider burning-rate error range than the JA2 tests shown in Figure 36.

![Figure 46. Time-location data for nitromethane burning rate at 25.7 MPa.](image)

Beginning at approximately 35.5 MPa, the flame front started showing distinct cellular structures [Figure 47 (top)]. Although the propellant surface was still sloshing in the tube, the cellular propagation began to slowly dominate the dynamics. By 40.8 MPa, the cellular propagation had completely taken over and the sloshing was no longer apparent. From 40.8 – 102 MPa, the
observed behavior remained relatively consistent with the flame progressing with the distinctive cellular flame front. Within this range, there was little variation in cell size (Figure 48) and the nominal burning surface was always at a large angle (30-60°) relative to the axial direction of the tube. This angled surface is in contrast to the smooth 90° surface angle that was observed at 18.2 MPa and below. An example of the cellular-propagating behavior shown in Figure 47 (bottom).

Figure 47. Nitromethane burning surfaces at 35.5 MPa (top), and 60.4 MPa (bottom).

Figure 48. Average cell diameters in the high-pressure burning regime of nitromethane did not vary significantly over the pressure range.
The full burning rate results for nitromethane in a 10.6 mm ID tube are shown in Figure 49. In the lowest burning regime, the UHPOC data aligns extremely well with previously published data. However, the UHPOC data has a significant divergence from other published data near the first slope-break region, particularly around 18 MPa where Rice and Cole [20] reported a burning rate almost 3x that which was observed in these experiments. This difference in behavior is not unexpected as small changes in environment or propellant purity may be reflected in the exact point in which the turbulent burning behavior begins. Above 20 MPa, the UHPOC data follows similar, but not identical, trends to the Rice and Cole data. Both data sets diverge at moderate pressures, but converge at higher pressures with the Boyer and Kuo data. This difference has been attributed to the use of glass tubes in both this study and the Rice and Cole study to hold the propellant versus the combustible straws used in the Boyer and Kuo study. The container difference could be affecting the burning rate in two ways. Because of the large angled burning surface, a combustible straw will begin to burn away before the entire burning surface has passed a location. This would likely distort the surface compared to a non-combustible tube which would preserve the surface’s inherent shape. Secondly, the glass tube would confine the product gasses where the combustible straw would not. This behavior could impact both heat and mass diffusion near the reaction zone.
5.3.1.2 Analysis

The UHPOC experiments showed three distinct burning regimes for nitromethane: a traditional burning region characterized by a smooth and flat burning surface, a transition region dominated by hydrodynamic instabilities, and a supercritical burning region dominated by a cellular-propagating surface. The pressure of 18.2 MPa was chosen as the first transition point as this pressure marked the change from a smooth burning surface to a surface with hydrodynamic instabilities. This transition pressure was slightly higher than the 15 MPa reported by Boyer and Kuo, and the Rice and Cole data was not published at these pressures. A second transition point of 40.8 MPa was chosen to separate the hydrodynamic-instability region and the cellular-propagation region; below this point, the hydrodynamic-instability behavior dominated, and above this point,
the cellular-propagation behavior dominated. This value is substantially lower than the 70 MPa transition point reported by Boyer and Kuo, although Boyer and Kuo’s use of combustible straws versus the glass tubes in this study limits the ability to directly compare the two data sets within this burning region. Using these two transition points, the observed burning rates have curve fits for the lower and upper regions of:

$$r_b (mm/s) = 0.1829 [P(MPa)]^{1.15} \quad (\text{for } 3.6 \leq P \leq 18.2 \text{ MPa}) \quad (6)$$

$$r_b (mm/s) = 11.04 [P(MPa)]^{0.679} \quad (\text{for } 40.8 \leq P \leq 102 \text{ MPa}) \quad (7)$$

In the low pressure region, the pressure exponent of 1.15 differs slightly from the 1.03 reported from the testing of Boyer and Kuo using similar methods. These two values fall within the experimental error of the tests, however. The pressure exponent of 0.679 for the highest pressure range is lower than the pressure exponent of 0.86 than the Boyer and Kuo data and falls outside of experimental error. This difference has been attributed to the difference in propellant containers mentioned previously. It should be noted that the data above 40 MPa, as shown in Figure 49, do not follow a strict exponential pattern as Equation 7 suggests but rather a constantly changing curve. It is possible that equations of another form could more accurately represent these data.

Due to the non-linear nature of the region between 18.2 – 40.8 MPa (on a log-log plot), a curve-fit for this data is not as straightforward as in the other regions. Because of the dramatic increase in the burning rate exponent above 18.2 MPa, a change in chemistry was considered. Kubota produced a simplified burning rate equation for energetic materials [7], which indicates the pressure exponent of approximately one from the 3.6 – 18.2 MPa regime relates to an overall second order reaction. Applying this model to the 18.2 – 40.8 MPa regime would produce a reaction order of ~4-5, which is unrealistic; therefore, the increased burning rate exponent for this range is likely due to a physical effect rather than chemical mechanism change. Because the pressures and temperatures involved are above the critical point for nitromethane, a supercritical combustion process was considered as the driving physical process for this region.
In the lowest burning regime, the nitromethane is burning with a traditional liquid-gas phase interface. This was hypothesized and validated by a numerical model by Boyer and Kuo [6]. If supercritical combustion is assumed for pressures above the first transition point, the flame would be acting directly on the supercritical vapor. It is hypothesized by Yetter [53] that the burning rate of a pure supercritical vapor should be similar to the flame speed of a freely propagating gaseous flame. In addition to the regime change, the turbulent and non-normal burning surfaces observed should increase the overall burning surface area and/or heat and mass transport rates of the flamelets, depending on the relative turbulence intensity, over that of a laminar burning regime [54].

Following this reasoning, the transition region should be bounded by two calculations: a traditional burning-rate calculation on the low pressure side and a freely propagating flame speed calculation on the high pressure side. The curve-fit listed in Equation 6 was used to represent the traditional burning rate calculations. The numerical burning rate model developed by Boyer and Kuo was also considered, but differed slightly from this experimental data by an average of 1.6%. Because of this difference, Equation 6 was viewed as a more appropriate basis for correlating the transition region for these data. The upper-bounds of the transition region were real-gas flame speed calculations provided by Dobbins and Smooke [55]. The flame speed calculation assumed an unburned propellant temperature of 298 K but did not include transport parameter modifications for a supercritical fluid. These calculations are described in more detail in Chapter 6.

To create a curve-fit for the transition pressure regime, Equations 8 and 9 were developed. Equation 8 computes the linear fraction \( x \) of the sample pressure \( P \) between the lower and upper pressure bounds for the transition region \( P_L \) and \( P_U \) respectively. The exponent \( h \) controls how strongly the change is represented by a linear transition. Equation 9 blends the burning rate \( R_b \) and the flame speed \( S_L \) models based on the fractional percentage developed in Equation 6 to arrive at the final burning rate correlation \( R_{b,c} \) for a particular pressure.
\[ x = 1 - \left( \frac{P - P_L}{P_U - P_L} \right)^h \]  

(8)

\[ R_{b,c} = R_b \times x + S_L \times (1 - x) \]  

(9)

Using the values of \( P_L = 18.2 \) MPa and \( P_U = 40.8 \) MPa previously mentioned, a wide range of values for the exponent \( h \) were calculated and compared with the experimental data. The smallest average error of 10\% occurred with an exponent of 0.79. These calculations resulted in the intermediate correlation plotted in Figure 50. This figure shows decent, but not yet acceptable, agreement between the correlation and the experimental data within the transition region. To decrease the average error, the effects of turbulence were next considered.

Figure 50. Correlation between a pure burning rate model and a pure flame speed model using a transition power of 0.79.

To determine the effect of turbulence on the flame speed, a Borghi diagram (Figure 51) was plotted for the data with turbulent burning surfaces. This diagram shows the data falling within a wrinkled laminar flame regime. In this regime, the turbulence is effectively increasing the burning surface area of the flame without dramatically affecting the heat or mass transfer rate through the flame. Therefore, an increase in burning surface should be roughly proportional to an increase in burning rate [54]. The videos of each experiment were analyzed to determine a rough estimate of
the burning surface area increase (Figure 52). Although the burning surface area did vary between experiments, multiple curve-fitting methods agreed that a constant 1.4x increase in the burning surface over the laminar surface described the full data set. This 1.4x factor was used to modify the laminar flame speed calculation and the transition curve was re-evaluated. The new transition power increased to $h = 0.95$ with an average error of 8%. Because the value of $h$ was so close to unity, the transition between the traditional and supercritical burning regimes, as a function of pressure, is nearly linear. The final curve for the transition region is plotted in Figure 53.

Figure 51. Experimental data fell within the wrinkled laminar flame regime.

Figure 52. Estimated fractional burning surface varied across experiments but had a correlation of a constant 1.4x.
Figure 53. Final transition region correlation with a transition power of $h = 0.95$.

For pressures above 40.8 MPa, the measured burning rates grew more rapidly than what the laminar flame speed calculations (using a constant $T_u = 298$ K) indicate. This divergence implies additional factors are influencing the propellant burning rate at these higher pressures. The suspected cause of this divergence is an increase of the laminar flame speed with increasing pressures. This suspicion is predicated on the belief that the thermal conductivity of the supercritical nitromethane increases as a function of pressure. Unfortunately, no published work could be found on the thermal conductivity of nitromethane within the supercritical regime, and attempts to model it (described in Chapter 6) were unsuccessful. Clues to its behavior had to therefore be inferred from other compounds. Figure 54 shows the supercritical conductivity of water as published by Pioro and Mokry [56]. Charts for Freon-12 [56], kerosene [57], n-hexane [58], and carbon dioxide [59] show similar trends, which implies the same trends may be universally applicable. Supercritical water shows an increase in thermal conductivity with increasing pressure across a broad range of temperatures. This increased conductivity would lead to higher enthalpy in the unburned propellant and would result in an increase in the laminar flame speed that would increase with pressure. The absolute enthalpy increase, and thus the absolute flame speed increase, is unable
to be determined without knowing the correct physical properties, but the trends appear to be headed in the right direction.

Figure 54. Thermal conductivity of water. [56]

The final curves represented by Equations 6-9 are plotted with the UHPOC experimental data in Figure 55. Although these correlations do not directly predict the other data sets described in Section 2.3, the methods used can be applied to get very good correlations for that data. For example, it is reasonable to assume that the values of $P_L$ and $P_U$ could vary between experiments given different purities of nitromethane and varying experimental conditions such as the pressurant used. By assuming a $P_L$ of 15 MPa and a $P_U$ of 50 MPa, keeping all other values constant, this process was able to predict the Rice and Cole data with an average error of only 4%.
Although much of the burning rate behavior appears to agree with the supercritical combustion hypothesis, the question remains as to why the transition to rapidly increasing burning rates happened at ~18 MPa when the critical pressure of nitromethane was only 6.3 MPa. One hypothesis for this behavior has been identified from analyzing the numerical combustion simulations described in Section 6.3. In these simulations, the propellant far upstream from the flame was not pure nitromethane, but a mixture of many different compounds that had diffused upstream. Figure 56 shows the major mixture components and how these percentages changed with pressure. Since the mixtures were not pure nitromethane, their critical properties were expected to differ from the pure nitromethane values and perhaps account for the observed experimental behavior.
To look for evidence that supported or refuted this hypothesis, the critical properties of the propellant mixtures were estimated. The estimation methods used and their caveats are described in detail in Sections 6.2.6 and 6.2.7. Although the method used to estimate critical temperatures (Li method) is generally accepted for most mixtures, the methods available to estimate critical pressures, particularly for mixtures that have methane components, can have large errors. [60] One of the best regarded methods for estimating the critical pressures of non-methane containing mixtures is the Kreglewski-Kay method. [40] Because these mixtures contain less than 10% methane, it is believed that general trends can be inferred from this method’s results.

Using the above methods, estimates for each mixture’s critical temperature and pressure were computed. The critical temperatures of the mixtures, shown in Figure 57, ranged from 480 – 506 K and were significantly lower than the 588 K of pure nitromethane. These temperatures decreased with increasing pressure, driven primarily by the decreasing nitromethane percentage in the mix and the increases in water and formaldehyde percentages. The critical pressures of the mixtures, shown in Figure 58, ranged from 14.2 – 16.2 MPa and were significantly higher than the 6.3 MPa of pure nitromethane. Similar to the temperature results, the critical pressure changes

Figure 56. Mole fractions of major components near propellant surface
appear to be primarily driven by the percentages of nitromethane, water, and formaldehyde in the mix which vary with pressure. Although it would be convenient to directly compare the ~16 MPa result from these estimations with the ~18 MPa experimental transition point, the unknown level of uncertainty from the estimation method would make the exercise difficult. However, the results from this analysis seem to support the hypothesis that the first slope break location was determined by the changing critical point of the propellant mixture as opposed to being a function of pure nitromethane properties.

Figure 57. Estimated critical temperatures of numerically simulated conditions
5.3.2 Impact of Tube Diameter

Previous research by Sabourin et al. [24] stated the size of a glass containment tube did not impact the burning rates of nitromethane. However, those experiment were only at lower pressures with smooth burning surfaces. Therefore, the influence of tube diameter while burning at higher pressures with turbulent surface conditions was investigated. Samples of nitromethane were burned in glass tubes with internal diameters that varied between 1 – 14 mm. All tubes were made from borosilicate glass and had similar wall thicknesses of ~1 mm with the exception of the 1-mm-ID tube which had a wall thickness of ~3 mm. For tube diameters of 5 mm and below, the NOSOL-363 booster used to ignite the sample would not fit within the tube. To work around this issue, a 10-mm diameter plastic cup was affixed around the entrance of the tube and filled with propellant. The booster was used to ignite the propellant in the cup which then propagated into the smaller diameter tube.

The burning rate results for the various tube diameters are plotted in Figure 59. In the first burning regime, below ~18 MPa, tube diameter was found to have no effect on the burning rates of
nitromethane. This result agreed with the findings of Sabourin et al. In this same region, it was observed that the burning rates for tube sizes of 2 mm, 5 mm, and 14 mm were, on average, 4.4% lower than the burning rates for the 11 mm tubes. Because the 11-mm tube tests were run 3-4 months before the other tube sizes, it is believed that this loss of performance was due to either slow decomposition or water absorption of the nitromethane after being exposed to atmosphere. Although no record of this behavior could be found in published literature, it matched similar results by Sabourin et al. during their testing. [53] Also within this same regime, the burning rates for the 1 mm tube were ~1% lower than those for the 2 mm, 5 mm, and 14 mm tubes. It is believed that higher heat loss from the larger wall-surface-to-burning–surface ratio caused a slightly lower burning rate than would otherwise be expected. The error bars shown in Figure 59 include these additional sources of uncertainty.

In the second burning region, at pressures above 18 MPa, tube diameter was found to have an impact on burning rates. Differences in the burning rates at a given pressure, and as a function of tube diameter, started off small near the lower inflection point and diverged gradually as pressure increased. Generally, an increasing tube diameter was associated with a faster transition from the traditional burning rate model to a model described by a freely propagating flame speed.

The transition point between the second and third burning regions appears to happen at a similar pressure (~40 MPa) across all tube sizes. Above this pressure, burning rates across all tube sizes grow steadily with pressure with more reasonable pressure exponents.

In the upper burning regime, larger tube diameters were associated with higher burning rates for a given pressure. This behavior is believed to be due to the larger turbulence scales, which are proportional to tube diameter, causing larger burning surface areas which increased burning rates. For all tube sizes, the burning rates in this region appeared to grow at similar rates. Because the 11-mm tube tests had more data points than the other tube sizes, the curve fits for this data set were scoped to the same range of 40 – 75 MPa to allow direct comparison of the results across tube
sizes. These data are plotted in Figure 60 and show very similar trends for all tube sizes. The burning rate slopes for this region across all tube sizes grew more rapidly than the estimated flame speed calculated with $T_U = 298K$. As described in a previous section, this accelerated growth of burning rates is believed to be caused by increases in flame speed with pressure due to higher thermal conductivity of the unburned supercritical vapor.

The transition region curves for each tube diameter, shown in Figure 59 and Figure 60, were calculated by using a modified version of the method described in Section 5.3.1.2. A lower transition pressure ($P_L$) of 19 MPa was chosen for all tube sizes because although an exact pressure was not determined for each tube size, they appeared to vary by less than 1 MPa. An upper transition pressure ($P_U$) of 40 MPa was used for all tube sizes since this pressure marked the beginning of the behavior change for all tube sizes. The upper-region curve fit, evaluated at 70 MPa, was used in place of the numerically calculated flame speed with the estimated burning surface modifier. Equation 6, evaluated at 19 MPa, was used in place of the experimental burning rate. Similar to the 10.6 tube size process, the values of $h$ in Equation 8 were determined by testing a range of possible values and minimizing the average error. Table 5-1 and Table 5-2 list the final results of these curve fits.

![Figure 59. Burning rates of nitromethane are affected by tube diameter.](image-url)
Figure 60. At pressures above 40 MPa, all tube sizes behave similarly.

Table 5-1. Second region curve-fits for various tube sizes

<table>
<thead>
<tr>
<th>Tube ID (mm)</th>
<th>Second region ((19 - 40 \text{ MPa}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>(x = 1 - \left(\frac{P(\text{MPa}) - 19}{40 - 19}\right)0.889) (r_{b,c}(\text{mm/s}) = 5.493 \times x + 56.78 \times (1 - x))</td>
</tr>
<tr>
<td>1.8</td>
<td>(x = 1 - \left(\frac{P(\text{MPa}) - 19}{40 - 19}\right)^{1.209}) (r_{b,c}(\text{mm/s}) = 5.493 \times x + 80.91 \times (1 - x))</td>
</tr>
<tr>
<td>5.0</td>
<td>(x = 1 - \left(\frac{P(\text{MPa}) - 19}{40 - 19}\right)^{1.155}) (r_{b,c}(\text{mm/s}) = 5.493 \times x + 104.9 \times (1 - x))</td>
</tr>
<tr>
<td>13.9</td>
<td>(x = 1 - \left(\frac{P(\text{MPa}) - 19}{40 - 19}\right)^{0.953}) (r_{b,c}(\text{mm/s}) = 5.493 \times x + 133.8 \times (1 - x))</td>
</tr>
</tbody>
</table>

Table 5-2. Third region curve-fits for various tube sizes

<table>
<thead>
<tr>
<th>Tube ID (mm)</th>
<th>Third region ((40 - 70 \text{ MPa}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>(r_b(\text{mm/s}) = 0.941[P(\text{MPa})]^{1.11})</td>
</tr>
<tr>
<td>1.8</td>
<td>(r_b(\text{mm/s}) = 3.829[P(\text{MPa})]^{0.83})</td>
</tr>
<tr>
<td>5.0</td>
<td>(r_b(\text{mm/s}) = 2.893[P(\text{MPa})]^{0.97})</td>
</tr>
<tr>
<td>13.9</td>
<td>(r_b(\text{mm/s}) = 3.497[P(\text{MPa})]^{0.99})</td>
</tr>
</tbody>
</table>

It is worth noting that across all tested tube sizes, the transition region appears to begin and end at the same pressures, 19 MPa and 40 MPa, respectively. This behavior lends additional
evidence to the earlier assertion that the transition pressures are due to thermochemical reasons rather than fluid mechanical phenomena. Additionally, it is hypothesized that results somewhere below the 1-mm-tube behavior would show the limiting behavior for nitromethane. As the size of the tube approaches the size of the cells measured in the supercritical combustion region, the burning rate would be minimally influenced by turbulence and the resulting increased surface area. However, heat transfer would still need to be accounted for.

Although the curve fits listed in Equation 7 and Table 5-2 provide the most accurate prediction results for the third burning regime if the exact same tube size is used, it is useful to have a general set of equations to help predicted untested sizes. Figure 61 plots burning rates across all tube sizes compared with curve fits at fixed pressures. These data show good agreement indicating that a general solution is possible. By determining the relationship between each of the constant pressure lines, Equations 10, 11, and 12 were developed. The predictions given by these equations were compared with experimental data (Table 5-3) and show acceptable agreement across all experimental data.

![Figure 61. Burning rates for a fixed pressure vary predictable across tube sizes.](image)
\[ r_p(mm) = a_P [TubeID(mm)]^{n_P} \text{ (for } 40 \leq P \leq 75MPa) \] (10)

Where:

\[ a_P = 1.502 \left[ P(MPa) \right] + 3.875 \] (11)

\[ n_P = 0.223 \left[ P(MPa) \right]^{0.0635} \] (12)

Table 5-3. Predictions of unified burning rate equations compared with experimental results.

<table>
<thead>
<tr>
<th>Tube ID, mm</th>
<th>RMS error, %</th>
<th>Max error, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.4</td>
<td>-13.2</td>
</tr>
<tr>
<td>2</td>
<td>5.7</td>
<td>9.9</td>
</tr>
<tr>
<td>5</td>
<td>3.9</td>
<td>5.1</td>
</tr>
<tr>
<td>11</td>
<td>3.2</td>
<td>-6.2</td>
</tr>
<tr>
<td>14</td>
<td>7.7</td>
<td>9.7</td>
</tr>
</tbody>
</table>

5.3.3 Sources of Error

As with any investigation, these studies contained several sources of error and uncertainty. As mentioned in Section 4.2, a certain amount of measurement uncertainty has been included in the error ranges presented within this publication. However, additional error sources were observed during experimentation that produced either difficult to quantify error or would require a separate study to investigate. These potential error sources are listed below:

1. Nitromethane samples contained an unknown amount of dissolved nitrogen gas during testing. This happened during pressurization of the chamber and could be observed as a small amount off-gassing for several minutes after unignited samples were removed from the chamber. The effect of this dissolved nitrogen on burning rates is unknown, as well as if the dissolved amount varies with temperature and/or pressures.
Investigating these questions could begin by using pressurants with different physical properties such as argon or helium.

2. Disturbances from the ignition process are potential causes of variations in measured burning rates. These disturbances could result in different burning surface angles which would result in changes to the total burning surface area. This error source likely had the biggest impact in the transition region as disturbances in the lowest burning regime would stabilize relatively quickly due to slow burning rates and higher viscosity. Similarly, higher pressures have burning rates so high that disturbances were dominated by the quick burning rate. Experiments with much longer tubes (200+ mm) would help determine if the observed effects are inherent to the flow or would eventually normalize over the longer burning time.

3. The purity of the nitromethane stock may have changed throughout the testing period. All tests for a given tube diameter happened within a few weeks of each other, however, several months elapsed between baseline (11-mm-dia tube) tests and the other testing. No published research could be found for storage effects of nitromethane, however, a small (4.4%) drop in burning rate for the lowest burning regime was observed between the beginning and end of testing. This difference was accounted for as an additional 4.4% error in the burning rate plots of tube diameters - 1 mm, 2mm, 5 mm and 14 mm. It is likely that the variance due to this error has an overall smaller size than the variance due to ignition disturbances.
In this chapter, the analytical and numerical modeling efforts for nitromethane are discussed. Until this study, very little work was found that covers the properties and behaviors of monopropellants in the high-pressure, trans-critical, and supercritical burning regimes. The most significant work thus far was by Boyer for the nitromethane monopropellant [22], but numerical work is still limited to moderate pressures. Because of the limited experimental coverage in the more extreme burning regimes, the physical properties of nitromethane had to be derived from generalized numerical models rather than observed from experimental data. Although the resulting properties were checked for reasonability against known values and related materials, they have not been experimentally verified.

The numerical results and underlying theories discussed here were primarily used to support investigations into observed phenomena. Efforts were also made to update Boyer’s existing models to run on a more modern code base. Lastly, modeling work performed by a supporting team at Yale is described due to its importance to the conclusions described in this work.

6.1 Theory

6.1.1 Burning Rates vs. Flame Speed in Supercritical Fluids

The burning rate behavior of nitromethane, as described in Section 5.3, appears to be bounded by a traditional burning rate model that includes a liquid-gas phase interface and a supercritical burning rate model that approaches a freely-propagating flame speed. These models
are discussed using generally accepted simplified theories from literature. As with all simplifications, the results are useful for general trends and order-of-magnitude assessments but may diverge from actual behavior. Specifically, the equations discussed in this section have underlying ideal-gas assumptions where the actual behavior is known to deviate from ideal behavior.

A simplified equation for the burning rate of a liquid propellant was given by Kubota [7] and is listed in Equation 13. This equation was developed by performing an energy balance within a system and assumed ideal gas, constant properties, and a single-step reaction. In this situation, the propellant is assumed to undergo a phase change from the liquid to gas before reacting.

\[
\dot{r}_b = \left[ \frac{k_g Q_g \omega}{\rho_p^2 C_{pgg}} \left( C_{pc} (T_s - T_u) - Q_s \right) \right]^{0.5}
\]  

Equation 13 is a simplified premixed flame speed equation as listed by Glassman et al. [61]. In contrast to Equation 13, this equation assumes all reactants are already in the gas phase and no phase change need occur before reacting. This equation is expected to model supercritical monopropellant combustion because although the propellant must transition from a liquid to a supercritical vapor, that transition happens far upstream of the flame (relative to the flame thickness). The supercritical vapor entering the reaction zone would undergo no further phase changes and thus the burning rate should approach a freely propagating flame speed. Additionally, because the propellant in question is a monopropellant, it can be considered a premixed, rather than diffusion, flame.

\[
S_L = \left[ \alpha_u \frac{\omega}{\rho} \left( \frac{T_f - T_i}{T_i - T_u} \right) \right]
\]  

Equations 13 and 14 have been considered as the lower and upper limits, respectively, when calculating the burning rates of a monopropellant at trans-critical pressures. Therefore, it is convenient to ratio the two equations to provide a better understanding of how that transition
occurs. [53] This ratio is shown in Equation 15 and should approach unity with increasing pressure. Perhaps the most interesting result from this analysis is that the ratio of burning-rate to flame-speed is proportional to the square root of almost all the terms. The one exception is that ratio of gas-density to liquid-density, which has a unity power. Experimental results for the 10.6 mm tube showed this transitioned happened with a power of 0.95, indicating that the density change is likely one of the dominating factors in predicting the increase of burning rate in the transition region as a function of pressure.

\[
\frac{r_b}{S_L} = \left[ \frac{C_p g (\rho_g / \rho_p)}{C_c (\rho_g / \rho_p)} \right]^2 \left( \frac{1}{1 - \left( \frac{Q_s}{C_c (T_s - T_u)} \right)} \right) \left( \frac{T_i - T_u}{T_s - T_u} \right) \left( \frac{T_f - T_s}{T_f - T_i} \right)^{0.5}
\]

(15)

### 6.1.2 Turbulence Effects and Flame Speed

Turbulence can affect flame speed in multiple different ways depending on the relative size of the turbulence scales to the size of the flame. Yortsos described three main regimes using the Kolmogorov microscale \((l_k)\) and integral scale \((l_o)\) as characteristic turbulence scales and the laminar flame thickness \((\delta_l)\) as the characteristic flame size [54]:

- **Wrinkled laminar flames:** \(\delta_l \leq l_k\)
- **Flamelets in eddies:** \(l_o > \delta_l > l_k\)
- **Distributed reaction:** \(\delta_l > l_o\)

Within the wrinkled laminar flame regime, the smallest turbulence scale is larger than the flame thickness. In this case, the turbulence only serves to distort the flame, increasing its surface area, as opposed to changing how the reaction occurs. In the distributed reaction regime, the flame thickness is larger than the largest turbulence scale. Within this regime, the turbulence serves to enhance both mass and energy transfer within the flame, increasing the reaction rates over the
laminar case. The final regime, flamelets in eddies, lies between the other two regimes and has some qualities of both. Experimental and numerical results from this study (Figure 51) showed that supercritical monopropellant combustion lies in the wrinkled laminar flame regime and thus increases in surface areas result in a proportional increase to burning rates.

6.2 Analytical Results

6.2.1 Liquid Density

The liquid density of nitromethane at ambient temperature was required to calculate the propellant’s kinematic viscosity. The density values were estimated for the experimental pressure range using the method of Thompson et al. [62] as compiled by Reid et al. [60]. This method is listed in Equations 16 – 19 using the values in Table 6-1 and a modified acentric factor ($\omega_{SRK}$) for nitromethane of 0.3295 [60].

$$v = v_s \left(1 - c \ln \frac{\beta + P}{\beta + P_{vp}}\right)$$  \hspace{1cm} (16)

$$\frac{\beta}{P_c} = -1 + a(1 - T_r)^\frac{1}{3} + b(1 - T_r)^\frac{2}{3} + d(1 - T_r) + e(1 - T_r)^4$$  \hspace{1cm} (17)

$$e = \exp(f + g\omega_{SRK} + h \ast \omega_{SRK}^2)$$  \hspace{1cm} (18)

$$c = j + k\omega_{SRK}$$  \hspace{1cm} (19)

Table 6-1. Equation variables for Thompson et al. method

<table>
<thead>
<tr>
<th>a</th>
<th>b</th>
<th>d</th>
<th>f</th>
<th>g</th>
<th>h</th>
<th>j</th>
<th>k</th>
</tr>
</thead>
<tbody>
<tr>
<td>-9.070217</td>
<td>62.45326</td>
<td>-135.1102</td>
<td>4.79594</td>
<td>0.250047</td>
<td>1.14188</td>
<td>0.0861488</td>
<td>0.0344483</td>
</tr>
</tbody>
</table>
The results of the liquid density estimations are presented in Figure 62. Throughout the entire test range, the density of nitromethane increased by only 5-6%. Although this change is not insignificant, it still about the same size as the error margin for the experimental burning rate measurements.

Figure 62. Saturated liquid density of nitromethane at 298 K.

6.2.2 Saturated Liquid Dynamic Viscosity

The dynamic viscosity of nitromethane at ambient temperature was required for calculating the kinematic viscosity of nitromethane. The dynamic viscosity values were estimated for the experimental pressure range using the method of Lucas [63] as listed by Reid et al. [60]. This method reported errors of less than 10% from 55 tested polar and nonpolar liquids (nitromethane is polar). Equations 20 – 24 and an acentric factor (\( \omega \)) for nitromethane of 0.310 [60] was used for these calculations.

\[
\frac{\mu}{\mu_{SL}} = \frac{1 + D(\Delta P_r/2.118)^A}{1 + C \omega \Delta P_r}
\]  

(20)

\[
\Delta P_r = \frac{P - P_{vp}}{P_c}
\]  

(21)
The results of the dynamic viscosity estimations are plotted in Figure 63. Although the shape of this graph looks similar the density results, the actual values changed significantly more; over the entire test range, viscosity increased by approximately 50%.

![Graph of Dynamic Viscosity](image)

Figure 63. Dynamic viscosity of nitromethane at 298 K.

### 6.2.3 Supercritical Vapor Dynamic Viscosity

The dynamic viscosity of supercritical nitromethane was estimated using the method of Zabaloy et al. [64] and Zabaloy et al. [65]. This method assumed a Lennard-Jones fluid and contained two adjustable parameters for bringing analytical predictions in-line with experimental observations. Because no experimental results could be found for the supercritical viscosity of
nitromethane, the adjustable parameters were left as the default. The method’s authors tested a wide variety of compounds such as methane, propane, n-octane, iso-butane, water, and nitrogen and reported an average error of 25% and a maximum error of 72% using the default parameters. These error ranges could be significant, but the resulting values were still useful for order-of-magnitude estimations. Equations 25 – 35, which require the variable values in Table 6-2, the coordinates in Table 6-3, and the values of \( b_{ij} \) listed in Table 6-4, were used in this estimation method.

\[
\eta^+ = \eta_0^+ + \sum_{i=2}^{10} \sum_{j=1}^{3} b_{ij} \frac{(\rho^+)^i}{(T^+)^{j-1}}
\]  
(25)

\[
\eta_0^+ = \frac{0.176288(T^+)^{0.5}}{\Omega_v}
\]  
(26)

\[
\Omega_v = [A(T^+)^{-B}] + C[\exp(-DT^+)] + E[\exp(-FT^+)]
\]  
(27)

\[
T^+ = \frac{k_b T}{\epsilon}
\]  
(28)

\[
p^+ = \frac{P\sigma^3}{\epsilon}
\]  
(29)

\[
\rho^+ = N_A\rho\sigma^3
\]  
(30)

\[
\epsilon = k_b \frac{T_c}{T_c^+}
\]  
(31)

\[
\frac{\sigma}{\sigma_c} = 1 + S_\sigma(T_r - 1)
\]  
(32)

\[
\eta = F_0 \eta^+ \frac{\sqrt{m\epsilon}}{\sigma^2}
\]  
(33)

\[
\sigma_c = \frac{k_b T_c P_c^+}{(P_c T_c^+)^{1/3}}
\]  
(34)

The adjustable parameters, which were left as default:

\[
S_\sigma = 0; \ F_0 = 1
\]  
(35)
Table 6-2. Variable values for Equation 24.

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.16145</td>
<td>0.14874</td>
<td>0.52487</td>
<td>0.77320</td>
<td>2.16178</td>
<td>2.43787</td>
</tr>
</tbody>
</table>

Table 6-3. Lennard-Jones PVT coordinates.

<table>
<thead>
<tr>
<th>$T_c^*$</th>
<th>$P_c^*$</th>
<th>$\rho_c^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3396</td>
<td>0.1405</td>
<td>0.3108</td>
</tr>
</tbody>
</table>

Table 6-4. Values of $b_{ji}$ for supercritical viscosity calculations.

<table>
<thead>
<tr>
<th>$i$</th>
<th>$j$</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>3</td>
<td>1.325875×10^0</td>
<td>4.529702×10^{-11}</td>
<td>4.759355×10^{-11}</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>0.411250×10^0</td>
<td>1.598922×10^{-2}</td>
<td>2.341807×10^{-11}</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>2.053585 10^{-4}</td>
<td>1.682684×10^{-7}</td>
<td>1.428941×10^{-11}</td>
</tr>
<tr>
<td>5</td>
<td>6</td>
<td>0.510490×10^0</td>
<td>1.477943×10^{-11}</td>
<td>3.471516×10^{-11}</td>
</tr>
<tr>
<td>6</td>
<td>7</td>
<td>0.441143×10^0</td>
<td>1.478254×10^{-12}</td>
<td>5.342499×10^{-6}</td>
</tr>
<tr>
<td>7</td>
<td>8</td>
<td>0.253873 10^{0}</td>
<td>4.255116×10^{-4}</td>
<td>1.003290×10^{-7}</td>
</tr>
<tr>
<td>8</td>
<td>9</td>
<td>0.110954×10^0</td>
<td>7.921571×10^{-4}</td>
<td>3.712390×10^{-2}</td>
</tr>
<tr>
<td>9</td>
<td>10</td>
<td>8.260164×10^{-2}</td>
<td>1.466775×10^0</td>
<td>2.822336×10^{0}</td>
</tr>
<tr>
<td>10</td>
<td>1</td>
<td>2.287980×10^{-13}</td>
<td>7.244097×10^{-2}</td>
<td>0.309918×10^0</td>
</tr>
</tbody>
</table>

The results of the supercritical viscosity calculations are plotted in Figure 64. This plot shows the expected trend of increasing viscosity with increasing pressure. The variance with temperature is more complicated. Below 60 MPa, viscosity first decreases and then increases with increasing temperature. Above 60 MPa, increasing temperature reduces viscosity over the entire temperature range.
Because no experimental reference could be found for supercritical properties of nitromethane, the above estimations were compared with sub-critical estimations to check for an order-of-magnitude agreement. The method of Letsou and Stiel [66] as compiled by Reid et al. [60] was used for this check by estimating the lower-temperature viscosity of saturated liquid nitromethane. Equations 36 – 39 and the acentric factor for nitromethane ($\omega = 0.310$) were used to compute these estimations and the results were compared with the above estimations as shown in Figure 65. This plot validates that the supercritical estimations do appear to be of the correct order-of-magnitude.

\[
\eta_{SL} k = (\eta_L k)^{(0)} + \omega (\eta_L k)^{(1)}
\]

\[
(\eta_L k)^{(0)} = 10^{-3}(2.648 - 3.725 T_r + 1.309 T_r^2)
\]

\[
(\eta_L k)^{(1)} = 10^{-3}(7.425 - 13.39 T_r + 5.933 T_r^2)
\]

\[
\xi = 0.176 \left( \frac{T_c}{M^3 p_c^4} \right)^{1/6}
\]
6.2.4 Kinematic Viscosity

The kinematic viscosity of nitromethane at ambient temperature was needed to do a Reynolds number analysis of the flows within the glass tubes. These viscosities were calculated using the estimated results discussed in Sections 6.2.1 and 6.2.2. These results are plotted in Figure 66. The change in kinematic viscosity, as a function of pressure, was mostly driven by the change in dynamic viscosity. These estimations only apply to ambient temperature nitromethane and likely vary significantly as the temperature of the propellant increases through the critical point. Attempts were made to estimate the kinematic viscosity of the propellant throughout the temperature range of 298 – 2000 K using the results from Section 6.2.3. Unfortunately, an acceptable analytical method to estimate supercritical densities could not be found and additional experimental measurements would need to be made to provide an accurate estimate for the propellant density at elevated temperatures.
6.2.5 Thermal Conductivity

Estimating the thermal conductivity of supercritical nitromethane was attempted using the method of Chung et al. [67] and Chung et al. [68]. The formulas and background can be found in the references and appear to be a good basis for estimating the conductivity of supercritical nitromethane. Unfortunately, the estimations using this method are highly dependent on an experimental “association parameter” that was not found in literature for nitromethane. Thus, no valid results could be obtained.

6.2.6 Critical Temperature

The critical temperatures of the nitromethane-based propellant mixtures, described in Figure 56, were estimated using the method of Li [36] as compiled by Reid at al. [60]. This method produces acceptable results for most mixtures, and Spencer et al. [69] found that critical
temperatures based on the Li method helped achieve better critical pressure estimations from the Kreglewski-Kay method. To estimate the mixture critical temperature, Equations 40 and 41 were calculated using the pure-component properties from Table 6-5. All pure component properties were taken from Reid et al. [60] except for the critical volume of formaldehyde which was calculated by Koo [70].

\[ \phi_j = \frac{y_j V_{cj}}{\sum_i y_i V_{ci}} \]  

(40)

\[ T_{cm} = \sum_j \phi_j T_{cj} \]  

(41)

Table 6-5. Pure Component properties used to calculate critical temperature and pressure.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( T_c, \text{K} )</th>
<th>( V_c, \text{cm}^3/\text{mol} )</th>
<th>( P_c, \text{bar} )</th>
<th>Accentric factor (( \omega ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)O</td>
<td>647.3</td>
<td>57.1</td>
<td>221.2</td>
<td>0.344</td>
</tr>
<tr>
<td>CO</td>
<td>132.9</td>
<td>93.2</td>
<td>35</td>
<td>0.066</td>
</tr>
<tr>
<td>NO</td>
<td>180</td>
<td>57.7</td>
<td>64.8</td>
<td>0.588</td>
</tr>
<tr>
<td>CH(_3)NO(_2)</td>
<td>588.15</td>
<td>173.2</td>
<td>63.1</td>
<td>0.31</td>
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<td>CH(_4)</td>
<td>190.4</td>
<td>99.2</td>
<td>46</td>
<td>0.011</td>
</tr>
<tr>
<td>H(_2)</td>
<td>33.2</td>
<td>65.1</td>
<td>13</td>
<td>-0.218</td>
</tr>
<tr>
<td>N(_2)</td>
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<td>89.8</td>
<td>33.9</td>
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<td>CH(_3)O</td>
<td>408</td>
<td>113</td>
<td>65.9</td>
<td>0.253</td>
</tr>
</tbody>
</table>

The estimated critical temperatures of the nitromethane-based mixtures were plotted previously in Figure 57. These temperatures are predicted to be significantly lower than the pure nitromethane critical temperature of 588 K. As the mixture near the propellant surface changed with pressure, so too did the critical temperature. A simplified sensitivity analysis showed that the mole fractions of nitromethane, water, and formaldehyde were the biggest influencers on the mixture’s critical temperature.
6.2.7 Critical Pressure

There are many methods for estimating the critical pressures of mixtures and no single method gives good results for all mixtures. This is particularly true for methane-containing mixtures, where even methods specifically derived for these mixtures can give less-than-adequate results. [40] The method published by Grieves et al. [71] has shown to give acceptable results for methane-containing mixtures, but is a trial-and-error graphical approach that is unreasonable for mixtures with large numbers of components. Therefore, the goal of estimating the critical pressures of the nitromethane-based propellant mixtures, described in Figure 56, was not to predict the actual pressures, but to determine the properties’ general trends with respect to pure nitromethane. With that philosophy, the Najafi et al. [40] formulation of the Kreglewski-Kay [37] method was used as an estimation method. It was expected that with methane making up less than 10% of the mixture, error could be kept to a reasonable level and the general trends could still be determined. For the chosen method, Equations 42 and 43 were calculated using the values in Table 6-5. This method is particularly sensitive to the mixture critical temperature calculation. As mentioned in the previous section, pairing the Kreglewski-Kay method with the Li critical temperature calculation has been shown to give good results.

\[
P_{cm} = \left[ 1 + (5.808 + 4.93(\omega_m)) \left( \frac{T_{cm} - \sum_{i=1}^{n} y_i T_{ci}}{\sum_{i=1}^{n} y_i T_{ci}} \right) \right] \sum_{i=1}^{n} y_i P_{ci} \tag{42}
\]

\[
\omega_m = \sum_{i=1}^{n} y_i \omega_i \tag{43}
\]

The results of the critical pressure estimations are plotted in Figure 58. The critical pressures of the mixtures (~16 MPa) are predicted to be significantly higher than the critical pressure of pure nitromethane (6.3 MPa). As the mixture near the propellant surface changed with
pressure, so too did the critical pressure. A simplified sensitivity analysis showed that the mole fractions of nitromethane, water, and formaldehyde were the biggest influencers on the mixture’s critical pressure, not only from the pressure calculation itself, but also from the change in the critical temperature estimation.

6.3 Numerical Results

A previously-developed numerical model by Boyer and Kuo [23], assuming ideal-gas, showed good agreement with burning rates below 15 MPa. This model used a FORTRAN 90 code to automate CHEMKIN 4.0.2 calculations. As part of this study, the Boyer and Kuo code was ported to run on more modern software packages. Specifically, the code was rewritten to operate on MATLAB 2018 and CHEMKIN 19.2 using the same CHEMKIN input files. The correlated results of the updated model (Equation 44, $R^2 = 0.99945$) show small differences to the original model (Equation 45). These two models were expected to show identical results, so this divergence was surprising. A detailed analysis of the chemistry files and input mechanisms showed no difference between the two code bases. Although the calculations between the FORTRAN and MATLAB codes appeared to be identical and because the original FORTRAN code could not be run with the available resources, it was not possible to compare the calculations directly. This leaves the possibility of some numerical difference between the code bases as the cause for the differing results. Another potential cause of the divergence is some bug fix or update within the CHEMKIN software itself. Detailed changelogs for the software are not publicly available, so this theory could not be confirmed or discarded.
The burning rate results of the original and revised code bases are plotted Figure 67. The original Boyer and Kuo model under-predicts the lowest pressure result at 3.5 MPa and over-predicts the higher results up through 18 MPa. Conversely, the revised code over-predicts the results at the lowest pressures and under-predicts the results up through 18 MPa. Due to the elevated pressures being studied, the ideal-gas assumption is likely producing significant errors in this model, especially above 18 MPa. Moving to real-gas equations for state and transport properties would be a next step into modeling this complex behavior.

\[ r_b \left( \frac{mm}{s} \right) = 0.261[P(MPa)]^{1.02} \quad (44) \]

\[ r_b \left( \frac{mm}{s} \right) = 0.148[P(MPa)]^{1.27} \quad (45) \]

Figure 67. Updated nitromethane burning-rate model differs slightly from the previous version.
6.4 Supporting Work

Much of the analysis contained in this work was supported by numerical modelling performed by Dobbins and Smooke [55]. This modelling effort studied nitromethane monopropellant combustion using the Boyer and Kuo mechanism with the addition of the Becker–Kistiakowski–Wilson (BKW) real-gas equation of state. Although this modeling effort is still under development, some of the early results are presented here.

Figure 68 plots the flame speeds of a freely-propagating nitromethane flame. These results show a large increase in flame speed by switching to the real-gas equation of state. It should be noted that the transport properties have not been adjusted for these calculations. A recent study by Liang et al. [45] states that adjustment of these transport properties may reduce the predicted flame speeds somewhat. Also visible in this figure are how the results vary when the unburned propellant temperature changes from 298 K to 350 K. The increase in propellant temperature produced the expected increase in flame speed. Finally, these results have an interesting prediction of nitromethane’s flame speed near 200 MPa. Around this pressure, the rate of increase in flame speed, as a function of pressure, begins to level off. This same trend is visible in the UHPOC and Boyer and Kuo data (Figure 49) which is an indication that this model is capturing at least some of the real-world behaviors.

The predicted flame thicknesses are plotted in Figure 69. Moving from an ideal-gas to a real-gas equation of state produced a noticeable decrease in flame thickness at pressures below 300 MPa. In contrast to the flame speed calculations, flame thicknesses did not change much when the unburned propellant temperature was adjusted. These flame thickness calculations provided an important perspective in which to view the experimental data. As discussed in Chapter 5, turbulence is expected to play a significant role in connecting analytical and experimental data. The ratio of the turbulence scales to the flame thickness helps decide how turbulence affects the flame.
Additionally, because the quenching distance of a flame is proportional to its flame thickness [54], this thickness sets a lower limit for experimental container sizes.

Figure 68. Estimated flame speeds of nitromethane by Dobbins and Smooke. [55]

Figure 69. Estimated flame thicknesses of nitromethane by Dobbins and Smooke. [55]
Chapter 7

Conclusions and Future Work

7.1 Conclusions

A new experimental chamber has been created to directly observe combustion events under ambient temperatures and at constant pressures up to 300 MPa. By directly observing these events, burning rates were able to be more precisely measured compared to traditional breakwire or Crawford-style bomb techniques. Several supporting systems were designed and built to operate this chamber including high-pressure gas systems and redundant control systems. To test the data gathering and analysis techniques, the JA2 modified double base gun propellant was tested at pressures between 14.1 – 207.7 MPa. Experimental burning rates could be correlated using a single pressure exponent and the observed burning rates were similar to previous published rates. By utilizing a windowed chamber, the first direct observations of the quality of JA2 combustion at elevated pressures were obtained.

The burning rates of nitromethane, when burned as a monopropellant, were gathered using the UHPOC at pressures between 3.6 – 101.7 MPa. Three distinct burning regimes were observed for nitromethane when burned in a 10.6 mm ID tube:

1. From 3.6 – 18.2 MPa, observed burning rates could be described with a single pressure exponent of 1.15 and agreed with previous publications within experimental error. These rates also agreed with the previously published numerical model that assumed ideal gas and a traditional liquid-gas phase interface.
2. From 18.2 – 40.8 MPa, observed burning rates rose sharply as a function of pressure. Correlations for the burning rates in this region appear to follow a near-linear transition, as
a function of pressure, between a burning rate that includes a liquid-gas phase interface to a supercritical burning rate that could be described by a freely-propagating flame speed.

3. From 40.8 – 102 MPa, observed burning rates could be described by a single pressure exponent of 0.679. The slope of this curve-fit was larger than the numerical predictions of flame speeds at those pressures leading to the theory that flame speeds are being increased due to enhanced heat transfer from the flame to the unburned propellant through the supercritical vapor.

Nitromethane was also tested across a variety of tube sizes from 1 – 14 mm ID tubes. The size of the tube was found to affect burning rates at pressures above ~18 MPa. The measured burning rates at the lowest tube size appeared to be bounded by nitromethane’s flame speed. Increasing tube sizes resulted in increased burning rates at a given pressure. Suspected causes of this behavior were believed to be increased turbulence effects as tube size increased.

To support the experimental analysis, numerical and analytical predictions for several nitromethane physical properties were developed. These predictions were not able to be experimentally verified during the study.

7.2 Future Work and Recommendations

As with many experimental studies, the results of this effort have raised as many questions as has been answered. Specifically, the nitromethane monopropellant has many avenues of follow-up topics to expand on the results found during this study:

- The slope of the observed burning rates in the highest pressure burning regime rose more rapidly than predicted by a numerical model for the freely-propagating flame speed. This behavior was believed to be caused by enhanced heat transfer of the
supercritical vapor increasing flame speed. Experiments using tubes instrumented with fine-wire thermocouples may determine if this theory has validity. Results would depend on if the thermal wave thickness is large enough to accurately measure.

- The supercritical behaviors observed here may be applicable to other propellant forms. Testing other liquid monopropellants, such as hydroxylammonium nitrate (HAN) aqueous solution, may show similar results at pressures above their critical pressure.

- The transition pressure between the first and second burning regimes is believed to be a function of the unburned vapor’s thermochemistry. Experiments designed to manipulate this transition pressure, such as varying the unburned propellant’s temperature would provide insight into this mechanism.

- As pressure is increased from 3 MPa, nitromethane transitions from a clear plume to luminous yellow plume indicating the presence of additional soot. Testing the amount of soot in the plume and whether or not this trend continues with ever increasing pressure will help to validate and refine existing combustion models.

- The UHPOC’s windows for these experiments were polycarbonate due to a flaw in the chambers original design. Improving this design will allow the use of quartz or sapphire windows which will in turn facilitate the use of more precise diagnostic tools.

- The numerical predictions described here were based on the BKW equation of state. BKW is not as accurate around the critical point, so alternate methods should be utilized to describe the behavior in this region. Additionally, inclusion of updated transport properties should improve the overall predictions.
• In practical devices, propellants are typically injected rather than burned in a pool. Extending this research to spray-injected delivery methods would be a step toward identifying and modeling behaviors in real-world devices.

• Heat-loss through the tubes has not been taken into account for any calculations. Ambekar, at al. [72] presented a model for the inclusion of heat transfer effects to the tube container which looks promising. Including these effects could provide reasons for why observed burning rates differ from predictions.

• The current numerical burning rate models diverge from experimental data around the 18 MPa mark. The data and theories from this study show that models could be extended by adding supercritical, turbulence, and heat transfer effects to better match experimental data.

• Pressurant gas was observed to dissolve in the nitromethane during pressurization of the chamber. Using different pressurants, such as argon, could help determine if the dissolved gas is affecting the burning rate measurements.

• Experimental physical properties of nitromethane in the supercritical state would be invaluable to validating and expanding the models presented here (thermal conductivity, density, viscosity, etc.).
## Appendix A

### Tabulated Test Results

#### A.1 JA2

<table>
<thead>
<tr>
<th>Pressure (MPa)</th>
<th>Burning Rate (mm/s)</th>
<th>Uncertainty (mm/s)</th>
<th>$R^2$ of Correlation</th>
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<td>0.9992</td>
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#### A.2 Nitromethane

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<th>Tube Dia. (mm)</th>
<th>Pressure (MPa)</th>
<th>Burning Rate (mm/s)</th>
<th>Uncertainty ± (mm/s)</th>
<th>$R^2$ of Correlation</th>
<th>Burning Surface Ratio</th>
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<td>24.6</td>
<td>21</td>
<td>1</td>
<td>0.9997</td>
<td>1.1</td>
</tr>
<tr>
<td>1.0</td>
<td>30.0</td>
<td>39</td>
<td>2</td>
<td>0.9999</td>
<td>1.1</td>
</tr>
<tr>
<td>1.0</td>
<td>39.9</td>
<td>59</td>
<td>3</td>
<td>0.9997</td>
<td>1.2</td>
</tr>
<tr>
<td>1.0</td>
<td>49.8</td>
<td>70</td>
<td>3</td>
<td>0.9998</td>
<td>1.0</td>
</tr>
<tr>
<td>1.0</td>
<td>60.1</td>
<td>90</td>
<td>4</td>
<td>0.9999</td>
<td>unk.</td>
</tr>
<tr>
<td>1.0</td>
<td>69.2</td>
<td>105</td>
<td>5</td>
<td>0.9999</td>
<td>unk.</td>
</tr>
</tbody>
</table>

Appendix B

MATLAB Code

B.1 Chemkin_Wrapper.m

```matlab
clear;
clc;
more off; %since Octave doesn't display stuff within the while loop until it is finished
    %use more off to make sure it goes straight to the screen and displays everything
    %while it is running.

%Execution parameters and other user settings
maxloops = 50;
Ti = 298; %initial temperature (k)
ChemkinInputFile  = '70_MPa_pre-mixed_burner__burner_stabilized.inp';
ChemkinOutputFile = '70_MPa_pre-mixed_burner__burner_stabilized.out';

%*Initialize shell environment
Set_Chemkin_Environment();
%location of local chem files for nitromethane
setenv('CHEM_FILES','"Y:\Public\Projects\ARO UHPOC\data\_Code and calculators\Chemkin Wrapper"');

%*Initialize variables
delta_rb = 1; %Initialize to some huge value so convergence loop runs...
rdelta_rb = 1; %relative delta
rb_tol = 2e-6; %delta-burning rate tolerance (assumes rb in m/s)
rb_rtol = 5e-4; %relative burning-rate tolerance
loopcount = 0;
error_message = '';
rb_history = 0;
rb_assumed_history = 0;

%* Preprocess chemistry meachansim, therm, and transport data files
% Preprocess chem.inp mechanism file and therm.dat data file (this is explained
% in "Getting Started 4.3")
% status = system('%REACTION_DIR%\chemkinpro.win64\bin\chem -i chem.inp -o chem.out
%  &-d %REACTION_DIR%\chemkinpro.win64\data\therm.dat')

% [status,cmdout] = system('%REACTION_DIR%\chemkinpro.win64\bin\chem -i Glarborg_hc_no_reburn.inp -o
Glarborg_hc_no_reburn.out -d %REACTION_DIR%\chemkinpro.win64\data\therm.dat')
disp('Preprocessing chemistry and therm data files....');
tic;
%base mechanism
%[status,cmdout] = system('%REACTION_DIR%\chemkinpro.win64\bin\chem -i %CHEM_FILES%\chem.inp -o
%CHEM_FILES%\chem.out -d %CHEM_FILES%\therm.dat');
```
%CH3NO additions
[status,cmdout] = system('%REACTION_DIR%\chemkinpro.win64\bin\chem -i
%CHEM_FILES%\NM_CH3NO_add_chem.inp -o %CHEM_FILES%\NM_CH3NO_add_chem.out -d
%CHEM_FILES%\NM_CH3NO_add_therm.dat');
toc

%Preprocess tran.dat file
[status,cmdout] = system('%REACTION_DIR%\chemkinpro.win64\bin\tran -o tran.out -d tran2.dat')
disp('Preprocesssing transport data file...')
tic;
[status,cmdout] = system('%REACTION_DIR%\chemkinpro.win64\bin\tran -o %CHEM_FILES%\tran.out -d
%CHEM_FILES%\tran.dat');
%CH3NO additions
[status,cmdout] = system('%REACTION_DIR%\chemkinpro.win64\bin\tran -o
%CHEM_FILES%\NM_CH3NO_add_tran.out -d %CHEM_FILES%\NM_CH3NO_add_tran.dat');
toc

%**Main loop - checks rb match for convergence between assumed value and calculated
%value from gas phase heat transfer
%Put in a do loop/while loop to make sure that it keeps on iterating if delta_rb>rb_tol
%while (abs(delta_rb) > rb_tol)
while (abs(rdelta_rb) > rb_rtol)
  disp('');
  disp(['Iteration # ', num2str(loopcount)]);
  %Check to see if maximum number of loops reached
  if (loopcount >= maxloops)
    error_message='Maximum loopcount reached with no convergence.';
    error(error_message);
    break;
  end

% ** Run premix burner stabilized CHEMKIN program
if (loopcount==0)
%run PREMIX to find new solution
  disp('Executing CKReactorBurnerStabilizedFlame.') ;
tic;
  SystemCommand = [%CHEMKIN_BIN%\CKReactorBurnerStabilizedFlame -i ', ChemkinInputFile, '-o ',
ChemkinOutputFile];
  [status,cmdout2] = system(SystemCommand);
toc
else %if loopcount>0 run with restart file and new input file
  disp('Executing CKReactorBurnerStabilizedFlame..')
  tic;
  SystemCommand = [%CHEMKIN_BIN%\CKReactorBurnerStabilizedFlame -i ', ChemkinInputFile, '-o ',
ChemkinOutputFile];
  [status,cmdout3] = system(SystemCommand);
toc
end

%Check for succesful execution
%Check for existence of XMLData.zip file
C = exist('XMLData.zip', 'file');
if (C == 0)
  disp('No XMLData.zip file exists...please check input files and output');
  disp('logs for possible errors, then restart');
  error_message = 'Missing XMLData.zip';
  error(error_message);
error(error_message);
end

% Check for existence of executable output logfile and look for signs of success
D = exist(ChemkinOutputFile,'file');
if (D == 0)
    disp('No oppdiff.out file exists please check input files and output');
    disp('logs for possible errors, then restart');
    error_message = 'Missing output logfile';
    error(error_message);
end

% Check for indication of successful convergence in CHEMKIn app output file:
% 'TWOPNT: SUCCESS. PROBLEM SOLVED.' seen at end of output for good run,
% so search for substring with this line.
% *be careful with this--look at some output files to make sure it doesn't
% converge, refine the grid, then *not* converge for final case. May need to
% go to end of output file, rewind a few lines, and scan them to make sure
% only final status of TWOPNT is captured
searchStr = 'TWOPNT: SUCCESS';
searchFile = fileread(ChemkinOutputFile);
searchResults = strfind(searchFile,searchStr);
% will spit out an empty matrix if the pattern is not found in the file
if isequal(size([],size(searchResults)))
    disp('No TWOPNT success found...may be a convergence problem');
    error_message = 'No TWOPNT: SUCCESS found';
    error(error_message);
    break;
else % if the results matrix is not empty
    disp('TWOPNT appears to have been successful. Continuing...');
end

% Extract solution data from XMLData.zip output file
% By default, GetSolution writes to comma-delimited row based file
% CKSoln.csv (see "Getting Started" 4.4) also run CKSolnTranspose
% to createcolumnar data to simplify reading. Unless full paths supplied,
% XMLData.zip and CKSolnList.txt preferences must be in working directory
% Hand modify CKSolnList.txt to produce only data needed for coupling the
% the interface

disp('Checking Solution...');

% Check for CKSolnList.txt prefs file--if doesn't exist, generate a "new"
% one based on solution and stop for modification
% % Check to see if it works without rerunning entire license and everythg
E = exist('CKSolnList.txt','file');

if (E == 0)
    error_message = 'Cannot find CKSolnList.txt file. Please copy one to the working directory.';
    error(error_message);
end

% Process output data in XML_zipfile using prefs file
% [status,cmdout] = system('%REACTION_DIR%\chemkinpro.win64\bin\tran -o tran.out -d tran2.dat')
disp('Extracting solution from XML...');
% use -nosen and -norop switches to skip sensitivity and rate-of-production data
% exporting mixture_thermal_conductivity doesn't work at all - no idea why.
[shell_cmd, cmdout5] = system('%REACTION_DIR%\chemkinpro.win64\bin\GetSolution -nosen -norop -p %CHEM_FILES%\CKSolnList.txt %CHEM_FILES%\XMLData.zip', '-echo');

%Transpose row lists in CKsoln.csv into columns
%By default, creates a set of column-based *.csv files
%(see "Getting Started" 4.4). Unless full paths supplied, CKSoln.csv
%must be in working directory
[shell_cmd, cmdout6] = system('%REACTION_DIR%\chemkinpro.win64\bin\CKSolnTranspose');
disp('...done');
%Get data out of excel spreadsheet
%Added 12/4/15
%Make sure these variables and order match those in CKSolnList.txt
%Use csvread to obtain the values in CKSoln_solution_no_1_1

Temp_1 = dlmread('CKSoln_solution_no_1.csv',';',[1,4,1,4]); %K - This is cell E2
Temp_2 = dlmread('CKSoln_solution_no_1.csv',';',[2,4,2,4]); %K - This is cell E3
dist_1 = dlmread('CKSoln_solution_no_1.csv',';',[1,0,1,0]); %cm - This is cell A2
dist_2 = dlmread('CKSoln_solution_no_1.csv',';',[2,0,2,0]); %cm - This is cell A3
Pressure = dlmread('CKSoln_solution_no_1.csv',';',[1,1,1,1]); %dyne/cm2 - This is cell B2
Pressure = Pressure * 0.1; %Pa

%Z = ['Distance 1(cm):', num2str(dist_1)];
%T = ['Temperature 1 (K):', num2str(Temp_1)];
%W = ['Distance 2(cm):', num2str(dist_2)];
%V = ['Temperature 2 (K):', num2str(Temp_2)];

%Set surface temperature to gas phase initial temperature from
%CHEMKIN output file
Ts = Temp_1; %K

%Find heat flux to liquid from gas phase (for interface energy balance)
%Make sure units are ok in energy and mass calcs
dTdx = (Temp_2-Temp_1)/(dist_2-dist_1); %K/cm
dTdx = dTdx*100; %K/m
T_ave = (Temp_2+Temp_1)/2; %K

%get k value and heat flux
%Read in entire file to find the last column. The number of columns
%varries for some reason I can't figure out at the moment.
clear entire_results;
entire_results = csvread('CKSoln_solution_no_1.csv',1,0);
kColumn = size(entire_results,2);
[k] = entire_results(1:2,kColumn);
k_avg = mean(k);
k_avg = k_avg * 1.0e-5; %Convert Erg/cm-K-s to W/m-K
q_flux = k_avg * dTdx; %W/m^2

disp(['Conductivity (W/m/K) Mixture:', num2str(k_avg)]);

%Calculate regression rate based on Ti, Ts, and heat of vaporization (Ts)
%call with necessary parameters to calculate condensed phase gasification
%i.e. Ts (or P, then find Ts for generality?)
[rb] = Find_rb(dTdx, Ts, Ti,q_flux); %m/s
disp(['Current rb (m/s): ' num2str(rb)]);

%**Compare calculated regression rate to assumed value (for gas phase input)
rho_liquid = Find_rho_liquid(Ti); %kg/m^3
flowrate = Find_inp_Value(ChemkinInputFile,'FLRT') * 10; %g/cm2/s * 10 = kg/m2/s
rb_assumed = flowrate / rho_liquid; %m/s
delta_rb = rb - rb_assumed; % m/s
rdelta_rb = delta_rb / rb_assumed; % m/s
disp(['delta_rb (m/s): ' num2str(delta_rb)]);

% save off data for troubleshooting
rb_history = [rb_history rb];
rb_assumed_history = [rb_assumed_history rb_assumed];

% If not converged, create/update input file with new conditions
% look for better convergence routine (newton like) ??
% keep history in an array?
% new_rb = rb_assumed + (rb_calc - rb_assumed) / 2
% Chemkin takes awhile so to make things go faster:
% use a scaling factor was 0.04 in Eric's code
disp(['rdelta_rb: ', num2str(rdelta_rb)]);
disp(['rb_rtol: ', num2str(rb_rtol)]);

if (abs(rdelta_rb) > rb_rtol)
  if loopcount < 10
    scaling_factor = 0.6;
  else
    scaling_factor = 0.05;
  end
  disp('Using rb_new method 1');
else
  rb_new = rb_assumed + (abs(delta_rb)/delta_rb)*0.00000005;
  disp('Using rb_new method 2');
end

% For very small values of delta_rb, make sure change in flowrate isn't too small and drops out due to significant digits after decimal in FLRT input statement
% assumes rb in m/s
if (abs(delta_rb*scaling_factor)>0.0000001)
  rb_new = rb_assumed + (scaling_factor * delta_rb);
  disp(['New rb guess is: ', num2str(rb_new)]);
else
  rb_new = rb_assumed + (abs(delta_rb)/delta_rb)*0.00000005;
  disp(['New rb guess is: ', num2str(rb_new)]);
end

% calculate new velocity off of new rb
new_flowrate = rho_liquid * rb_new; % kg/m2/s
new_flowrate = new_flowrate / 10; % Change units to g/cm2/s for chemkin
disp(['New flowrate guess is (g/cm2/s): ', num2str(new_flowrate)]);

% Determine surface temperature associated with new guess for conditions
% This value is an input to the PREMIX code, set in the PREMIX input file
% as the initial temperature profile point (at x=0)
new_Ts = Find_Ts(new_flowrate, Pressure, Ti, Ts);

% Input file modify/write routines....
% Use the restart from previous run setting by adding RSTR keyword to input file
% rewrite old input file with loopcount suffix
% Read txt into line 88 where the fuel velocity will be changed
filename = ChemkinInputFile;
%write new flowrate
newValStr = num2str(new_flowrate);
for i = length(newValStr)+1:-1:2
    newValStr(i) = newValStr(i-1);
end
newValStr(1) = ' ';  
A = fileread(filename);
search = 'FLRT';
k = 0; %reset index
k = strfind(A, search);
k = k+length(search);
frontHalf = A(1:k);
k = k+1;

while A(k) ~= ''
    k = k+1;
end
backHalf = A(k:end);
%A = strcat(frontHalf, newValStr, char(13), backHalf);
A = strcat(frontHalf, newValStr, backHalf);
%save file
fileID = fopen(filename, 'w');
fwrite(fileID, A);
fclose(fileID);

%write new surface temperature
newValStr = num2str(new_Ts);
for i = length(newValStr)+1:-1:2
    newValStr(i) = newValStr(i-1);
end
newValStr(1) = ' ';  
A = fileread(filename);
search = 'TPRO 0.0 ';
k = 0; %reset index
k = strfind(A, search);
k = k+length(search)-1;
frontHalf = A(1:k);
k = k+1; %trailing space

while A(k) ~= ''
    k = k+1;
end
backHalf = A(k:end);
A = strcat(frontHalf, newValStr, backHalf);
%save file
fileID = fopen(filename, 'w');
fwrite(fileID, A);
fclose(fileID);

loopcount = loopcount+1;  %add this at the end so it actually iterates on the loopcount and doesn’t do it before the actual for loop
end
end

% Determine situation and write out final status/results
disp(' ');
function Set_Chemkin_Environment()
    % for 19.1
    setenv('REACTION_DIR', '"C:\Program Files\ANSYS Inc\v191\reaction"');
    setenv('CHEMKIN_BIN', '"C:\Program Files\ANSYS Inc\v191\reaction\chemkinpro.win64\bin"');
    setenv('CHEMKIN_VERS', '19.1');
    setenv('BUILD_DATE_FILE', '"C:\Program Files\ANSYS Inc\v191\reaction\chemkinpro.win64\build_date.txt"');
    setenv('CHEMKIN_RELEASE_NUMBER', '19.1 (18-Apr-2018)');
    setenv('CHEMKIN_TITLE', 'ANSYS Chemkin-Pro');
    setenv('RD_JRE_BIN', '"C:\Program Files\ANSYS Inc\v191\reaction\..\EKM\programs\jre1.8.0_144\bin"');
    setenv('PATH', [getenv('PATH') ';' getenv('CHEMKIN_BIN')]);
end

% for 19.2
% setenv('REACTION_DIR', '"C:\Program Files\ANSYS Inc\v192\reaction"');
% setenv('CHEMKIN_BIN', '"C:\Program Files\ANSYS Inc\v192\reaction\chemkinpro.win64\bin"');
% setenv('CHEMKIN_VERS', '19.2');
% setenv('BUILD_DATE_FILE', '"C:\Program Files\ANSYS Inc\v192\reaction\chemkinpro.win64\build_date.txt"');
% setenv('CHEMKIN_RELEASE_NUMBER', '19.2 (30-Jul-2018)');
% setenv('CHEMKIN_TITLE', 'ANSYS Chemkin-Pro');
% setenv('RD_JRE_BIN', '"C:\Program Files\ANSYS Inc\v192\reaction\..\jre\1.8.0\bin"');
% setenv('PATH', [getenv('PATH') ';' getenv('CHEMKIN_BIN')]);
end

B.3 Find_Ts.m

function Ts = Find_Ts(flowrate, P, Ti, Ts_old)
    % find_Ts(flowrate, P, Ti, Ts_old)
    % flowrate in g/cm^2-s
    % P = pressure in Pa - unused
    % Ti = initial temperature in K
    % Ts_old = previous surface temp - unused

    disp('Convergence satisfied.');
    Pressure = dlmread('CKSoln_solution_no_1.csv', ',', [1,1,1,1]); % dyne/cm^2 - This is cell B2 % dyne/cm^2
    Pressure = Pressure*0.1; % Convert dyne/cm^2 to Pa; 10 dyne/cm^2 = 1Pa

    Pressure2 = Pressure*1e-6; % convert to megapascals
    P = ['Pressure (Pa):', num2str(Pressure)];
    A = ['Pressure (MPa):', num2str(Pressure2)];
    R = ['Regression rate (m/s):', num2str(rb)];
    disp(P);
    disp(A);
    disp(R);
    disp('see CHEMKIN output for details');
    disp('******************');

    % disp('B.2 Set_Chemkin_Environment.m');
    % disp('B.3 Find_Ts.m');
    disp('**********************');
% like the pyrolysis law Miller&Anderson used (JPP 2004).

R = 1.9872; %Universal Gas Constant (cal/mol-K)

%1. empirical pyrolysis law? Ts=f(P)?
% data not resolved enough for this

%2. equilibrium assumption--Ts=Ts sat where P_{vap}=P
% similar to Zarko, I think...
% would need to invert P_{vap}=f(Tsat) correlation in DIPPR to calculate explicitly
% or can just cheat and put correct value in PREMIX input file and keep it the same...
% this should duplicate previous program behavior
%Ts = Ts_{old}

%3. pyrolysis law (in the Arrhenius form suggested by Miller&Anderson, JPP 2004):
% rb = Aexp(-Ea/RTs) (better to curve-fit to FLRT or mdot, but this'll work)
% solve for Ts from flux (burning rate):
% Ts = (-Ea/R)*((1/ln(rho*flowrate/A)) where rb = rho*flowrate

A = 527.51; %pre-exponential parameter (cm/s)
Ea = 9071; %surface activation energy (cal/mol)
rho = Find_rho_liquid(Ti); %kg/m3
Ts = (-Ea / R) * (1 / log((rho * flowrate) / A)); %K
disp(['New Ts (K):',num2str(Ts)]);
end

function [rho_liquid] = Find_rho_liquid(T)
%Find density of liquid of C2H4 at given surface temperature in g/cm^3
MW = 61.04; %kg/kmol for CH3NO2
%for testing, use an approximate constant value
%rho_liquid = 1.1371 * 1000; %g/cm3 * 1000 = kg/m3
A = 1.3793;
B = 2.3918E-01;
C = 5.8815E+02;
D = 2.9030E-01;

%DIPPR property given in kmoles/cubic meter
molar_rhoe = A / B^(1 + (1 - (T / C))^D); %kmol/m3
rho_liquid = (MW * molar_rhoe); %kg/m3
end

B.4 Find_rh0_liquid.m

B.5 Find_inp_Value.m

%---------------------------------------------------------------%
function [Val] = Find_inp_Value(filename, Param)

    %Open file and read in contents
    input_file = fileread(filename);

    % get index of parameter and increment index to end of parameter
    index = strfind(input_file, Param);
    index = index + length(Param) + 1; % +1 for trailing space

    %beginning of value assuming no additional spaces
    loc_begin = index;

    %Find index where value ends by looking for a space
    while input_file(index) ~= ' '
        index = index+1;
    end

    loc_end = index;

    %return the number to the caller
    Val = str2num(input_file(loc_begin:loc_end));

end

B.6 Find_Cp-liquid.m

function [Cp] = Find_Cp_liquid(T)

    %DIPPR coefficients
    A = 1.1627E+05;
    B = -1.3530E+02;
    C = 3.4500E-01;

    %NM molecular weight
    MW = 61.04; %kg/kmol

    %DIPPR curve fit: Equation 100
    molar_Cp = A + (B * T) + (C * T^2); %J/kmol-K
    %DIPPR property given in J/kmol-K,
    Cp = (molar_Cp / MW); %J/kg-K

end
Figure 70. Overall schematic for hardware control panel.
Figure 71. Schematic for Hand Valve Actuator (HVA) control system.
Figure 72. Pinouts for HVA control boxes.
Figure 73. Schematic for isolation valve LED circuits.

Note: For the dump valve, Red and Green LEDs are switched
Appendix D

UHPOC Standard Operating Procedures

D.1 General Safety Procedures

1. Always wear appropriate PPE when entering the chamber or handling propellants.
2. Always wear safety goggles whenever any gas bottles are turned on.
3. Limit the amount of propellant for any given experiment to the minimum amount needed. This minimizes the over pressurization risk.
4. Never enter the chamber when the system is pressurized.
   There are rare occasions when this is necessary – if so, consult with the lab manager to determine additional safety procedures that must be followed.
5. Visually inspect the plumbing and electrical systems weekly to look for any signs of wear or distress.
   Never inspect plumbing or wiring while the system is energized or pressurized.
6. Before any test, understand the hazards of the propellant and any combustion products.
   This knowledge is critical should an unexpected event occur.

D.2 Bottom end-closure installation

General note, do not let spring-loaded plate compress fully. Damage to the turntable and possibly the full assembly will result.

1. Prepare sample in strand burner
2. Slide end-closer assembly until it hits the stops on the horizontal rails.
3. Set/Verify the Variac for the winch to ~15%. This slows the lifting rate of the winch.
4. Begin lifting assembly – be aware that it will begin to tilt as soon as it is off of the ground.
5. Once the plug is near the opening, hold the assembly vertically to prevent it from being caught on the edge of the opening.
6. Continue raising the assembly until the threaded collar has contacted the opening and the springs are almost, but not fully, compressed.
7. Manually lift the threaded collar and rotate it until it catches in the threads of the opening.
8. Use a bar, inserted into the access holes on the collar, to screw the collar into the chamber. Do not insert the bar more than 1” into the holes at it will catch on the inner plug causing the sample to be rotated out of position. If the plug turns when the threaded collar turns, either hold the plug in place or add more anti-seize to lubricate it.

As the springs decompress, the assembly will become harder to turn. After the springs have decompressed approximately half-way, lift the base plate more to take off some of the weight.

Caution: when the threaded collar is about half-way screwed in, the lifting assembly will have the plug fully seated within the chamber. At this point, do not raise the lifter any more as it will break the lifting assembly. Continue screwing the collar in until it is fully installed. The last few rotations will be harder, but the assembly should still move smoothly.

D.3 Compressor Startup and Chamber Filling

1. Perform all pre-test data collection (Room temp, sample size, etc.)
2. Test that internal illumination is operational (if using)
3. Install sample per “Bottom end-Closure” installation SOP
4. Turn on power strip on bottom of control panel
5. Turn on master power to control panel
6. Turn on Red air compressor for control gas and let it pump up.
7. Turn off red compressor when it reaches ~100 psi. It has plenty of volume so doesn’t need to run while testing.
8. Verify HV2 is open. This is the valve between the air compressor and the plumbing panel.
9. Set pressure levels on LabVIEW to read zero; begin monitoring pressure
10. Outside the test cell, close HV1, the isolation valve between the N2 source and the buffer bottle
11. Set the high-speed camera to use ruler-capture settings
12. Turn on the fiber light
13. Cover the camera and run the CSR process on the high-speed camera
14. If using polycarbonate windows:
   Open the upstream isolation valve
   Close downstream isolation valve and dump valve
   Pressurize chamber to ~200 psi using the green buffer bottle to spread out mineral oil and verify the scale is visible.
15. Once windows are verified, close the upstream isolation valve and open the green buffer bottle.
16. Verify sample is visible through window and through camera(s).
17. Verify all data-collection equipment is in place and operational
18. Verify hydraulic fluid level on compressor is full (above the temperature scale on the window)
19. Open the rolling metal door to the chamber by ~1 ft.
20. Turn on exterior warning light
21. Open both valves on outside of building for exhaust and relief valve plumbing
22. Turn on cooling water for compressor. Ensure flow rate is ~1-2 gal/min.
23. Close the door to the test cell
24. Verify 3-way valve on high-pressure system is closed to the test cell.
25. Open in-building vent (HV3) for high-pressure plumbing
26. Ensure valve between test cell and HPCL high-p plumbing is closed (HV4)
27. Open the source N2 bottles and verify you have enough gas for the test (compressor will not operate below 800 PSI)
28. Close the Downstream isolation valve and dump valve
29. Fully close (decrease) the downstream needle valve
30. Make sure the upstream needle valve is at least partially open. There is no “openness” indicator, so you if you are unsure, running it in the “increase” direction until it stops ensures it is fully open.
31. If not using polycarbonate windows, now pressurize the chamber to ~200 psi by opening the isolation valve.
32. Open dump valve to let the chamber evacuate to below 100 psi. This removes the air/moisture that was in the chamber prior to being sealed.
33. Open HV1 between the N2 bottles and the buffer bottle
34. Open the upstream isolation valve to begin filling the chamber
35. Wait for the chamber pressure to level off.
36. Turn on the breaker to power the gas compressor.
   The compressor does not turn off automatically, so this process must be monitored
37. Begin capturing high-speed video with a trigger set to capture all past data. Trigger the camera if a failure happens during pressurization.
38. Turn off the breaker to the compressor power once the desired pressure has been reached.

Target Pressure _________________________

39. Close the Upstream isolation valve.
40. Wait for the pressure to equalize in the system before beginning test.
41. Ensure all three isolation valves on the control panel are closed.
42. Close HV1 between N2 bottles and buffer bottle
43. Close the source N2 bottles

D.4 Test Execution procedures

1. Ensure door to test cell is fully closed
2. Turn on Variac and adjust to proper setting
   JA2 and Nitromethane use ~17-18 for most pressures.
   If testing below 2000 psi, try a lower setting such as 10-15.
3. Turn on internal illumination (if using)
4. Capture lit video of ruler and save to .mp4 format
5. Record chamber pressure
6. Change high-speed camera recording settings.
7. Start high-speed video capture
8. Start Labview data collection
9. Arm ignitor
10. Ignite
11. Trigger high-speed camera as soon as flame extinguishes
12. Turn off ignitor
13. Disarm ignitor
14. Stop data collection
15. Turn off internal illumination (if using)
16. Turn Variac off
17. Save burn video to .mp4 and .cine (RAW) format
18. Convert LabView data file from TDMS raw format.
19. Save data to thumb drive and move to the data repository on the main network

**D.5 End of test procedures**

1. Open the downstream isolation valve.
2. Open the downstream needle valve until gas begins to exit the chamber. Do not open fully while at high pressures to limit the stress on the low-pressure exhaust plumbing.
3. When chamber falls below 3000 psi and you can enter the room briefly using appropriate PPE and close the green buffer bottle.
4. Open the Upstream isolation valve. Also open the upstream needle valve if it was closed before the test.
5. Wait until the chamber pressure and compressor pressure has been fully released. Can open the dump valve to speed things up if necessary.
6. Once the pressure has been released, open the dump valve (assuming it wasn’t open already from step 5).
7. Close the upstream and downstream isolation valves
8. Close the downstream needle valve.
9. Let test cell air out for a few minutes after venting completes because there is a LOT of nitrogen in the area.
10. Turn off exterior warning light
11. Collect any post test data needed (window deflection, etc.)
12. Clean inside and outside of windows with soft gauze and a mild soap and water solution
13. Clean sample holder in strand burner
14. Inspect windows for damage or fatigue

If testing is done for the day
1. Close both valves on the exterior of building for exhaust and relief valve plumbing
2. Close vent valve (HV3) inside building for high-pressure plumbing
3. Turn off cooling water to the compressor
4. Verify fluid hydraulic levels on compressor are full
5. Shut down the master on the control panel
6. Turn off the power strip on the bottom of the control panel
7. Close the rolling metal door to the chamber.

D.6 Bottom end-closure removal

General note, do not let spring-loaded plate compress fully. Damage to the turntable and possibly the full assembly will result.
1. Raise lifting mechanism until the center round support is fully seated on the inner plug. The springs on the movable support plate will be slightly compressed.

2. Use a bar, inserted into the access holes on the collar, to unscrew the collar from the chamber.

   Do not insert the bar more than 1” into the holes at it will catch on the inner plug causing it to be rotated along with the collar. If the plug turns when the threaded collar turns, either hold the plug in place or add more anti-seize to lubricate it.

   As the springs get close to full compression, lower the lifter to give the springs more travel room. Lower a little bit at a time, corresponding to each round of unscrewing. When the collar fully unscrews, it will drop onto the movable plate and you want to limit the amount of distance it drops.

3. Continue lowering the lifter until the widest part of the plug is about to exit the opening.

   Hold the assembly vertically while lowering the lifter until the plug is fully out of the opening. Allow the mechanism to fully settle in whatever orientation it prefers. Failure to hold the assembly will cause it to tilt dramatically after exiting the opening, causing damage to the sealing surface of the plug.

4. Lower the lifter until all four support legs are on the floor. Don’t continue running the winch past this point to prevent the cable from coming off of the rollers.

**D.7 Compressor Maintenance**

**General Notes:**

- During the winter, and any other time it is expected to get below freezing outside, keep the heater running in the test cell. The compressor is water cooled, and bad things will happen if the water in the compressor freezes.
• If testing is not occurring, run the compressor for at least 30 minutes every week. It can be run safely with the gas bottles turned off.

• If the compressor is shutdown or stored for longer than two weeks, it needs to be protected from corrosion.
  o The best way to do this is to run the compressor using lightweight oil or other corrosion inhibiting fluid. This will leave a film that will protect the barrel bores and other parts that may corrode.
  o When the compressor is restarted, all the internal parts should be cleaned unless the protective fluids compatible with the compressed gas system requirements.

• The compressor should be protected from extreme changes in temperature that could cause condensation to occur.

Yearly Maintenance:

The end of the spring semester / beginning of summer (April-May) is the timeframe for yearly compressor maintenance

• The strainer and hydraulic reservoir should be cleaned yearly.

• The hydraulic oil should be replaced yearly. Compatible oils are listed in the compressor manual.

D.8 Loss of System Control

Blowout or venting of combustion products to room:

1. Notify lab manager and PI immediately.

2. Do not enter room until it can be deemed safe.
3. If either the propellant or products are toxic and/or harmful, follow lab procedures for handling and cleanup.

Loss of system control:

The UHPOC system is designed to fail to a safe state should all control be lost to the system. However, should control be lost:

1. Notify the lab manager immediately.
2. Do not enter room until it can be deemed safe.
3. If unable to manipulate and observe system via one of the control systems (hardware or software), use the control switch on the hardware panel to switch control to the other system. These systems are independent and redundant, so they should be able to take over control for each other to bring the system back to a safe state.
4. If neither control system is able to manipulate the system, cut all electrical power to the hardware control panel. This will turn off all valves in the chamber, causing the system to fail to an open state.
5. In the unlikely event the dump valve is stuck, cutting power to the panel will not help. You can attempt to retain control of the system by restarting the hardware control panel.
6. If all control attempts have failed and the system is still pressurized, work with the lab manager to call in specialized safety personnel.

Unable to determine system state although appear to still have control:

1. Notify the lab manager immediately.
2. Do not enter room until it can be deemed safe.
3. If you are unable to see source and chamber pressure through either the analog gauges or digital readouts, open the downstream isolation and/or dump valves to vent chamber. The evacuation of gasses is easy to hear, so use that as a guide to whether the camber is venting.

4. Wait a minimum of 30 minutes after opening vents before entering room. The valves can sometimes freeze up with long depressurization events from high pressures, so this wait time ensures that the chamber is fully depressurized and not just slowed down due to a stuck valve.
References


