ABSTRACT

VOGEL, PATRICK DYLAN. Numerical Simulation of a Hypervelocity Scramjet Engine. (Under the direction of Dr. Jack R. Edwards.)

Reynolds-averaged Navier-Stokes (RANS) methods are used to simulate flow in a dual-mode scramjet engine operating in the hypersonic flight regime at two different flight conditions. The engine is a freejet design based off of the University of Virginia’s direct-connect Dual Mode Scramjet (DMSJ) engine with the addition of an extended isolator, and a forebody / inlet. Menter’s two equation $k-\omega$ turbulence model is used in both its baseline (BSL) and shear-stress transport (SST) forms for different cases. Reaction chemistry was modeling using a finite-rate approach based off of the law of mass action with the combustion of hydrogen in air being modeled using a 9 species, 19 reaction model by Jachimowski. A silane-hydrogen blend fuel was also utilized to take advantage of the decreased ignition and reaction times caused by silane’s pyrophoric nature. This was initially modeled using a 16-species, 39-reaction model by Jachimowski and McLain and a 15-species, 45-reaction model by Chinitz. However, these models were found to lack the ability to simulate the pyrophoric nature of silane at low temperatures and pressures. To remedy this, the Chinitz model was modified to match ignition times of a 25-species, 70-reaction mechanism by Britten, Tong and Westbrook (BTW), before the full BTW model was ultimately implemented. Both of these models were able to achieve good agreement with the available experimental pressure data at the exit of the combustor when using solid phase thermodynamic data for SiO$_2$; however, they failed to replicate the early stages of the combustion process and resulted in combustion occurring far upstream of what was indicated by the experimental data. Tare results indicated general agreement with data, with the BSL model proving to be slightly more accurate. An investigation of the transient effects of the start of the experimental facility indicated that they had no effect on the initial ignition and combustion of the fuel, and the system was able to converge to the same solution as in the steady-state analysis.
BIOGRAPHY

Patrick Vogel was born on August 13, 1987 in Nashville, Tennessee. As a child, he grew a strong interest in math and science, particularly anything related to atmospheric or space flight. He attended Tennessee Technological University as an undergraduate where he received a BS in mechanical engineering with an area of concentration in aerospace engineering in 2010. Here his interest in aerospace propulsion systems grew and he was introduced to the concept of computational modeling of complex engineering problems. He attended North Carolina State University to pursue his Master’s in aerospace engineering under the direction of Dr. Jack Edwards where he has focused on computational fluid dynamics and aerospace propulsion.

Outside of school, Patrick enjoys hiking, camping, playing soccer and racquetball, and running.
ACKNOWLEDGEMENTS

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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>List of Tables</td>
<td>vi</td>
</tr>
<tr>
<td>List of Figures</td>
<td>vii</td>
</tr>
<tr>
<td>Nomenclature</td>
<td>xii</td>
</tr>
<tr>
<td>Chapter 1 Introduction</td>
<td>1</td>
</tr>
<tr>
<td>Chapter 2 Governing Equations</td>
<td>4</td>
</tr>
<tr>
<td>2.1 Navier-Stokes Equations</td>
<td>4</td>
</tr>
<tr>
<td>2.2 Turbulence modeling</td>
<td>7</td>
</tr>
<tr>
<td>2.2.1 Reynolds and Favre Averaging</td>
<td>7</td>
</tr>
<tr>
<td>2.2.2 Menter Two-Equation RANS Model</td>
<td>9</td>
</tr>
<tr>
<td>2.3 Chemical Kinetics</td>
<td>11</td>
</tr>
<tr>
<td>2.3.1 Hydrogen / Air Combustion</td>
<td>12</td>
</tr>
<tr>
<td>2.3.2 Silane - Hydrogen / Air Combustion</td>
<td>12</td>
</tr>
<tr>
<td>Chapter 3 Numerical Formulation</td>
<td>17</td>
</tr>
<tr>
<td>3.1 Discretization of Governing Equations</td>
<td>17</td>
</tr>
<tr>
<td>3.2 Flux Reconstruction</td>
<td>19</td>
</tr>
<tr>
<td>3.2.1 Low-Diffusion Flux-Splitting Scheme (LDFSS)</td>
<td>19</td>
</tr>
<tr>
<td>3.2.2 Viscous Fluxes</td>
<td>22</td>
</tr>
<tr>
<td>3.3 Higher-Order Extension</td>
<td>22</td>
</tr>
<tr>
<td>3.4 Time Integration</td>
<td>23</td>
</tr>
<tr>
<td>Chapter 4 Experimental and Computational Details</td>
<td>26</td>
</tr>
<tr>
<td>4.1 Experimental Overview</td>
<td>26</td>
</tr>
<tr>
<td>4.2 Model Geometry</td>
<td>27</td>
</tr>
<tr>
<td>4.3 Boundary Conditions</td>
<td>29</td>
</tr>
<tr>
<td>4.4 Initial Conditions</td>
<td>30</td>
</tr>
<tr>
<td>4.4.1 Steady Conditions</td>
<td>32</td>
</tr>
<tr>
<td>4.4.2 Transient Conditions</td>
<td>32</td>
</tr>
<tr>
<td>Chapter 5 Results and Discussion</td>
<td>33</td>
</tr>
<tr>
<td>5.1 Mach 7 Test Case</td>
<td>33</td>
</tr>
<tr>
<td>5.1.1 Tare Flow</td>
<td>33</td>
</tr>
<tr>
<td>5.1.2 Silane - Hydrogen / Air Mixing</td>
<td>36</td>
</tr>
<tr>
<td>5.1.3 Silane - Hydrogen / Air Combustion</td>
<td>38</td>
</tr>
<tr>
<td>5.2 Mach 10 Test Case</td>
<td>58</td>
</tr>
<tr>
<td>5.2.1 Tare Flow</td>
<td>58</td>
</tr>
<tr>
<td>5.2.2 Fuel / Air Mixing</td>
<td>60</td>
</tr>
<tr>
<td>5.2.3 Hydrogen / Air Combustion</td>
<td>62</td>
</tr>
<tr>
<td>5.2.4 Silane - Hydrogen / Air Combustion</td>
<td>64</td>
</tr>
</tbody>
</table>
LIST OF TABLES

Table 2.1 Modeling constants for Menter BSL and SST models ..................................... 11
Table 2.2 Third-body reactions and efficiencies for the Jachimowski and McLain silane - hydrogen / air reaction mechanism ............................................................. 14
Table 2.3 Gas phase to solid phase condensation of SiO$_2$ implemented in BTW reaction mechanism .................................................................................................................. 16
Table 4.1 Simulated Flight Conditions .................................................................................. 30
Table 4.2 Freestream Test Conditions ..................................................................................... 31
Table 4.3 Injector CFD Conditions ......................................................................................... 31
Table 5.1 Mach 7, $\phi = 1.1$ case: Comparison of combustor wall pressure readings using gas phase SiO$_2$ .............................................................................................................. 44
Table 5.2 Mach 7, $\phi = 1.1$ case: Comparison of combustor wall pressure readings using solid phase SiO$_2$ .............................................................................................................. 51
Table A.1 Gas phase to solid phase condensation of SiO$_2$ implemented in BTW reaction mechanism ................................................................................................................... 79
Table B.1 Ignition times for the BTW model and the modified Chinitz model at a pressure of 20,000 Pa ......................................................................................................................... 81
Table B.2 Reactions used to modify Chinitz reaction mechanism .............................................. 81


**LIST OF FIGURES**

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>Diagram of HYPULSE test facility</td>
<td>27</td>
</tr>
<tr>
<td>4.2</td>
<td>Experimental engine / pedestal assembly</td>
<td>28</td>
</tr>
<tr>
<td>4.3</td>
<td>Pressure (PCB) and heat flux gauge (HFG) locations, fuel plume imaging plane locations (green), TDLAS plane locations (pink). Test cabin window location (blue) is for Mach 5 tests. [28]</td>
<td>28</td>
</tr>
<tr>
<td>4.4</td>
<td>Engine centerplane mesh spacing</td>
<td>29</td>
</tr>
<tr>
<td>4.5</td>
<td>Engine boundary conditions</td>
<td>30</td>
</tr>
<tr>
<td>5.1</td>
<td>Mach 7 Isolator centerplane pressure and Mach number contours for SST turbulence model</td>
<td>34</td>
</tr>
<tr>
<td>5.2</td>
<td>Comparison of injector side centerplane wall pressure, Mach 7 tare case</td>
<td>34</td>
</tr>
<tr>
<td>5.3</td>
<td>Mach 7 Tare Schlieren image (top) versus BSL (middle) and SST (bottom) model density gradient magnitudes</td>
<td>35</td>
</tr>
<tr>
<td>5.4</td>
<td>Mixing centerplane nitrogen mass fraction results for equivalence ratios of 0.8 and 1.1</td>
<td>37</td>
</tr>
<tr>
<td>5.5</td>
<td>Mixing centerplane pressure results for equivalence ratios of 0.8 and 1.1</td>
<td>37</td>
</tr>
<tr>
<td>5.6</td>
<td>Mixing centerplane temperature results for equivalence ratios of 0.8 and 1.1</td>
<td>37</td>
</tr>
<tr>
<td>5.7</td>
<td>Centerplane temperatures for Jachimowski reaction mechanism at an equivalence ratio of 0.8</td>
<td>37</td>
</tr>
<tr>
<td>5.8</td>
<td>U-velocity centerplane results for 1/2 activation energy, 0.8 equivalence ratio case</td>
<td>38</td>
</tr>
<tr>
<td>5.9</td>
<td>Temperature centerplane results for 1/2 activation energy, 0.8 equivalence ratio case</td>
<td>39</td>
</tr>
<tr>
<td>5.10</td>
<td>Pressure centerplane results for 1/2 activation energy, 0.8 equivalence ratio case</td>
<td>39</td>
</tr>
<tr>
<td>5.11</td>
<td>Mach 7, $\phi = 1.1$ case: Temperature centerplane results for the Chinitz model (top), the modified Chinitz model (middle), and the BTW model (bottom) using gas phase SiO$_2$ modeling</td>
<td>40</td>
</tr>
<tr>
<td>5.12</td>
<td>Mach 7, $\phi = 1.1$ case: Pressure centerplane results for the Chinitz model (top), the modified Chinitz model (middle), and the BTW model (bottom) using gas phase SiO$_2$ modeling</td>
<td>41</td>
</tr>
<tr>
<td>5.13</td>
<td>Mach 7, $\phi = 1.1$ case: Comparison of injector-side centerplane wall pressure using gas phase SiO$_2$</td>
<td>42</td>
</tr>
<tr>
<td>5.14</td>
<td>Mach 7, $\phi = 1.1$ case: SiO$_2$ fuel plume imaging versus SiO$_2$ mass fractions using gas phase SiO$_2$ modeling (top: $x=12h$; bottom: $x=24h$)</td>
<td>43</td>
</tr>
<tr>
<td>5.15</td>
<td>Mach 7, $\phi = 1.1$ case: Schlieren image versus density gradient magnitudes using gas phase SiO$_2$ modeling</td>
<td>44</td>
</tr>
<tr>
<td>5.16</td>
<td>Mach 7, $\phi = 1.1$ case: Temperature centerplane results for the Chinitz model (top), the modified Chinitz model (middle), and the BTW model (bottom) using solid phase SiO$_2$ modeling</td>
<td>45</td>
</tr>
</tbody>
</table>
Figure 5.17 Mach 7, $\phi = 1.1$ case: Pressure centerplane results for the Chinitz model (top), the modified Chinitz model (middle), and the BTW (bottom) using solid phase SiO$_2$ modeling

Figure 5.18 Mach 7, $\phi = 1.1$ case: SiO$_2$ mass fractions for the BTW model with gas phase modeling and gas phase to solid phase condensation

Figure 5.19 Mach 7, $\phi = 1.1$ case: Heat release of several species for BTW model using gas phase modeling and gas to solid condensation

Figure 5.20 Mach 7, $\phi = 1.1$ case: Comparison of injector-side centerplane wall pressure using solid phase SiO$_2$

Figure 5.21 Mach 7, $\phi = 1.1$ case: SiO$_2$ fuel plume imaging using solid phase SiO$_2$ modeling (top: $x=12h$; bottom: $x=24h$)

Figure 5.22 Mach 7, $\phi = 1.1$ case: Schlieren image versus solid phase SiO$_2$ density gradient magnitudes

Figure 5.23 Series of centerplane temperature (left) and pressure (right) results for transient case using the modified Chinitz model and an equivalence ratio of 1.1

Figure 5.24 Mach 7, $\phi = 1.1$ transient case: Comparison of injector-side wall pressure for steady-state and transient analysis

Figure 5.25 Series of centerplane temperature (left) and pressure (right) results for transient case using Chinitz model with 1/2 activation energies and an equivalence ratio of 1.1

Figure 5.26 Inlet / isolator centerplane pressure (top) and Mach number (bottom) for Mach 10 tare case using Menter’s BSL model

Figure 5.27 Mach 10 tare case: centerplane, injector-side wall pressure comparison

Figure 5.28 Mach 10 silane - hydrogen / air mixing case: combustor centerplane temperature

Figure 5.29 Mach 10 silane - hydrogen / air mixing case: combustor centerplane pressure

Figure 5.30 Mach 10 silane - hydrogen / air mixing case: combustor centerplane N$_2$ mass fraction

Figure 5.31 Mach 10 mixing case: centerplane, injector-side wall pressure comparison

Figure 5.32 Mach 10 H$_2$ combustion case: combustor OH mass fraction

Figure 5.33 Mach 10 H$_2$ combustion case: combustor centerplane temperature

Figure 5.34 Mach 10 H$_2$ combustion case: centerplane, injector-side wall pressure comparison

Figure 5.35 Mach 10 SiH$_4$ combustion case: combustor OH mass fraction

Figure 5.36 Mach 10 SiH$_4$ combustion case: combustor temperature

Figure 5.37 Mach 10 SiH$_4$ combustion case: centerplane, injector-side wall pressure comparison

Figure 5.38 Mach 10 SiH$_4$ combustion case: combustor SiO$_2$ mass fraction

Figure B.1 Modified reaction rates
NOMENCLATURE

Roman Letters

\( a \)  
Speed of Sound

\( A \)  
Pre-Exponential Constant

\( A_{CV} \)  
Area of Cell Face, Pre-Exponential Constant

\( A_1 - A_5 \)  
Specific Heat Polynomial Constants

\( \tilde{A} - \tilde{G} \)  
Flux Jacobians

\( C_n \)  
Species Concentration

\( C_p \)  
Specific Heat at Constant Pressure

\( e \)  
Total Energy

\( E_1, E_2, E_3 \)  
Numerical Fluxes

\( E_a \)  
Activation Energy

\( g \)  
Gibbs Free Energy

\( h \)  
Enthalpy

\( k \)  
Turbulent Kinetic Energy

\( k_f, k_b \)  
Forward and Backward Reaction Rate Constants

\( L, D, U \)  
Lower, Diagonal, and Upper Matrix Components

\( M \)  
Third Body Species

\( M_W \)  
Molecular Weight

\( n \)  
Temperature Exponent

\( \bar{n} \)  
Normal Vector

\( P \)  
Pressure

\( Pr \)  
Prandtl Number

\( q \)  
Heat Flux Vector
\( R \)  Specific Gas Constant

\( R_u \)  Universal Gas Constant

\( \bar{R} \)  Unsteady Residual

\( \bar{\bar{R}} \)  Steady-State Residual

\( RR \)  Reaction Rate

\( S \)  Source Term Vector

\( Sc \)  Schmidt Number

\( S_{ij} \)  Strain Rate Tensor

\( t \)  Time

\( T \)  Temperature

\( TB \)  Third Body Efficiency

\( t_{ij} \)  Stress Tensor

\( u, v, w \)  Velocity

\( U \)  Normal Velocity

\( \bar{U} \)  Conservative Variable Vector

\( V \)  Species Diffusion Velocity

\( \bar{V} \)  Primitive Variable Vector

\( V_{CV} \)  Cell Volume

\( x, y, z \)  Spatial Location

\( X \)  Mole Fraction

\( Y \)  Mass Fraction

**Greek Letters**

\( \Delta \)  Difference Operator

\( \delta_{ij} \)  Kronecker Delta
<table>
<thead>
<tr>
<th>Symbol</th>
<th>English Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\dot{\omega}$</td>
<td>Species Production Rate</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>Turbulent Dissipation</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Viscosity</td>
</tr>
<tr>
<td>$\mu_T$</td>
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</tr>
<tr>
<td>$\nu$</td>
<td>Kinematic Viscosity</td>
</tr>
<tr>
<td>$\nu', \nu''$</td>
<td>Stoichiometric Coefficients</td>
</tr>
<tr>
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<td>Turbulent Kinematic Viscosity</td>
</tr>
<tr>
<td>$\omega$</td>
<td>Specific Dissipation Rate</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Equivalence Ratio</td>
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<tr>
<td>$\psi_{ij}$</td>
<td>Mixing Coefficient</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Pseudo Time</td>
</tr>
<tr>
<td>$\tau_{ij}$</td>
<td>Reynolds-Stress Tensor</td>
</tr>
</tbody>
</table>

**Superscripts**

<table>
<thead>
<tr>
<th>Superscript</th>
<th>English Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c$</td>
<td>Convective Component</td>
</tr>
<tr>
<td>$k$</td>
<td>Sub-Iteration Level</td>
</tr>
<tr>
<td>$n$</td>
<td>Time Level</td>
</tr>
<tr>
<td>$p$</td>
<td>Pressure Component</td>
</tr>
</tbody>
</table>

**Subscripts**

<table>
<thead>
<tr>
<th>Subscript</th>
<th>English Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1/2$</td>
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</tr>
<tr>
<td>$i, j, k$</td>
<td>Cell Indices, Spatial Component</td>
</tr>
<tr>
<td>$i, v$</td>
<td>Inviscid or Viscous Flux</td>
</tr>
<tr>
<td>$L, R$</td>
<td>Left and Right Cells</td>
</tr>
<tr>
<td>$n$</td>
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</tr>
</tbody>
</table>
$T$ Turbulent

**Accents**

\[ \bar{\text{\text{\text{-}}} \text{Time-Averaged Term}} \]

\[ \vec{\text{\text{\text{-}}} \text{Vector}} \]

\[ \tilde{\text{\text{\text{-}}} \text{Mass-Averaged Term}} \]

\[ ' \text{Time-Fluctuating Term} \]

\[ " \text{Mass-Fluctuating Term} \]

**Abbreviations**

- **BSL** Baseline Model
- **BTW** Britten, Tong, and Westbrook Model
- **DNS** Direct Numerical Simulation
- **ILU** Incomplete Lower / Upper
- **LDFSS** Low-Diffusion Flux-Splitting Scheme
- **LES** Large Eddy Simulation
- **NR** Number of Reactions
- **NS** Number of Species
- **RANS** Reynolds-Averaged Navier-Stokes
- **SST** Shear-Stress Transport Model
- **TVD** Total Variation Diminishing
The development of hypersonic airbreathing propulsion systems has long been a goal of the aerospace community. The principle method of hypersonic airbreathing propulsion, the scramjet engine, was first examined in the 1950’s and 60’s with great interest [14]. This was fueled by the scramjet’s promise of cheaper, reusable space vehicles and high-speed, long range reconnaissance and strike, and was buoyed by the space race and Cold War atmosphere. However, difficulties in generating net thrust, maintaining combustion in a supersonic flow, engine wall cooling, and the fact that the engine must first be brought up to supersonic speeds using other propulsion methods kept the idea in the research stages. This was compounded by the difficulty and high costs associated in ground testing articles at hypersonic speeds. Traditional wind tunnels cannot generate the high energy flow needed, so more advanced testing methods must be employed. These include combustion- or arc-heated tunnels, where the flow is heated to the correct enthalpies by either the combustion of fuel or the use of an electric current, or shock tunnels where shock waves are used to heat the test air. Each of these methods has drawbacks including the vitiation of the test air with combustion products or extremely short test durations, and each can simulate only portions of the hypersonic flight regime.

Due to these challenges, it was not until the 1990’s that test flights started to take place. Even then, early flight programs were more focused on validating ground test data than producing a usable scramjet engine. Some of the most notable scramjet programs include the Russian Central Institute of Aviation Motors CIAM Hypersonic Flying Laboratory program which made several flights from 1991 to 1998 correlating flight data to ground test data and demonstrating supersonic combustion [26]. The University of Queensland’s HyShot program has likewise correlated flight and ground test data and demonstrated supersonic combustion for several different engine configurations across a series of successful tests from 2002 to 2007 [13, 24]. NASA tested its scramjet powered X-43A experimental aircraft in 2004, successfully demonstrating net
thrust generation and aerodynamic control at hypersonic speeds [20]. More recently, the U.S. Air Force tested its scramjet powered X-51 experimental aircraft from 2010 to 2012 achieving a burn time of 140 seconds, the longest burn time yet achieved in a scramjet flight test.

With the increasing power of computers and the increasing accuracy and sophistication of the algorithms employed by them, the field of computational fluid dynamics (CFD) is coming to play an increasingly important role in hypervelocity research and was instrumental in the development of the X-43A and X-51. Its advantages over ground testing include much faster turn-around times allowing for more rapid testing of a range of geometries and flight conditions, cheaper simulations, and the ability to extract any desired variable at any location in the flow. However, the accurate simulation of hypersonic flow has proven to be difficult due to the many complexities involved, all of which must be modeled with great precision. These include turbulence, chemical interactions and combustion, compressibility, diffusion-limited mixing, and severe wall heat transfer. There also exist only a limited number of data sets at hypersonic conditions to allow for model verification, limiting knowledge of the accuracy of results.

Previous validation work has been carried out by Star [30], where the effects of varying the turbulent Prandtl and Schmidt numbers, turbulence inflow characteristics, and thermal wall boundary conditions were examined in detail in a scramjet-like design and compared to experimental data from Odam [23]. Computational work by Engman [8] has examined combustion in a scramjet combustor making comparisons to experimental data from DLR’s Institute of Propulsion Technology. Fulton et al. [11] have numerically examined a scramjet combustor of very similar design to the one used in this work operating in its dual-mode regime using RANS and LES / RANS methods and compared to experimental data from the University of Virginia’s Supersonic Combustion Facility.

The work presented herein focuses on three-dimensional computational modeling of a dual-mode scramjet engine operating in the hypervelocity regime (greater than Mach 7 flight enthalpy). Comparisons are made to available data from concurrent experimental tests being done at NASA’s HYPULSE facility for both tare (no injection) and combust ing cases. This will serve to verify model performance at the hypersonic test conditions chosen as well as identify possible areas of improvement. The majority of the work shown are steady results giving a single time-averaged solution; however, the effects of the start of the experimental facility were also modeled using transient, time-accurate simulations. North Carolina State University’s in-house REACTMB program has been utilized as the computational flow solver. This program has been previously used to model a wide range of reacting and non-reacting flows using RANS and LES/RANS turbulence modeling including simulations of scramjet engines [11, 25, 27, 34]. Turbulence has been modeled using both the baseline (BSL) and the shear-stress transport (SST) variation of Menter’s $k – \omega$ two-equation RANS model and the combustion of two different fuels was modeled using a finite-rate approach based on the law of mass action. The first fuel
examined was gaseous hydrogen and the second was a gaseous blend of 20% silane and 80% hydrogen by volume (80% silane and 20% hydrogen by mass).

Silane is a chemical traditionally associated with the semiconductor industry where it used in the manufacture of silicon wafers; however, the aerospace community has also used it as a fuel additive, or as a fuel itself, to aid in igniting and maintaining combustion of hydrogen fuels in scramjet engines when low combustor temperatures and pressures make hydrogen combustion difficult or uncertain. It has successfully been used both in ground testing as well as in flight tests of the X-43A [3, 15], and has been numerically examined by Biasca [4] in computational modeling of scramjet combustion. It is a pyrophoric substance which will very rapidly combust when exposed to air, even at low temperatures and pressures. This process generates heat and free radicals, both of which will drive the combustion of hydrogen to occur faster than it would have otherwise. While direct experimental comparisons between silane and hydrogen ignition times at the same test conditions could not be found, every numerical reaction mechanism examined predicted that appreciably shorter ignition times could be achieved with the addition of silane to hydrogen. This difference was most pronounced for greater proportions of silane and lower initial temperatures and pressures.

This thesis is broken into five other chapters. Chapter 2 covers the governing equations used to simulate fluid flow, RANS turbulence modeling, and chemical reaction modeling. Chapter 3 deals with the discretization of the governing equations into numerical systems solvable by computers and the advancement of this system in time. Chapter 4 gives details of the experimental tests and numerical simulation of these tests. Chapter 5 covers the computational results achieved with comparisons to experimental results. Lastly, Chapter 6 gives summaries and conclusions.
The equations governing the dynamics of a reacting fluid flow are covered in this chapter. Among these are the Navier-Stokes equations, closure equations for the expanded Reynolds-averaged Navier-Stokes equations, and the Law of Mass Action which forms the basis of the finite-rate chemical kinetic models used.

### 2.1 Navier-Stokes Equations

The Navier-Stokes equations are the fundamental equations of fluid flow. These are a set of coupled differential equations resulting from the laws of conservation of mass, momentum, and energy being applied over a continuum. They are given in differential form using tensor notation below.

- The continuity (mass conservation) equation:
  \[
  \frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_j} (\rho u_j) = 0 \tag{2.1}
  \]

- The momentum equations (one for each of the three spatial dimensions):
  \[
  \frac{\partial}{\partial t} (\rho u_i) + \frac{\partial}{\partial x_j} (\rho u_i u_j) = -\frac{\partial P}{\partial x_i} + \frac{\partial t_{ij}}{\partial x_j} \tag{2.2}
  \]

- The energy equation:
  \[
  \frac{\partial}{\partial t} \left[ \rho \left( e + \frac{1}{2} u_i u_j \right) \right] + \frac{\partial}{\partial x_j} \left[ \rho u_j \left( h + \frac{1}{2} u_i u_j \right) \right] = \frac{\partial}{\partial x_j} (u_i t_{ij}) + \frac{\partial q_j}{\partial x_j} \tag{2.3}
  \]
This only considers the total mixture of the fluid. In order to account for multiple species, the species mass conservation equations, one for each species, are used in place of the continuity equation:

$$\frac{\partial \rho_n}{\partial t} + \frac{\partial}{\partial x_j} (\rho_n u_j + \rho_n V_{j,n}) = \dot{\omega}_n$$  \hspace{1cm} (2.4)$$

Here $\rho_n$ is the mass density of a species $n$, $V_{j,n}$ is the species diffusion velocity, and $\dot{\omega}_n$ is the species production rate. The ideal gas law is used as the equation of state, relating the thermodynamic state variables:

$$P = \rho RT$$  \hspace{1cm} (2.5)$$

The mixture gas constant, $R$, is the average of the species gas constants:

$$R = R_u \sum_{n=1}^{NS} \frac{Y_n}{M_{W,n}}$$  \hspace{1cm} (2.6)$$

where $R_u$ is the universal gas constant, $Y_n$ is the species mass fraction, $M_{W,n}$ is the species molecular weight, and $NS$ is the number of species. The total mixture density is the sum of the species mass densities:

$$\rho = \sum_{n=1}^{NS} \rho_n$$  \hspace{1cm} (2.7)$$

and the species mass fraction is the ratio of the species mass density to the total mixture density:

$$Y_n = \frac{\rho_n}{\rho}$$  \hspace{1cm} (2.8)$$

The total energy, $e$, and total enthalpy, $h$, are functions of temperature and are found using the following relations:

$$e = h - \frac{P}{\rho}$$  \hspace{1cm} (2.9)$$

$$h = \sum_{n=1}^{NS} Y_n h_n$$  \hspace{1cm} (2.10)$$

$$h_n = h_{n,0} + \int_{T_0}^{T} C_{p,n} dT$$  \hspace{1cm} (2.11)$$

$$C_{p,n} = R_u \left( A_{1,n} + A_{2,n} T + A_{3,n} T^2 + A_{4,n} T^3 + A_{5,n} T^4 \right)$$  \hspace{1cm} (2.12)$$
Here $T^o$ and $h_{f,n}^o$ are reference temperatures and enthalpies, $Cp_n$ is the species specific heat, and $A_{1,n}, A_{2,n}, A_{3,n}, A_{4,n},$ and $A_{5,n}$ are constants valid over a given temperature range for each species.

By assuming the mixture is a Newtonian fluid, the viscous stress tensor can be written as:

$$t_{ij} = 2\mu S_{ij} - \frac{2}{3} \mu \frac{\partial u_k}{\partial x_k} \delta_{ij}$$

where $\mu$ is the dynamic viscosity and $\delta_{ij}$ is the Kronecker delta such that $\delta_{ij} = \begin{cases} 0, & \text{if } i \neq j \\ 1, & \text{if } i = j \end{cases}$.

$S_{ij}$ is the rate of strain tensor, given as:

$$S_{ij} = \frac{1}{2} \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right)$$

Molecular viscosity is a function of temperature for each species and is calculated using Sutherland’s law:

$$\mu_n = \mu_{ref,n} \left( \frac{T}{T_{ref,n}} \right)^{3/2} \frac{T_{ref,n} + S_n}{T + S_n}$$

where $\mu_{ref,n}$, $T_{ref,n}$, and $S_n$ are constants for each species. The mixture viscosity is found using Wilke’s law:

$$\mu = \sum_{n=1}^{NS} X_n \mu_n \left( \sum_{n=1}^{NS} X_n \psi_{ij} \right)^{-1}$$

Here $X_n$ is the species mole fraction, $X_n = Y_n M_{W,n} / M_W$, where $M_W$ is the mixture molecular weight and $\psi_{ij}$ is the mixing coefficient:

$$\psi_{ij} = \left( 1 + \sqrt{\frac{\mu_i}{\mu_j}} \left( \frac{M_{W,i}}{M_{W,j}} \right)^{1/2} \frac{1}{8} \left( 1 + \frac{M_{W,i}}{M_{W,j}} \right) \right)^2$$

The heat flux is given as:

$$q_j = \mu \sum_{n=1}^{NS} Y_n C_{p,n} \frac{\partial T}{\partial x_j}$$

where $Pr$ is the the Prandtl number, a constant of 0.72 in this study. Species diffusion is a function of species mass fraction gradients:

$$V_{j,n} = -\frac{\mu Y_n}{Sc} \frac{\partial Y_n}{\partial x_j}$$
where $Sc$ is the Schmidt number, a constant of 0.50 in this study.

### 2.2 Turbulence modeling

The above equations can be used to directly solve for an exact representation of any turbulence. However, this would require an extremely high resolution mesh in order to capture the smallest scales of turbulence. As this is not feasible for most problems due to the high computational resources required, turbulence is often modeled. This allows coarser meshes, greatly reducing computational costs and run times. By only modeling the smallest scales of turbulence and resolving the larger scales, a Large Eddy Simulation (LES) solution is produced, while modeling all scales of turbulence is done using Reynolds-Averaged Navier-Stokes (RANS) methods. Resolving all scales of turbulence is called Direct Numerical Simulation (DNS). For this work, only RANS modeling has been employed.

#### 2.2.1 Reynolds and Favre Averaging

As the name suggests, Reynolds-Averaged Navier-Stokes methods are based on Reynolds averaging. This is accomplished by splitting a flow variable, $q$, into a Reynolds-averaged mean term, $\bar{q}$, and a fluctuating term, $q'$:

$$ q = \bar{q} + q' $$

$$ \bar{q} = \frac{1}{t_f} \int_{t_f} q(t) \, dt $$

where $t_f$ is a finite time. While this accounts for time-dependent fluctuations, compressible fluids also experience density-dependent fluctuations. This is accounted for by using Favre averaging. Similar to Reynolds averaging, the flow variable is split into a Favre-averaged mean term, $\tilde{q}$, and a Favre fluctuating term, $q''$:

$$ q = \tilde{q} + q'' $$

$$ \tilde{q} = \frac{\int_{t_f} \rho(t) q(t) \, dt}{\int_{t_f} \rho(t) \, dt} = \frac{\bar{pq}}{\bar{p}} $$

One important result of these splittings is that $\bar{q}' = 0$ and $\bar{pq}'' = 0$, though $\tilde{q}'' \neq 0$ and $\tilde{q}' \tilde{q}_j' \neq 0$ in general.

The compressible RANS formulation is obtained by decomposing $\rho$, $P$, $t_{ij}$, $q_i$, and $\dot{\omega}_n$ using
Reynolds averaging and \( u_i, V_{i,n}, Y_n, e, h, \) and \( T \) using Favre averaging:

Reynolds-averaged:

\[
\begin{align*}
\rho &= \bar{\rho} + \rho' \\
P &= \bar{P} + P' \\
t_{ij} &= \bar{t}_{ij} + t'_{ij} \\
q_i &= \bar{q}_i + q'_i \\
\dot{\omega}_n &= \bar{\dot{\omega}}_n + \dot{\omega}'_n
\end{align*}
\] (2.24)

Favre-averaged:

\[
\begin{align*}
u_i &= \bar{\tilde{u}}_i + \tilde{u}_i'' \\
V_{i,n} &= \bar{\tilde{V}}_{i,n} + \tilde{V}_{i,n}'' \\
Y_n &= \bar{\tilde{Y}}_n + \tilde{Y}_n'' \\
e &= \bar{\tilde{e}} + e'' \\
h &= \bar{\tilde{h}} + h'' \\
T &= \bar{\tilde{T}} + T''
\end{align*}
\] (2.25)

By plugging in the decomposed flow variables into the governing equations, performing Favre averaging, and rearranging, the Favre-averaged Navier-Stokes equations (still referred to as RANS) are obtained:

\[
\begin{align*}
\frac{\partial \rho_n}{\partial t} + \frac{\partial}{\partial x_j} (\rho_n \bar{u}_j + \bar{\rho}_n \bar{V}_{j,n}) &= \bar{\omega}_n \\
\frac{\partial \bar{p}}{\partial t} + \frac{\partial}{\partial x_j} (\bar{p} \bar{u}_j) &= 0 \\
\frac{\partial}{\partial t} (\bar{p} \bar{u}_i) + \frac{\partial}{\partial x_j} (\bar{p} \bar{u}_i \bar{u}_j) &= -\frac{\partial P}{\partial x_i} + \frac{\partial}{\partial x_j} \left[ \bar{t}_{ij} - \rho \bar{u}_j'' \bar{u}_i'' \right] \\
\frac{\partial}{\partial t} \left( \bar{p} \left( \bar{e} + \frac{1}{2} \bar{u}_i \bar{u}_i \right) \right) + \frac{\partial}{\partial x_j} \left[ \bar{p} \bar{u}_j \left( \bar{h} + \frac{1}{2} \bar{u}_i \bar{u}_i \right) + \bar{u}_j \frac{\rho \bar{u}_j'' \bar{u}_i''}{2} \right] &= \frac{\partial}{\partial x_j} \left( \bar{t}_{ij} - \rho \bar{h}'' \bar{u}_j'' + t_{ij} \bar{u}_i'' + \frac{\rho \bar{u}_j'' \bar{u}_i''}{2} \right) \\
\bar{P} &= \bar{p} R \bar{T}
\end{align*}
\] (2.26-2.30)

It is immediately obvious several more unknowns have been generated in the momentum and energy equations. These must be solved for, but generating new transport equations would only result in the creation of even more unknowns. Therefore, these new terms must be modeled in some fashion. This is done by relating these terms to their laminar counterparts through the use of dimensional analysis and general understanding of the physics involved. For instance the \( -\rho \bar{u}_j'' \bar{u}_i'' \) term in the momentum and energy equation has the dimensions of a stress tensor and is termed the Favre-averaged Reynolds-stress tensor:
\[ \rho \tau_{ij} \equiv -\rho \bar{u}''_i u''_j \] (2.31)

Using the Boussinesq assumption, this can be modeled similarly to the laminar viscous stress tensor:

\[ \rho \tau_{ij} = 2 \mu_T \left( S_{ij} - \frac{1}{3} \frac{\partial \bar{u}_k}{\partial x_k} \delta_{ij} \right) - \frac{2}{3} \rho k \delta_{ij} \] (2.32)

where \( \mu_T \) is the turbulent eddy viscosity. The \( \frac{\rho \bar{u}''_i u''_i}{2} \) term is the kinetic energy per unit volume of the turbulent fluctuations:

\[ \rho k \equiv \frac{\rho \bar{u}''_i u''_i}{2} \] (2.33)

In the energy equation, the \( \rho \bar{h}'' u''_j \) term is analogous to molecular heat transport and is known as the turbulent heat flux:

\[ q_{Tj} \equiv \rho \bar{h}'' u''_j \] (2.34)

This also is modeled similarly to its laminar counterpart:

\[ q_{Tj} = \frac{\mu_T C_p}{P_T} \frac{\partial T}{\partial x_j} \] (2.35)

where \( C_p \) is the mixture specific heat and \( P_T \) is the turbulent Prandtl number, a constant of 0.90 in this study.

### 2.2.2 Menter Two-Equation RANS Model

Several different turbulence closure models exist to solve for the turbulent eddy viscosity, \( \mu_T \), in the Reynolds stress tensor given above. Two models by Menter [22] were examined in this study: the Menter Baseline model (BSL) and the Menter Shear-Stress Transport model (SST). These models use Wilcox’s \( k-\omega \) model [33] near the wall and the \( k-\epsilon \) model in the outer part of the boundary layer, combining the best parts of the two modeling approaches. This is accomplished by transforming the \( k-\epsilon \) model into a \( k-\omega \) form, multiplying the two \( k-\omega \) equations by a blending function \( F_1 \) and the transformed \( k-\epsilon \) equations by \( (1 - F_1) \), and then adding the two sets together. This results in:

\[
\frac{\partial \rho k}{\partial t} + \frac{\partial \rho k u_j}{\partial x_j} = \tau_{ij} \frac{\partial u_i}{\partial x_j} - \beta^* \rho \omega k + \frac{\partial}{\partial x_j} \left[ \left( \mu + \sigma_k \mu_T \right) \frac{\partial k}{\partial x_j} \right]
\] (2.36)
\[
\frac{\partial \rho \omega}{\partial t} + \frac{\partial \rho \omega u_j}{\partial x_j} = \frac{\gamma}{\nu_T} \tau_{ij} \frac{\partial u_i}{\partial x_j} - \beta \rho \omega^2 + \frac{\partial}{\partial x_j} \left[ (\mu + \sigma_\omega \mu_T) \frac{\partial \omega}{\partial x_j} \right] \\
+ 2 \left( 1 - F_1 \right) \rho \sigma_\omega \frac{1}{\omega} \frac{\partial k}{\partial x_j} \frac{\partial \omega}{\partial x_j} \quad (2.37)
\]

Here \( \tau_{ij} \) is found with:

\[
\tau_{ij} = \mu_T \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \frac{2}{3} \frac{\partial u_k}{\partial x_k} \delta_{ij} \right) - \frac{2}{3} \rho k \delta_{ij} \quad (2.38)
\]

The blending function is found by:

\[
F_1 = \tanh \left( \arg_1 \right) \quad (2.39)
\]

\[
\arg_1 = \min \left[ \max \left( \frac{\sqrt{k}}{0.09 \omega y}, \frac{500 \nu}{y^2 \omega} \right), \frac{4 \rho \sigma_\omega k}{C_{D_{k\omega}} y^2} \right] \quad (2.40)
\]

where \( y \) is the distance to the next surface and \( C_{D_{k\omega}} \) is the positive portion of the cross-diffusion term of Eq. 2.37:

\[
C_{D_{k\omega}} = \max \left( 2 \rho \sigma_\omega \frac{1}{\omega} \frac{\partial k}{\partial x_j} \frac{\partial \omega}{\partial x_j}; 10^{-20} \right) \quad (2.41)
\]

The differences between the BSL model and the SST model come into play through the definition of the eddy viscosity and the values for the modeling constants, found in Table 2.1. This is because the SST model satisfies Bradshaw’s assumption that the shear stress in a boundary layer is proportional to the turbulent kinetic energy. This leads to a reduction in the calculated shear stress over the BSL model in regions where the production of \( k \) is larger than its dissipation and usually results in better behavior in separation regions caused by adverse pressure gradients often generated by shock wave boundary layer interactions. The eddy viscosity is in the BSL model is found by:

\[
\mu_T = \rho \nu_T = \rho \frac{k}{\omega} \quad (2.42)
\]

while it is defined as:

\[
\mu_T = \rho \nu_T = \rho \frac{0.31 k \max (0.31 \omega, \Omega F_2)}{\max (0.31 \omega, \Omega F_2)} \quad (2.43)
\]

in the SST model. \( F_2 \) is another blending function given as:
Table 2.1: Modeling constants for Menter BSL and SST models

<table>
<thead>
<tr>
<th>Model Constant</th>
<th>(inner) BSL $k - \omega$</th>
<th>(outer) $k - \epsilon$</th>
<th>(inner) SST $k - \omega$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_k$</td>
<td>0.5</td>
<td>1.0</td>
<td>0.81</td>
</tr>
<tr>
<td>$\sigma_\omega$</td>
<td>0.5</td>
<td>0.856</td>
<td>0.5</td>
</tr>
<tr>
<td>$\beta$</td>
<td>0.0750</td>
<td>0.0828</td>
<td>0.0750</td>
</tr>
<tr>
<td>$\beta^*$</td>
<td>0.09</td>
<td>0.09</td>
<td>0.09</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>0.41</td>
<td>0.41</td>
<td>0.41</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>0.5532</td>
<td>0.4404</td>
<td>0.5532</td>
</tr>
</tbody>
</table>

\[ F_2 = \tanh \left( \arg_2^2 \right) \tag{2.44} \]

\[ \arg_2 = \max \left( \frac{2 \sqrt{k}}{0.09 \omega_y} \frac{500 \nu}{y^2 \omega} \right) \tag{2.45} \]

### 2.3 Chemical Kinetics

The Law of Mass Action [19] forms the basis of the finite rate chemical kinetic scheme used. This states that the rate of a given reaction is proportional to the product of the concentrations of the reactant species with each concentration being raised to a power equal to its corresponding stoichiometric coefficient. This reaction rate is then incorporated into the species conservation equations as the production term, $\dot{\omega}_n$. For an exchange / recombination reaction of the form $A + B \leftrightarrow C + D$, the Law of Mass Action gives:

\[ RR_i = k_{f,i} \prod_{n=1}^{NS} C_n^{v'_n,i} - k_{b,i} \prod_{n=1}^{NS} C_n^{v''_n,i} \tag{2.46} \]

and for a reaction requiring a third body to initiate, $A + B + M \leftrightarrow C + D + M$:

\[ RR_i = \left( k_{f,i} \prod_{n=1}^{NS} C_n^{v'_n,i} - k_{b,i} \prod_{n=1}^{NS} C_n^{v''_n,i} \right) \left( \sum_{n=1}^{NS} C_n TB_{n,i} \right) \tag{2.47} \]

Here the subscript $i$ refers to a reaction $i$ and the subscript $n$ refers to a species $n$, $C_n$ is the species molar concentration, the species density divided by its molecular weight, $C_n = \frac{\rho_n}{M_{W,n}}$, $v'_n,i$ and $v''_n,i$ are the stoichiometric coefficients of the reactants and products, respectively, and $TB_{n,i}$ is the third body efficiency. The $k_{f,i}$ and $k_{b,i}$ terms are the forward and backward specific
reaction-rate constants. The forward reaction rate is a function solely of temperature and is given by the Arrhenius rate law:

\[ k_{f,i} = A_i T^{n_i} \exp \left( \frac{E_{a,i}}{R_u T} \right) \]  (2.48)

where \( A_i \) is the pre-exponential constant, \( n_i \) is the temperature exponent, and \( E_{a,i} \) is the activation energy of the reaction. These are given by the reaction models discussed later and can be found in Appendix A. The backward rate constant is found using the forward rate coefficient and the equilibrium constant:

\[ k_{b,i} = \frac{k_{f,i}}{k_{eq,i} |P|} \left( \frac{P_\infty}{R_u T} \right)^{m_i' - m_i''} \]  (2.49)

\[ k_{eq,i} |P| = \exp \left( -\frac{\Delta g_i}{R_u T} \right) \]  (2.50)

\[ \Delta g_i = \sum_{n=1}^{NS} \left( v_{n,i}'' - v_{n,i}' \right) g_n \]  (2.51)

where \( P_\infty \) is a pressure of 1 atm, \( g_n \) is the Gibbs free energy for species \( n \). The species production rate is then found to be:

\[ \dot{\omega}_n = \sum_{i=1}^{NR} \left( v_{n,i}'' - v_{n,i}' \right) RR_i \]  (2.52)

It should be noted that the effects of any turbulent fluctuations have been ignored, \( k_f(T) = k_f(\tilde{T}) \).

2.3.1 Hydrogen / Air Combustion

The combustion of hydrogen (H\(_2\)) in air is modeled using a 19 reaction, 9 species model by Jachimowski [16]. It uses six third-body dissociation / recombination reactions with third-body efficiencies of one for every species except for H\(_2\) and H\(_2\)O for which it is 2.5 and 16.0, respectively. Reactions and Arrhenius coefficients are given in Appendix A. Note, all reactions involving nitrogen have been neglected in this study.

2.3.2 Silane - Hydrogen / Air Combustion

The combustion of the blend of 20% silane (SiH\(_4\)) and 80% hydrogen in air was examined using several different chemical reaction mechanisms. The first two are a 39 reaction, 16 species model by Jachimowski and McLain [17] and a 45 reaction, 15-species model by Chinitz [6]. These
models were developed using analogues to the relatively well understood combustion of methane (CH$_4$) due to the similarity in chemical structure between silane and methane with activation energies and thermodynamic data scaled appropriately. Both models were also refined to match experimental data from shock tube tests performed by McLain, et. al, [21] leading to both models having similar ranges of initial conditions, 800 K to 1200 K and 1.0 atm to 1.35 atm for the Jachimowski and McLain model and 800 K to 1250 K and 0.5 atm to 1.35 atm for the Chinitz model. However, the Chinitz model predicts significantly shorter ignition times than the Jachimowski and McLain model, especially at lower temperatures and pressures, and results in significantly different combustion physics overall, possibly due to the differences in their modeling of the direct reaction of SiH$_4$ and O$_2$. The Jachimowski and McLain model treats it as a hydrogen abstraction:

$$\text{SiH}_4 + \text{O}_2 \leftrightarrow \text{SiH}_3 + \text{HO}_2$$

while the Chinitz model suggests the formation of water:

$$\text{SiH}_4 + \text{O}_2 \leftrightarrow \text{SiH}_2\text{O} + \text{H}_2\text{O}$$

The Jachimowski and McLain model has six third-body reactions with the reactions and third-body efficiencies given in Table 2.2. The Chinitz model has ten third-body reactions with all species having a third-body efficiency of one for each reaction.

While both of these mechanisms are able to replicate the shock tube data of McLain et al. [21] accurately, they fail to reproduce the pyrophoric nature of silane at lower temperatures and pressures. Unfortunately, it is at these conditions where silane is most needed in order to ignite or maintain the combustion of the more slowly reacting hydrogen. It is also at these conditions where much of the work described herein takes place. Hartman et al. have suggested a completely separate reaction pathway takes place at low temperatures and pressures compared to the high temperature and pressure pathway that occurs in the shock tube tests [12]. They suspect this pathway is driven by vibrationally hot silylperoxy radical, xSiH$_3$O$_2$, and go as far to outline a reaction mechanism as well as provide upper pressure explosion limits and combustion product yields for a range of equivalence ratios. This work was then used by Britten, Tong, and Westbrook (BTW) to develop a full reaction mechanism consisting of 70 reactions and 25 species [5]. This mechanism achieves very good agreement with both the shock tunnel tests of McLain et al. [21] and the product yields of Hartman et al. [12] and predicts long ignition time delays (0.1 sec to 1 sec) for the explosion limit data of Hartman et al. [12] using an adiabatic, constant volume reactor code. They expect that if heat losses of the reactor vessel were taken into account, their model would suppress ignition entirely at the explosion limits.

As computational costs increase significantly with the number of variables that must be solved, implementing the 25 species of the BTW model requires roughly double the number of
Table 2.2: Third-body reactions and efficiencies for the Jachimowski and McLain silane-hydrogen / air reaction mechanism

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Coefficient</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>(H + OH + M \leftrightarrow H_2O + M)</td>
<td>(6.36)</td>
<td>(1.00)</td>
</tr>
<tr>
<td>(M = H_2O)</td>
<td>(M = H_2)</td>
<td>(4.0e-6)</td>
</tr>
<tr>
<td>(M = H_2O)</td>
<td>(M = All) others</td>
<td>(6.0e-6)</td>
</tr>
<tr>
<td>(H + O_2 + M \leftrightarrow HO_2 + M)</td>
<td>(2.19)</td>
<td>(1.00)</td>
</tr>
<tr>
<td>(M = H_2)</td>
<td>(M = H_2O)</td>
<td>(13.75)</td>
</tr>
<tr>
<td>(M = All) others</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(H_2O_2 + M \leftrightarrow OH + OH + M)</td>
<td>(1.00)</td>
<td></td>
</tr>
<tr>
<td>(M = All)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(HSiO + M \leftrightarrow H + SiO + M)</td>
<td>(1.00)</td>
<td></td>
</tr>
<tr>
<td>(M = All)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(SiO + O + M \leftrightarrow SiO_2 + M)</td>
<td>(1.00)</td>
<td></td>
</tr>
<tr>
<td>(M = All)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
processors over the 16 species Jachimowski and McLain model or the 15 species Chinitz model. It was therefore decided to first attempt to modify the Chinitz model so that it would match ignition times of the BTW model at low temperatures and then revert back to the original Chinitz model once temperatures have risen above 800 K. While this would not produce the most accurate solution, it was hoped that this would give a good estimation of the results produced by the much more computationally expensive model. This is described in greater detail in Appendix B.

The phase of the saturated combustion product SiO$_2$ is also examined in detail. SiO$_2$, most commonly known as sand, is known to be a solid at flame temperatures. Since all silane reactions take place in the gas phase, different models have handled SiO$_2$ in different ways. The Jachimowski and McLain and the Chinitz models both ignore the solid phase completely and just treat it as a gas. The BTW model, among others, assumes the nucleation occurs fast enough that SiO$_2$ can be considered to be formed in its solid phase and that the solid particles formed are small enough that they have no effect on the gas phase fluid dynamics [1, 5, 18]. This allows for the thermodynamic data of gas phase SiO$_2$ to be simply substituted with its solid phase thermodynamic data while not needing to model any solid particle effects on the flow, potentially resulting in a greater amount of heat release due to solid phase SiO$_2$ having a much more negative enthalpy of formation than gas phase SiO$_2$, -903.7 kJ/mole vs. -318.0 kJ/mole [12]. For comparison, the enthalpy of formation of water vapor is -241.8 kJ/mole. The Chinitz and modified Chinitz models were examined using both 100% gas phase SiO$_2$ and 100% solid phase SiO$_2$ to give lower and upper bounds as to what could be reasonably expected. This was done without any modification to their reactions, allowing SiO$_2$ to form and be consumed as if it were a gas in both cases.

The BTW model was then later implemented using both 100% gas phase SiO$_2$ and with the addition of a finite rate reaction condensing SiO$_2$ from its gas phase to solid phase, shown in Table 2.3. As this is the only reaction involving SiO$_2$(s), once it condenses into its solid phase, it can no longer be involved in any other reactions that might consume it. This model has ten third-body reactions with every species having a third-body efficiency of one for each reaction. It also specifies Arrhenius coefficients to be used to calculated the backward rate constant instead of allowing it to be calculated using an equilibrium rate. This is done similarly to the forward rate constant, Eq. 2.53, with the subscript ‘b’ on the Arrhenius coefficients indicating it is for the backward rate.

$$k_{b,i} = A_{v,b} T^{\gamma_{i,b}} \exp \left( \frac{-E_{a,i,b}}{R T} \right)$$  (2.53)
Table 2.3: Gas phase to solid phase condensation of SiO$_2$ implemented in BTW reaction mechanism in cal, cm$^3$, mol, s units

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$A_f$</th>
<th>$n_f$</th>
<th>$E_{a,f}$</th>
<th>$A_b$</th>
<th>$n_b$</th>
<th>$E_{a,b}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$(g) ⇔ SiO$_2$(s)</td>
<td>1.00 * 10$^8$</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>
Chapter 3 covers how the governing equations covered in Chapter 2 are discretized into a finite volume formulation and solved using NCSU’s REACTMB flow solver. The Low Diffusion Flux Splitting Scheme (LDFSS) is used to solve the inviscid fluxes while viscous fluxes are solved directly. Extension to higher order is accomplished using a Total Variation Diminishing scheme (TVD) allowing for greater spatial accuracy. The system of equations formed is solved using an incomplete Lower / Upper (ILU) decomposition method and integrated in time using an implicit Euler scheme. These are all described in greater detail in the subsequent sections.

3.1 Discretization of Governing Equations

A finite volume method is used to discretize the governing equations, turning them into a form solvable by computers. This is done by dividing the system into discrete volumes called mesh cells and representing these volumes using information stored at the cell center. By using the integral form of the Navier-Stokes equations and applying it over a mesh cell, a discrete algebraic formulation can be achieved. Starting with the integral form:

\[ \int_{V_{CV}} \left( \frac{\partial \vec{U}}{\partial t} + \frac{\partial \vec{E}_1}{\partial x} + \frac{\partial \vec{E}_2}{\partial y} + \frac{\partial \vec{E}_3}{\partial z} \right) dV_{CV} = \vec{S} \]  \hspace{1cm} (3.1)

This can be transformed using the Green-Gauss Theorem:

\[ \int_{V_{CV}} \left( \frac{\partial \vec{U}}{\partial t} \right) dV_{CV} + \int_{A_{CV}} \left( \vec{E}_k \cdot \vec{n}_k \right) dA_{CV} = \vec{S} \]  \hspace{1cm} (3.2)

In these equations \( V_{CV} \) refers to the volume of a given mesh cell, \( A_{CV} \) is the area of a face of the cell, \( \vec{U} \) is the vector of conservative variables, \( \vec{E}_1, \vec{E}_2, \) and \( \vec{E}_3 \) are fluxes in the \( x, y, \) and \( z \)
directions with $\vec{E}_k \cdot \vec{n}_k$ representing these fluxes normal to a face of the cell, and $\vec{S}$ is the source term vector. The $\vec{U}$, $\vec{E}_1$, $\vec{E}_2$, and $\vec{S}$ vectors are given below:

$$\vec{U} = \begin{bmatrix}
\rho_1 \\
\vdots \\
\rho_{NS} \\
\rho u \\
\rho v \\
\rho w \\
\rho e
\end{bmatrix}$$  \hspace{1cm} \text{(3.3)}$$

$$\vec{E}_1 = \vec{E}_{1,i} - \vec{E}_{1,v} = \begin{bmatrix}
\rho_1 u \\
\vdots \\
\rho_{NS} u \\
\rho u^2 + P \\
\rho v u \\
\rho w u \\
\rho h u
\end{bmatrix} - \begin{bmatrix}
-\rho_1 V_{x_1} \\
\vdots \\
-\rho_{NS} V_{x_{NS}} \\
t_{xx} \\
t_{yx} \\
t_{xx} \\
utt_{xx} + vtt_{yx} + wtt_{xx} - q_x
\end{bmatrix}$$  \hspace{1cm} \text{(3.4)}$$

$$\vec{E}_2 = \vec{E}_{2,i} - \vec{E}_{2,v} = \begin{bmatrix}
\rho_1 v \\
\vdots \\
\rho_{NS} v \\
\rho u v \\
\rho w v \\
\rho h v
\end{bmatrix} - \begin{bmatrix}
-\rho_1 V_{y_1} \\
\vdots \\
-\rho_{NS} V_{y_{NS}} \\
t_{xy} \\
t_{yy} \\
t_{zy} \\
utt_{xy} + vtt_{yy} + wtt_{zy} - q_y
\end{bmatrix}$$  \hspace{1cm} \text{(3.5)}$$

$$\vec{E}_3 = \vec{E}_{3,i} - \vec{E}_{3,v} = \begin{bmatrix}
\rho_1 w \\
\vdots \\
\rho_{NS} w \\
\rho u w \\
\rho w v \\
\rho w^2 + P \\
\rho h w
\end{bmatrix} - \begin{bmatrix}
-\rho_1 V_{z_1} \\
\vdots \\
-\rho_{NS} V_{z_{NS}} \\
t_{xz} \\
t_{yz} \\
t_{zz} \\
utt_{xz} + vtt_{yz} + wtt_{zz} - q_z
\end{bmatrix}$$  \hspace{1cm} \text{(3.6)}$$
\[
\vec{S} = \begin{bmatrix}
\dot{\omega}_1 \\
\vdots \\
\dot{\omega}_{NS} \\
0 \\
0 \\
0 \\
0
\end{bmatrix}
\] (3.7)

where the subscript \(i\) denotes the inviscid flux vector and \(v\) denotes the viscous flux vector.

Eq. 3.2 is then converted to its discrete formulation:

\[
V_{CV_c} \frac{\partial \vec{U}_c}{\partial t} + \sum_{j=1}^{NF_c} \left( \vec{E}_k \cdot \vec{n}_k \right)_{j,c} A_{CV_{j,c}} = \vec{S}_c
\] (3.8)

where the subscript \(c\) refers to a given cell, the subscript \(j\) refers to a specific face of that cell, and \(NF\) is the total number of faces of the cell (6 in this case as a three-dimensional structured grid is used).

### 3.2 Flux Reconstruction

#### 3.2.1 Low-Diffusion Flux-Splitting Scheme (LDFSS)

The inviscid fluxes are mixed in character, behaving as either elliptic or hyperbolic equations depending on the local Mach number. Therefore, care must be taken in order to make sure information propagates in the correct direction. The Low-Diffusion Flux-Splitting Scheme (LDFSS) by Edwards \[7\] is used to solve these fluxes. This is a first order, upwind method that splits the flux into “convective” and “pressure” terms so that the flux across a cell face is expressed in the “\(i\)” direction as:

\[
\vec{E} = A \left( \rho U \vec{E}^c + P \vec{E}^p \right)
\] (3.9)

where \(A\) is the area of the cell face, \(U\) is the velocity normal to the face, and:
\[ \vec{E}_c = \begin{bmatrix} Y_1 \\ \vdots \\ Y_{NS} \\ u \\ v \\ w \\ H \\ k \\ \omega \end{bmatrix} \]  \hfill (3.10)

\[ \vec{E}_P = \begin{bmatrix} 0 \\ \vdots \\ 0 \\ \vec{n}_x \\ \vec{n}_y \\ \vec{n}_z \\ 0 \\ 0 \end{bmatrix} \]  \hfill (3.11)

At the cell interface, the convective flux is:

\[ \vec{E}^c_{1/2} = a_{1/2} \left[ \rho_L C^+ E^c_L + \rho_R C^- E^c_R \right] \]  \hfill (3.12)

with the subscripts \( L \) and \( R \) denoting values at the left and right cells and \( a_{1/2} \) is the interface speed of sound:

\[ a_{1/2} = \frac{1}{2} (a_L + a_R) \]  \hfill (3.13)

\( C^\pm \) gives Mach number splittings:

\[ C^+ = C^+_V L - M^+_L \]  \hfill (3.14)

\[ C^- = C^-_V L - M^-_L \]  \hfill (3.15)

with:

\[ C^+_V L = \alpha^+_L (1 + \beta_L) M_L - \beta_L M^+_L \]  \hfill (3.16)
\[ C_{VL} = \alpha_R^{-} (1.0 + \beta_R) M_R - \beta_R M_R^- \quad (3.17) \]

and:

\[ M_{\frac{1}{2}}^+ = M_{\frac{1}{2}} \left( \frac{2P_R}{P_L + P_R} - \delta \frac{|P_L - P_R|}{P_R} \right) \quad (3.18) \]

\[ M_{\frac{1}{2}}^- = M_{\frac{1}{2}} \left( \frac{2P_L}{P_L + P_R} - \delta \frac{|P_L - P_R|}{P_L} \right) \quad (3.19) \]

\[ \alpha_{L,R}^\pm \text{ and } \beta_{L,R} \text{ are sonic-point transition functions:} \]

\[ \alpha_{L,R}^\pm = \frac{1}{2} [1.0 \pm \text{sign} (M_{L,R})] \quad (3.20) \]

\[ \beta_{L,R} = -\max [0.0, 1.0 - \text{int} (|M_{L,R}|)] \quad (3.21) \]

\( M_{L,R} \) and \( M_{\frac{1}{2}} \) are the left/right contravariant Mach numbers and the split Mach number, respectively:

\[ M_{L,R} = \frac{1}{a_{\frac{1}{2}}} \left[ n_x u_{L,R} + n_y v_{L,R} + n_z w_{L,R} \right] \quad (3.22) \]

\[ M_{L,R}^\pm = \pm \frac{1}{4} (M_{L,R} \pm 1.0)^2 \quad (3.23) \]

and:

\[ M_{\frac{1}{2}} = \frac{1}{4} \beta_L \beta_R \left( \sqrt{\frac{1}{2} (M_{L}^2 + M_{R}^2)} - 1.0 \right)^2 \quad (3.24) \]

The pressure flux across the interface is given as:

\[ E_{P}^F = E^P \left[ D_{L}^+ P_{L} + D_{R}^- P_{R} \right] \quad (3.25) \]

where \( P_L \) and \( P_R \) are left and right cell pressures and:

\[ D_{L,R}^\pm = \alpha_{L,R}^\pm (1.0 + \beta_{L,R}) - \beta_{L,R} P_{L,R}^\pm \quad (3.26) \]

where \( \alpha_{L,R}^\pm \) and \( \beta_{L,R} \) are the same as above and \( P_{L,R}^\pm \) is Van Leer’s subsonic pressure splitting [32]:

\[ P_{L,R}^\pm = \frac{1}{4} (M_{L,R} \pm 1.0)^2 (2.0 \mp M_{L,R}) \quad (3.27) \]
3.2.2 Viscous Fluxes

The viscous fluxes are parabolic in nature and are simply discretized using a second-order central-differencing method about the cell interface. These are then summed with the inviscid fluxes at each face to give the total flux.

3.3 Higher-Order Extension

The inviscid flux formulation is a first-order method where variable values at cell interfaces are the same as their value at the cell center (variables are constant across a cell). Since the viscous fluxes are second-order, the inviscid fluxes must be extended to higher-order as well to maintain second-order spatial accuracy. This is accomplished using a Total Variation Diminishing (TVD) scheme to reconstruct values for the primitive variables at the cell interface. The primitive variable vector is:

$$\vec{V} = \begin{bmatrix} P_1 \\ \vdots \\ P_n \\ u \\ v \\ w \\ T \\ k \\ \omega \end{bmatrix}$$

(3.28)

where $P_k$ is the species partial pressure, $P_k = \rho_k R_k T$. Reconstruction at cell interfaces is accomplished by:

$$\vec{V}_{L,i+1/2} = \vec{V}_i + \frac{1}{2} \minmod \left( \vec{V}_{i+1} - \vec{V}_i, \vec{V}_i - \vec{V}_{i-1} \right)$$

$$\vec{V}_{R,i+1/2} = \vec{V}_{i+1} - \frac{1}{2} \minmod \left( \vec{V}_{i+2} - \vec{V}_{i+1}, \vec{V}_{i+1} - \vec{V}_i \right)$$

(3.29)

where the minmod function is defined so that:

$$\minmod (a, b) = \begin{cases} 
  a & \text{if } |a| < |b| \text{ and } ab > 0 \\
  b & \text{if } |b| < |a| \text{ and } ab > 0 \\
  0 & \text{if } ab \leq 0
\end{cases}$$

(3.30)
3.4 Time Integration

The solution was advanced in time using an implicit Euler method. Though implicit methods are harder to implement and much more costly per iteration than explicit methods, they are stable for much larger time steps and are better suited to solving "stiff" systems where different aspects of the system may have widely varying time scales, i.e. fluid flows with chemical reactions taking place. This typically allows the system to converge more quickly than it would for an explicit formulation despite its higher per iteration costs. It can first be written using the steady-state residual:

\[
\frac{\partial \tilde{U}}{\partial t} = -\tilde{R}_{i,j,k} \tag{3.31}
\]

where \(\tilde{R}_{i,j,k}\) is the steady-state residual solved using the fluxes discussed in Section 3.1 and solved in Section 3.2:

\[
\begin{align*}
\tilde{R}_{i,j,k} &= \frac{E_{i+1/2,j,k} - E_{i-1/2,j,k}}{\Delta x} + \frac{F_{i,j+1/2,k} - F_{i,j-1/2,k}}{\Delta y} \\
&\quad + \frac{G_{i,j,k+1/2} - G_{i,j,k-1/2}}{\Delta z} - S_{i,j,k} \tag{3.32}
\end{align*}
\]

The unsteady residual is then given as:

\[
\begin{align*}
\tilde{R}_{i,j,k}^{n+1} &= \frac{U_{i,j,k}^{n+1} - U_{i,j,k}^{n}}{\Delta t} + \tilde{R}_{i,j,k}^{n+1} \tag{3.33}
\end{align*}
\]

where the superscript \(n\) refers to the current time step and \(n + 1\) refers to the time step being solved. This is solved using a pseudo time step to converge the unsteady residual using sub-iterations before advancing the solution in time. This can be written as:

\[
\frac{\partial \tilde{U}}{\partial \tau} = -\tilde{R}_{i,j,k} \tag{3.34}
\]

and then discretized as:

\[
\frac{\Delta U_{i,j,k}^{n+1,k+1}}{\Delta \tau} = \frac{U_{i,j,k}^{n+1,k+1} - U_{i,j,k}^{n+1,k}}{\Delta \tau} = - \left( \frac{U_{i,j,k}^{n+1,k+1} - U_{i,j,k}^{n+1,k}}{\Delta \tau} - \frac{U_{i,j,k}^{n+1,k} - U_{i,j,k}^{n+1,k}}{\Delta \tau} \right) \tag{3.35}
\]

where \(\tau\) is the pseudo time step, and the superscript \(k\) refers to the current sub-iteration. Only one sub-iteration was used for steady calculations. This is updated at each cell according to:
\[
\begin{align*}
-\vec{R}_{i,j,k}^{n+1} &= - \left[ \frac{a_{\text{time}}}{\Delta t} \left( \vec{U}_{i,j,k}^{n+1} - \vec{U}_{i,j,k}^{n} \right) + \vec{R}_{i,j,k}^{n+1} \right] \\
&= \left( \frac{a_{\text{time}}}{\Delta t} + \frac{1}{\Delta \tau} \right) \begin{bmatrix}
\frac{\partial \vec{U}_{i,j,k}^{n+1}}{\partial V_{i,j,k}} - \frac{\partial \vec{S}_{i,j,k}^{n+1}}{\partial V_{i,j,k}} + \vec{A}_{i,j,k}^{n+1} \Delta V_{i,j,k}^{n+1,k+1} \\
\vdots \\
\vec{B}_{i,j,k}^{n+1,k+1} - \vec{C}_{i,j,k}^{n+1,k+1} + \vec{D}_{i,j,k}^{n+1,k+1} + \vec{E}_{i,j,k}^{n+1,k+1}
\end{bmatrix}
\end{align*}
\]

(3.36)

where \( \vec{A} - \vec{G} \) are flux Jacobians whose calculations are described in [7] and \( a_{\text{time}} \) is a constant of 1 for unsteady calculations and 0 for steady calculations. This results in the creation of a linear system of the form:

\[
A \vec{x} = \vec{b}
\]

(3.37)

where:

\[
A = \left[ \left( \frac{a_{\text{time}}}{\Delta t} + \frac{1}{\Delta \tau} \right) \vec{U}^{n+1,k} - \vec{S}^{n+1,k} + \vec{A}^{n+1,k} \right]
\]

(3.38)

\[
\vec{x} = \Delta \vec{V}^{n+1,k+1}
\]

(3.39)

\[
\vec{b} = -\vec{R}^{n+1,k}
\]

(3.40)

\( \vec{V} \) is an ordering of \( \vec{V}_{i,j,k} \) over the grid nodes, \( \vec{U} \) is an appropriately ordered block-diagonal matrix of \( \frac{\partial \vec{U}_{i,j,k}}{\partial V_{i,j,k}} \), \( \vec{S} \) is a block-diagonal matrix of \( \frac{\partial \vec{S}_{i,j,k}}{\partial V_{i,j,k}} \), \( \vec{A} \) is a septadiagonal matrix of the flux Jacobians, \( \vec{A}_{i,j,k} - \vec{G}_{i,j,k} \), and \( \vec{R} \) is an ordering of the unsteady residual vector, \( \vec{R}_{i,j,k} \).

Due to the very large size of \( A \) in Eq. 3.37, it is impractical to solve the system by directly inverting \( A \). Instead, an approximation of \( A \) is made, referred to as \( A' \), using an Incomplete Lower/Upper (ILU) decomposition method, taking advantage of its sparseness. This is given as:

\[
A' = (D + L)(D)^{-1}(D + U)
\]

(3.41)

where \( D \) is the block diagonal, and \( L \) and \( U \) are the lower and upper block triangular, respectively. These are defined as:

\[
D = \left[ \left( \frac{a_{\text{time}}}{\Delta t} + \frac{1}{\Delta \tau} \right) \frac{\partial \vec{U}}{\partial V} - \frac{\partial \vec{S}}{\partial V} + \vec{A} \right] + \vec{B} + \vec{C} + \vec{D} + \vec{E}
\]

(3.42)
\[ L = \tilde{F} \quad (3.43) \]

\[ U = \tilde{G} \quad (3.44) \]

Thus, Eq. 3.36 can now be approximated by the following, easier to solve, system:

\[
\left( D^{n+1,k} + L^{n+1,k} \right) \left( D^{n+1,k} + U^{n+1,k} \right)^{-1} \Delta \vec{V}^{n+1,k+1} = -\vec{R}^{n+1,k} + \frac{a_{\text{time}}}{\Delta t} \left( \vec{U}^{n+1,k} - \vec{U}^{n,k} \right) \quad (3.45)
\]

This can then be solved using a forward and backward sweep over the system:

Forward:

\[
\Delta \vec{V}^{n+1,k+1/2}_m = \left( D^{n+1,k} \right)^{-1} \left[ -\vec{R}^{n+1,k}_m + \frac{a_{\text{time}}}{\Delta t} \left( \vec{U}^{n+1,k}_m - \vec{U}^{n,k}_m \right) - L^{n+1,k} \Delta \vec{V}^{n+1,k+1/2}_m \right] \quad (3.46)
\]

Backward:

\[
\Delta \vec{V}^{n+1,k+1}_m = \Delta \vec{V}^{n+1,k+1/2}_m - \left( D^{n+1,k} \right)^{-1} U^{n+1,k} \Delta \vec{V}^{n+1,k+1}_m \quad (3.47)
\]

where the subscript \( m \) is the vector index. Finally, the primitive variable vector can be updated:

\[
\vec{V}^{n+1,k+1}_{i,j,k} = \vec{V}^{n+1,k}_{i,j,k} + \Delta \vec{V}^{n+1,k+1}_{i,j,k} \quad (3.48)
\]

allowing the conservative variable vector to be updated, \( \vec{U}^{n+1}_{i,j,k} = \vec{U} \left( \vec{V}^{n+1,k+1}_{i,j,k} \right) \).
This work was done in conjunction with concurrent experimental tests being conducted at NASA’s HYPULSE facility. Therefore, care was taken in order to replicate details of the tests as closely as possible. This chapter covers many of the details of the experimental tests and how these conditions were modeled for computational runs.

4.1 Experimental Overview

Experimental runs were conducted at NASA’s HYPULSE facility (diagram shown in Figure 4.1). This is a shock heated facility capable of running as either a reflected shock tunnel or as an expansion shock tunnel simulating Mach 5 to Mach 12 conditions or Mach 12 to Mach 25 conditions, respectively [31]. Since the test gas is heated through the use of shock wave, there are no vitiation effects as would exist in a combustion heated facility. While some NO and O are produced from the shock heating process, their effects on combustion are negligible [2, 9] and have not been modeled in this work. Shock facilities do have one major drawback, however, and that is their run duration. Operating in its reflected shock mode only allows for a maximum of 5 to 10 milliseconds of runtime at test conditions before pressures and flow rates begin to drop off. While this can greatly hamper testing, it does still allow for about 10 transits of the full engine configuration at test conditions, simply due to the very high velocities associated with hypersonic flight. This allows for most aspects of the flow to reach a steady state, even though some aspects, such as wall heat flux, do not [29].
4.2 Model Geometry

The flowpath is a free-jet design based on the University of Virginia direct-connect Dual Mode Scramjet (DMSJ) with an identical injector/combustor section and an extended isolator. However, this is a free-jet design, so it includes the addition of a forebody and inlet as well, allowing for the simulation of an entire scramjet engine. The forebody consists of a 10 degree unswept wedge 0.566 m (22.30 in) in length leading to the rectangular isolator section which is 0.418 m (16.47 in) in length. The cowl consists of a 0.053 m (2.10 in) ramp angled 5 degrees. This results in two weaker shocks being generated as opposed to a single stronger shock, giving a reduced adverse pressure gradient on the forebody boundary layer and helping to reduce the likelihood of separation as the flow enters the isolator. The internal flowpath has a constant width of 0.038 m (1.50 in) with the isolator section being 0.025 m (1.00 in) in height. Fuel injection is performed using a single 10 degree unswept compression ramp 0.006 m (0.25 in) in height, \( h \), and \( 2h \) in width (0.013 m, 0.50 in). The combustor section maintains its constant area for \( 10h \) before starting a 2.9 degree divergence on the fuel injector wall for another \( 48h \) before exiting to atmosphere.

The test apparatus is built of uncooled aluminum and carbon steel, as the short test times render the use of any thermal protection or cooling systems unnecessary. The cowl and sidewalls are machined of a single piece and joined to the injector wall. Optical access is accomplished by windows in the sidewall aligned with test cabin windows at the HYPULSE facility. A diagram of the engine assembly can be seen in Figure 4.2.

A wide range of sensors were used to provide data for analysis. Close-coupled, high-frequency, PCB pressure transducers are arranged primarily along the centerplane of the injector-side wall with multiple off-center and cowl wall positions as well. Heat flux gauges are spaced along centerplane of the injector-side wall upstream of the injector and along the cowl wall downstream of the injector. Focusing Schlieren imaging was used to capture density gradients, revealing
shock structure, in the region surrounding the injector. Fuel plume imaging was used at two axial locations to capture solid-phase silica, $\text{SiO}_2$, as it is formed from the combustion of the silane fuel. Locations for these sensors can be seen in Figure 4.3. [28]

A three-dimensional structured mesh, consisting of the geometry given above as well as spillage regions around the inlet of the engine, was created for the computational modeling. The spillage regions allow for the accurate simulation of actual engine mass capture. Over 11.2 million mesh cells are used with 4.5 million in the combustor region, 2.7 million in the isolator region, and 3.7 million in the forebody and inlet area. The fuel injector is modeled as a high
pressure cylinder connecting to a diverging nozzle, and the mesh used to resolve the interior of the injector contains 0.3 million cells. In both the experimental apparatus and computational model, the injector nozzle accelerates the gaseous fuel stream to a Mach number of 1.7 and is designed so that the fuel is under-expanded as it exits into the low pressure, high velocity core flow. This leads to the fuel plume rapidly expanding as it enters the combustor so that greater mixing of the fuel and air can be achieved. The computational mesh along the engine centerplane can be seen in Figure 4.4 along with a zoomed in view of the combustor. Both of these only show every third grid line in order to better show mesh density.

4.3 Boundary Conditions

As all turbulence is being modeled, it is only necessary to model half the flow. A symmetry boundary condition is therefore used along the geometric centerplane of the engine, allowing cell count and computational costs to be decreased. A supersonic inlet boundary condition enforced the freestream conditions given in the next section at the inlet to the engine. Extrapolation boundary conditions were used for the engine outlet and spillage regions, though, due to the angle of attack used, some of the spillage boundary acted as an inflow and some acted as an outflow, with the location of the change being unknown a priori. While this worked fine for steady results, it caused some artifacts along the boundary at the start of transient runs. However, airflow entering the engine was far enough away that it was unaffected. The fuel injector boundary enforced stagnation pressures and temperatures and no-slip conditions were used for solid walls. Due to the very short duration of testing possible, wall temperatures were
set to a constant of 300 K. Experimental data showed a maximum temperature increase of about 50 K in the combustor heat flux gauges over the course of the test window, indicating this assumption is valid. These boundary conditions can be seen in Figure 4.5.

![Figure 4.5: Engine boundary conditions (blue: no-slip wall; red: extrapolation; purple: stagnation pressure - stagnation temperature; orange: symmetry; green: supersonic inlet)](image)

4.4 Initial Conditions

Two different test conditions, corresponding to two different simulated flight conditions, were examined. Flight conditions are given in Table 4.1. These were simulated using corresponding test conditions, given in Table 4.2. These conditions were chosen so that the correct flow enthalpy could be achieved within the engine in ground tests, even though conditions up stream of the engine would be different than what would be seen in flight, i.e. 

\[
(c_p T_0)_{flight} = (c_p T + \frac{1}{2} u^2)_{testing}
\]

Two equivalence ratios were numerically examined for the Mach 7 case. The 0.8 equivalence ratio was the original target equivalence ratio for the experimental tests; however, an equivalence ratio of 1.1 was actually achieved in testing.
Table 4.2: Freestream Test Conditions

<table>
<thead>
<tr>
<th>Simulated Flight Mach Number</th>
<th>7</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Velocity (m/s)</td>
<td>2122.3</td>
<td>2751.0</td>
</tr>
<tr>
<td>Angle of Attack (deg)</td>
<td>0.93</td>
<td>0.90</td>
</tr>
<tr>
<td>Pressure (Pa)</td>
<td>1179.0</td>
<td>2751.0</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>208.9</td>
<td>547.2</td>
</tr>
<tr>
<td>Chemical Composition (mass fraction)</td>
<td>76% N₂, 24% O₂</td>
<td>80% N₂, 20% O₂</td>
</tr>
<tr>
<td>Equivalence Ratio</td>
<td>0.8 and 1.1</td>
<td>0.65</td>
</tr>
</tbody>
</table>

Table 4.3: Injector CFD Conditions

<table>
<thead>
<tr>
<th>Mach 7</th>
<th>Stagnation Pressure</th>
<th>Stagnation Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>φ=0.80 H₂</td>
<td>1.41 MPa</td>
<td>298.86 K</td>
</tr>
<tr>
<td>20% SiH₄ / 80% H₂</td>
<td>1.76 MPa</td>
<td>298.86 K</td>
</tr>
<tr>
<td>φ=1.10 H₂</td>
<td>3.14 MPa</td>
<td>298.86 K</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mach 10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>φ=0.65 H₂</td>
<td>1.64 MPa</td>
<td>298.86 K</td>
</tr>
<tr>
<td>20% SiH₄ / 80% H₂</td>
<td>2.05 MPa</td>
<td>298.86 K</td>
</tr>
</tbody>
</table>
4.4.1 Steady Conditions

Steady runs form the majority of results presented in the next chapter. These are computationally faster to run compared to transient cases due to the use of local time steps. This varies the time step being used across the engine so that it adjusts to the wave speeds present in a given cell, i.e., the time step being used to advance the solution in a given cell is only a function of conditions in that cell. These runs were initiated by first setting all cells to the freestream values given in Table 4.2 except for the injector, which was set to the proper injector stagnation pressure and temperature and species mass densities given in Table 4.3. This is then allowed to converge using only the air and fuel species with no chemical reactions, so that a mixing solution is obtained. Combusting runs were then initiated from their appropriate mixing run. This allows for faster convergence and reduced computational costs versus considering combustion, and all of the chemical species it entails, from the start. Tare runs without any injection were accomplished by changing the stagnation pressure/temperature boundary condition in the injector to that of a solid wall and were then started in similar manner to the mixing runs.

4.4.2 Transient Conditions

Transients runs were also undertaken in order to better model the actual experimental process. Here a global time step is used so that time steps are equal across the engine allowing for a time-accurate solution to be obtained. Since a shock tunnel is being used, fuel injector pressures must be brought to near their steady state values before testing begins in order to ensure the correct equivalence ratio during the very short test window. This involves ramping injector pressures up over a period of approximately 10 ms as the engine is in a near vacuum initial state. This was modeled by changing the supersonic inlet boundary condition to an extrapolation condition and setting the pressure in the device to 500 Pa and velocities to near zero. Injector pressure was increased from 50kPa to its steady value as time increased, closely matching experimental data available. To model the shock of air hitting the engine, the boundary condition at the engine inlet is changed back to a supersonic inlet condition using the appropriate values from Table 4.2.
5.1 Mach 7 Test Case

Results were first obtained for the Mach 7 flight conditions, corresponding to the first phase of ground testing. Test conditions are listed in Table 4.2 with the flight conditions being simulated in Table 4.1. Hydrogen combustion could not be achieved in either ground testing or computational modeling and no hydrogen results are shown for this condition.

5.1.1 Tare Flow

A tare flow with no fuel injection was first run in order to generate baseline comparisons for the two turbulence models. Pressure and Mach number results for the inlet and isolator area along the centerplane are shown in Figure 5.1 for the SST model. Virtually no difference in these contours could be seen between the BSL and the SST models. It can be seen that the cowl creates two separate shocks that then propagate as a shock train down the isolator. An expansion wave is formed as the flow is diverted from the forebody to the isolator, leading to a small region of flow separation just downstream of the forebody/isolator transition caused by the large adverse pressure gradient between the expansion region and a reflected shock from the cowl. The Mach number contour clearly shows the growth of the boundary layer as the air flows downstream towards the injector. These results are typically uncoupled from any injection or combustion occurring in the combustor due to the supersonic nature of the flow; however, very large pressures in the combustor can result in a displacement of the shock train as it reacts to the greater back pressure.

Pressures along the centerplane of the injector-side wall can be seen in Figure 5.2 with the geometry of the engine shown below for reference. The experimental data, run PQJ43, is the average of pressures that have been normalized with respect to the target test condition.
Figure 5.1: Mach 7 Isolator centerplane pressure and Mach number contours for SST turbulence model

Figure 5.2: Comparison of injector side centerplane wall pressure, Mach 7 tare case
across a 5 ms test window for a single experimental run. Error bars indicate a range of one standard deviation from the mean pressure. It can clearly be seen that, while both models match shock locations of the experimental data in the isolator fairly well, they predict lower peak pressures. The BSL model performs slightly better than the SST model, with slightly higher peak pressure predictions. The difference between the two is most likely due to the SST model under-predicting turbulent shear stress in the regions of strong adverse pressure gradients such as in the shock / boundary-layer interactions, especially in the separation bubble at the forebody / inlet transition. The most significant difference between the two models exists along the injector ramp, with the BSL model predicting pressures 10% higher than the SST model by the end of the ramp, indicated by the vertical black line at $x = 1.02m$. This is likely due to the SST model predicting greater shock induced seperation along the injector ramp; however, without any experimental data in this region, it is difficult to determine which model is more accurate. Within the combustor, both models continue to slowly diverge from the experimental data as the flow approaches the rear of the engine suggesting that small differences between the model and experimental shock trains are able to build up across each shock, producing larger differences as the flow proceeds downstream.

Figure 5.3: Mach 7 Tare Schlieren image (top) versus BSL (middle) and SST (bottom) model density gradient magnitudes

Schlieren imagery is compared to density gradient magnitude results for both turbulence models in Figure 5.3. Both turbulence models are seen to produce nearly identical shock locations, and while experimental and modeling results look very similar, it can be seen that the principal isolator shock hits the near the base of the injector ramp in the CFD results.
and closer to the center of the ramp for the experimental result. It can also be seen that the shock resulting from the flow that is diverted around the back of the injector impacting the injector-side wall reflects off of the cowl wall further upstream in the modeling results than it does in the experimental results. This difference is likely the primary cause of the wall pressure differences further down the combustor.

Subsequent mixing and combusting runs at the Mach 7 test condition have used the SST variation of Menter’s turbulence model, as the SST model is often noted for its better performance in adverse pressure gradients and regions of separation.

5.1.2 Silane - Hydrogen / Air Mixing

Mixing cases for equivalence ratios of 0.8, the original target equivalence ratio, and 1.1, the equivalence ratio achieve in experimental testing, were first run by considering only the air and fuel species and disallowing any reactions. This allows for quicker convergence for combusting cases and may more accurately replicate the start of the experimental system. These results show the fuel from the injector creating a ’tear-drop’ shaped plume that covers about one third of the vertical area near the injector nozzle as it expands, clearly seen in nitrogen mass fraction contours for both equivalence ratios in Figure 5.4. The black lines indicate levels of 75%, 85% and 95% of the free-stream nitrogen mass fraction. Mixing initially occurs very quickly with the lower equivalence ratio with the entirety of the fuel plume having reached the 75% mark by $x = 10.9h$ and the 85% mark by $x = 20.6h$. It is obvious that, due to the angle of injection, the fuel plume is completely enveloped by the air stream so that mixing occurs from all sides. This occurs to a much lesser extent with the higher equivalence ratio due to the greater size of the fuel plume reducing mixing along the injector-side wall. This, and the greater mass of fuel being injected, cause mixing to occur much more slowly, with the entirety of the fuel plume not reaching 75% of the free-stream nitrogen mass fraction until $x = 33.7h$ and the system never fully reaching the 85% value.

Shocks generated by blockage of the core flow by the fuel plume reflect, coalescing together so that a high pressure region is formed along the bottom wall, just below the start of the divergence of the injector-side wall, shown in combustor centerplane pressure contours in Figure 5.5. This is enhanced by further expansion of the fuel stream, which serves to compress the core flow region before turning to follow the diverging combustor wall.

Temperature contours in Figure 5.6 show the expansion of the mixing region as the cold fuel mixes with the warmer core flow, leading to the reduction of both the area occupied and the temperature of the core flow. Both pressure and temperature contours reveal that conditions are very cold for combustion purposes with pressures of approximately 20 kPa to 25 kPa and temperatures of between 300 K and 500 K in the mixed region. This presents a problem for
Figure 5.4: Mixing centerplane nitrogen mass fraction results for equivalence ratios of 0.8 and 1.1

Figure 5.5: Mixing centerplane pressure results for equivalence ratios of 0.8 and 1.1

Figure 5.6: Mixing centerplane temperature results for equivalence ratios of 0.8 and 1.1
the Jachimowski and McLain and Chinitz mechanisms since they were developed for initial conditions well in excess of this - pressures above 50 kPa for the Chinitz mechanism and 100kPa for the Jachimowski and McLain mechanism and temperatures above 800 K. Also noteworthy is the absence of a recirculation region that might aid in ignition and flame stabilization by holding some of the fuel - air mixture, giving it more time to ignite.

5.1.3 Silane - Hydrogen / Air Combustion

Gas-Phase SiO$_2$, $\phi = 0.8$

Once mixing runs were completed for the $\phi=0.8$ case, reactions were turned on and activation energies were set to 1/2 of their original values in order to force ignition of the fuel. Once a stable flame was achieved, activation energies were returned to normal to allow for the correct modeling of reaction chemistry. The Jachimowski and McLain reaction mechanism proved to be unable to sustain combustion with the incoming air pushing the flame down the combustor faster than the flame could advance back towards the injector. This leads to the flame eventually leaving the combustor completely and the solution converging to essentially the same as the pure mixing solution. The only discernible differences are moderately higher temperatures along the low-momentum wall regions and only slightly elevated fuel plume temperatures with no changes seen in pressure, seen in Figure 5.7. The model from Chinitz was then tried in the hope that its slightly quicker ignition times would serve to maintain combustion. However, it too proved unable to anchor the flame with it once again blowing out the back of the combustor, eventually producing a solution virtually indistinguishable from that given by the Jachimowski model.

![Jachimowski Combustion](image)

Figure 5.7: Centerplane temperatures for Jachimowski reaction mechanism at an equivalence ratio of 0.8

Centerplane results using 1/2 activation energies are shown in Figures 5.8, 5.9, and 5.10.
Figure 5.8: u-velocity centerplane results for 1/2 activation energy, 0.8 equivalence ratio case

Figure 5.9: Temperature centerplane results for 1/2 activation energy, 0.8 equivalence ratio case
While these cannot be said to accurately predict the combustion process, they may give some insight into the expected flame structure and the differences between the two models. Looking first at axial velocity results, large differences between the two models can immediately be spotted. The Chinitz model shows a large area of recirculation in the area between the combustor and the start of combustor wall divergence that is not seen in the Jachimowski and McLain results. This pushes the fuel stream coming out of the injector further into the core flow, compressing it down and elevating pressures. Temperature contours show that both models react as fast as the fuel and air can mix due to the much higher reaction rates caused by the reduced activation energies. A thin region of elevated temperatures can be seen starting all the way from the beginning of the shear layer between the fuel plume coming out of the injector and the core flow. The Chinitz model produces much higher temperatures than the Jachimowski and McLain model in this reacting region throughout the combustor. Similar to the mixing results, an area of peak pressure is found along the cowl wall about 10h downstream of the injector as a result of interactions between shock waves coming off the injector and fuel plume and the volumetric expansion and deflection of the reacting plume, which serves to constricts the supersonic core flow.

**Gas-Phase SiO$_2$, $\phi = 1.1$**

Runs at an equivalence ratio of 1.1 were performed in order match equivalence ratios obtained in the experimental tests. The Chinitz model, the modified Chinitz model described in Appendix B, and the BTW model were used to simulate combustion at this equivalence ratio using both
gas phase and solid phase modeling of the combustion product SiO$_2$. Gas phase results are presented here with solid phase results in the next section. The Jachimowski and McLain model was not used due to its higher ignition times and less favorable results in the $1/2$ activation energy $\phi = 0.8$ case.

![Temperature centerplane results for the Chinitz model (top), the modified Chinitz model (middle), and the BTW model (bottom) using gas phase SiO$_2$ modeling](image)

Figure 5.11: Mach 7, $\phi = 1.1$ case: Temperature centerplane results for the Chinitz model (top), the modified Chinitz model (middle), and the BTW model (bottom) using gas phase SiO$_2$ modeling.

Unfortunately, the Chinitz model achieved the same results seen in the $\phi = 0.8$ case; namely, after starting from a $1/2$ activation energy, combusting solution, it was unable to maintain combustion using full activation energies, with the flame again blowing out the back of the combustor. The modified Chinitz model and the BTW model showed a marked improvement over this by being able to maintain combustion when started from the combusting solution, though they were still unable to ignite on their own. Temperature contours in Figure 5.11 again
show only a slight increase in temperature over that of the mixing case for the standard Chinitz model, while both the modified Chinitz model and the BTW models appear similar, showing strong heat release in the heavily mixed region between the fuel plume and core flow. These both indicate a flame detached a short ways from the injector with the fuel plume of the modified Chinitz model not being fully enveloped by the flame until $x = 14h$ and the BTW model not being fully enveloped until $x = 6h$.

![Pressure contour plots](image)

**Figure 5.12:** Mach 7, $\phi = 1.1$ case: Pressure centerplane results for the Chinitz model (top), the modified Chinitz model (middle), and the BTW model (bottom) using gas phase SiO$_2$ modeling.

Centerplane pressure contours for the three models are shown in Figure 5.12. Again, virtually no pressure rise is seen in the Chinitz model results due to the absence of combustion. Significant differences can be seen between the results of the modified Chinitz model and the BTW model with the modified Chinitz model showing that the isolator shock train has been pushed a short ways upstream. The reason for this is not immediately clear, as this is usually due
to high pressures in the combustor. However, this is not seen in the BTW model, despite its flame extending further upstream and its high pressure regions near the cowl wall being located further upstream and being higher in pressure. Both models show a shock train propagating through the forward part of the combustor, though it appears to gradually weaken so that it can no longer be seen at the rear of the combustor where results between the two models appear very similar.

![Figure 5.13: Mach 7, $\phi = 1.1$ case: Comparison of injector-side centerplane wall pressure using gas phase SiO$_2$](image)

Pressures along the centerplane of the injector-side wall can be seen in Figure 5.13. The experimental data, PQ.I41 and PQ.I42, are the average pressure results of two experimental runs with error bars of one standard deviation. These points were obtained in the same way as the tare wall pressure results by normalizing the experimental data with respect to the target test conditions and then taking the average over a 5 ms test window. The Chinitz model shows virtually no increase in pressure over the mixing results due its failure to maintain combustion. Other than the pressure rise at the rear of the isolator due to the displacement of the isolator shock train, the modified Chinitz and BTW models appear similar. However, they both result in poor agreement with experimental data throughout the combustor. They indicate a pressure rise far upstream of what is seen in the experimental data which shows very minimal pressure rise until approximately 25$h$ downstream of the injector followed by a very sudden increase in pressure. This likely indicates the silane-hydrogen fuel is slowly breaking down and forming radicals as it mixes with the air stream. This continues until a critical point is reached, allowing for an extremely rapid chain branching explosion to occur. Since the fuel and air is well mixed
by this point, much of it can combust at once, helping it to reach higher pressures compared to the more gradual rise of the two combusting computational solutions, where combustion occurs essentially in conjunction with reactant mixing. Experimental data also indicates greater pressures at the rear of the combustor, suggesting a greater amount of heat release. This could be due to more significantly more mixing occurring, allowing more fuel to combust, but it more likely indicates problems with the combustion models or the gas phase assumption for SiO$_2$.

Data from the combustor pressure transducers with corresponding modeling results is given in Table 5.1, summarizing the poor agreement between modeling results and experimental data in the combustor, especially in the front section.

Fuel plume imaging of SiO$_2$ and SiO$_2$ mass fraction contours are given in Figure 5.14. The first experimental image, taken at x=12h, upstream of the large pressure rise, shows no evidence of SiO$_2$ formation, while the second, taken in the region at the start of the pressure rise at x=24h, shows the beginning of SiO$_2$ formation in the highly mixed horseshoe shaped region at the edges of the fuel plume. Computational results show SiO$_2$ at both locations, again indicating that they predict combustion far upstream of what is seen in the experimental tests. Between the modified Chinitz and BTW models, results differ greatly. The BTW model shows the greatest amount of SiO$_2$ in the reacting plume, similarly to the experimental results, though the plume appears to be much larger in the BTW results. The modified Chinitz model shows much less SiO$_2$ formation, with it concentrated in the cool, fuel-rich center of the fuel plume with no SiO$_2$ in the high temperature reacting plume. It was seen in the rear of the combustor that virtually no SiO$_2$ existed, suggesting it was consumed as temperature increased, releasing an O atom
and allowing for a greater formation of water, as the flow is fuel-rich. This is likely unrealistic and suggests problems with either the backward reaction rates in reactions that result in the formation of SiO$_2$ or problems with the thermodynamic data used for SiO$_2$. Fuel plume imaging further downstream would confirm whether SiO$_2$ continues to build up as combustion progresses or whether the formation of water is preferred.

Figure 5.15 shows Schlieren imagery from the experimental results and density gradient magnitudes from the numerical results for the two combusting models and for the pure mixing case. Experimental results show shocks forming at the base of the injector and at the fuel plume where it expands past the injector to block some of the core flow. These coalesce together in a manner very similar to that observed in the numerical mixing results. It also appears that fuel flow is parallel to the top wall in the experimental and mixing images while both combusting CFD images show it angled into the core flow. This suggests the experimental results lack the recirculation region near the injector that is seen in the combusting cases but not seen in the mixing results, further suggesting the gradual breakdown of the silane-hydrogen fuel into radicals with ignition and combustion not occurring until much further downstream.
Figure 5.15: Mach 7, $\phi = 1.1$ case: Schlieren image (top) versus density gradient magnitudes using gas phase SiO$_2$ modeling (2nd from top: modified Chinitz model; 3rd from top: BTW model; bottom: mixing only)
Solid-Phase SiO$_2$, $\phi = 1.1$

As mentioned in section 2.3.2, silane’s saturated combustion product, SiO$_2$, is a solid at flame temperatures. It has been suggested that the condensation from gas to solid occurs so quickly that the gas phase can be ignored and it can be assumed to instantaneously form in its solid phase. This assumption has been applied to the Chinitz and the modified Chinitz models, while a finite rate reaction converting gas phase SiO$_2$ to solid phase has been applied to the BTW model. In each case, the solid particles formed have been considered to be small enough that their effects on fluid dynamics is negligible, allowing the system to still be treated as a mixture of only gases. As with the gas phase modeling, no reaction model examined was able to self ignite.

![Temperature centerplane results for the Chinitz model (top), the modified Chinitz model (middle), and the BTW model (bottom) using solid phase SiO$_2$ modeling](image)

Figure 5.16: Mach 7, $\phi = 1.1$ case: Temperature centerplane results for the Chinitz model (top), the modified Chinitz model (middle), and the BTW model (bottom) using solid phase SiO$_2$ modeling
Temperature contours for the centerplane of the combustor can be seen in Figure 5.16. Even with the greater heat release generated by the solid phase consideration due to its more negative heat of formation, the Chinitz model was still unable to maintain combustion with the flame eventually blowing out the back of the combustor and the solution again resembling the mixing solution. Both the modified Chinitz and BTW models show much higher temperatures throughout the combustor owing to the greater heat release. This has resulted in the flame firmly anchoring to the back of the injector with combustion starting as soon as any oxygen and fuel mix. The high temperature plume near the injector appears to be larger for the BTW model results, suggesting that combustion may initially be occurring at a faster rate than in the modified Chinitz model.

![Temperature Contours](image)

Figure 5.17: Mach 7, $\phi = 1.1$ case: Pressure centerplane results for the Chinitz model (top), the modified Chinitz model (middle), and the BTW (bottom) using solid phase SiO$_2$ modeling

Pressure contours are shown in Figure 5.17. Similar to the gas phase results, pressure
solutions in the injector region are quite different between the modified Chinitz model and the BTW model, despite the similar temperature results. Both of these solutions still show a peak pressure along the cowl wall near the injector and that the isolator shock train has been pushed upstream, out of frame, by the high combustor pressures, but the BTW model gives much higher pressures than the modified Chinitz model in the injector region. This is likely due to the slightly higher heat release near the injector experienced by the BTW model, causing slightly more blockage of the core flow by the fuel plume and the reacting plume surrounding it. This in turn leads to a disproportionately higher pressure rise at the blockage. Toward the rear of the combustor, both models strongly resemble each other and pressure is seen to have a very strong dependence on the x-location while being nearly constant in the y- and z-directions.

![Image](image_url)

Figure 5.18: Mach 7, $\phi = 1.1$ case: SiO$_2$ mass fractions for the BTW model with gas phase modeling and gas phase to solid phase condensation

Figure 5.18 shows mass fractions for both gas and solid phase SiO$_2$ for the BTW model incorporating 100% gas phase modeling and a gas phase to solid phase transition. It is clearly seen that the virtually all SiO$_2$ exists in its solid form when using the gas to solid condensation, even at the start of combustion near the injector. This strongly supports the assumption of
instantaneous formation of SiO\(_2\) into its solid phase as suggested by [1, 5, 18]. Comparing the
gas phase modeling to the gas to solid modeling shows significantly more SiO\(_2\) is formed when
considering the solid phase. This is due to a preference in the formation of water over gas phase
SiO\(_2\), but not solid phase SiO\(_2\), as the high equivalence ratio, limited residence time in the
combustor, and the nature of diffusion limited flames result in the system being unable to fully
oxidize.

![Graph showing heat release comparison between gas phase and gas to solid condensation]

Figure 5.19: Mach 7, \(\phi = 1.1\) case: Heat release of several species for BTW model using gas
phase modeling and gas to solid condensation (heat release by all other species was negligible,
<1% of total)

Figure 5.19 shows the overall amount of heat being released by the production and / or
destruction of many of the species in the BTW model for both the gas phase and the gas to solid
phase considerations. The largest difference between the two is with the heat release caused by
SiO\(_2\), as would be expected. The gas to solid phase consideration shows four times greater heat
release caused by SiO\(_2\) versus the gas phase consideration. This is due to the greater amount
of SiO\(_2\) formation and due to the nearly three times greater enthalpy of formation of the solid
phase over the gas phase. This results in SiO\(_2\) causing even greater heat release than water. The
differences seen in the heat release caused by water are likewise due to the greater formation of
water when using the gas phase modeling. Overall, using the gas to solid phase modeling results
in an overall heat release of 66733 J/s while the gas phase consideration gives 39055 J/s.

Wall pressures along the centerplane of the injector-side wall are shown in Figure 5.20. This
uses the same experimental data as Figure 5.13 as well as results from the Chinitz and modified
Figure 5.20: Mach 7, $\phi = 1.1$ case: Comparison of injector-side centerplane wall pressure using solid phase SiO$_2$

Table 5.2: Mach 7, $\phi = 1.1$ case: Comparison of combustor wall pressure readings using solid phase SiO$_2$

<table>
<thead>
<tr>
<th>x(m)</th>
<th>Experimental Data Pressure (Pa)</th>
<th>Modified Chinitz Model Pressure (Pa)</th>
<th>Percent Error</th>
<th>BTW Model Pressure (Pa)</th>
<th>Percent Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.03</td>
<td>12284</td>
<td>92440</td>
<td>652.6%</td>
<td>124126</td>
<td>910.5%</td>
</tr>
<tr>
<td>1.07</td>
<td>25642</td>
<td>104315</td>
<td>306.8%</td>
<td>138289</td>
<td>439.3%</td>
</tr>
<tr>
<td>1.09</td>
<td>25432</td>
<td>109940</td>
<td>332.3%</td>
<td>129713</td>
<td>410.0%</td>
</tr>
<tr>
<td>1.10</td>
<td>23634</td>
<td>114289</td>
<td>383.6%</td>
<td>122909</td>
<td>420.0%</td>
</tr>
<tr>
<td>1.11</td>
<td>20900</td>
<td>116793</td>
<td>458.8%</td>
<td>118024</td>
<td>464.7%</td>
</tr>
<tr>
<td>1.18</td>
<td>72396</td>
<td>89982</td>
<td>24.3%</td>
<td>92625</td>
<td>27.9%</td>
</tr>
<tr>
<td>1.21</td>
<td>103360</td>
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<td>17.8%</td>
<td>85265</td>
<td>17.5%</td>
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<td>1.24</td>
<td>79588</td>
<td>79252</td>
<td>0.4%</td>
<td>78847</td>
<td>0.9%</td>
</tr>
<tr>
<td>1.28</td>
<td>73676</td>
<td>71189</td>
<td>3.4%</td>
<td>70319</td>
<td>4.6%</td>
</tr>
<tr>
<td>1.38</td>
<td>58033</td>
<td>57109</td>
<td>1.6%</td>
<td>55679</td>
<td>4.1%</td>
</tr>
</tbody>
</table>
Chinitz models using the instantaneous solid phase SiO$_2$ formation assumption, results from the BTW model using the gas to solid reaction, and pure mixing results. It is obvious that the large pressures seen in the injector region in Figure 5.17 has resulted in an even worse agreement with the experimental data in the rear of the isolator and beginning of the combustor for the modified Chinitz and BTW models. However, much better agreement is achieved at the combustor exit with pressures 23.4% higher than was seen using the gas phase consideration. This is arguably more important, as it reveals that the models may be predicting a similar equilibrium as the experimental runs, despite the differences at the start of the combustion process.

Table 5.2 lists the average pressure readings in the combustor of the two experimental runs with corresponding results and percent errors from the modified Chinitz and BTW models. This quantifies the agreement between the experimental data and modeling, revealing the two models produced percent errors of less than 5% across the final three pressure transducers. Agreement is slightly better using the modified Chinitz model, possibly due to its slightly less combustion at the front of the combustor allowing for slightly more efficient mixing of the fuel and air.

![Fuel Plume Imaging](image1.png)

(a) Fuel Plume Imaging  (b) modified Chinitz model  (c) BTW model

![Fuel Plume Imaging](image2.png)

(d) Fuel Plume Imaging  (e) modified Chinitz model  (f) BTW model

Figure 5.21: Mach 7, $\phi = 1.1$ case: SiO$_2$ fuel plume imaging using solid phase SiO$_2$ modeling (top: $x=12h$; bottom: $x=24h$)

Fuel plume and Schlieren imagery, Figure 5.21 and Figure 5.22, again show that the modified Chinitz and BTW models are not correctly replicating the start of the combustion process. Both models still show combustion at the $x = 12h$ location and the total size of the plumes at
both locations are still larger than the experimental data. Both models also show far greater SiO\textsubscript{2} formation over what was seen in the gas phase modeling, and the modified Chinitz model results now results in a horseshoe shape similar to the shape of the BTW model. The regions of heavy SiO\textsubscript{2} formation, colored red, in the BTW model results at the \( x = 24h \) location do appear to be similar in size and shape to the experimental image, though the models show more SiO\textsubscript{2} along the injector-side wall while the experimental image appears to show more SiO\textsubscript{2} nearer the cowl wall.

The density gradient magnitude images appear very smeared out due to the isolator shock train being pushed far upstream. No clear evidence of a shock train, or any shocks at all, can be seen, even any resulting from the injector ramp. This is due to the flow being partially choked so that it is subsonic in the region near the injector wall.

**Transient Analysis**

Time-accurate simulations were undertaken to determine whether the starting process of the experimental facility could influence the results achieved. Due to the very short test duration, fuel injector pressure must be brought to near its steady value before testing begins in order to ensure the correct equivalence ratio during the test window. Matching conditions seen in the experimental tests as closely as possible, the fuel injection pressure was slowly ramped up over a period of approximately 10 ms with the test chamber being initialized at near vacuum, room-temperature conditions. While the vast majority of the fuel is blown out the back of the engine due to the geometry of the fuel injector, a significant amount is able to propagate towards
the front of engine. This fills much of the isolator section, pushing out some of the air, with tendrils of fuel making it about one half of the way down the forebody before the shock hits the engine. When the shock of air hits the engine, a separate compression wave is formed, preceding in front of the main slug of air at approximately twice its speed. This leads to a region of higher pressure and temperature sitting between the front shock and the mass of air. This region hits the fuel that has propagated out the front of the engine, igniting it and pulling it back down into the engine with it.

As the flame front continues down the engine, any oxygen it encounters is consumed. As it approaches the combustor region, little oxygen remains in its vicinity. The hot combustion products mix with the fuel, but, due to the lack of any recirculation regions, they, and any radicals formed by the high temperatures, are just blown out the back of the engine, seemingly having no lasting effect on the injector region. By the time any oxygen is able to mix with the fuel, it encounters what is essentially ‘cold’ fuel unaffected by the propagation of the flame front. This leads to the failure of the modified Chinitz model using both gaseous and solid phase SiO$_2$ to ignite, similar to the response observed when started from a mixing solution for the steady cases. Both cases also tend towards their steady state results, virtually identical to each other and very similar to the pure mixing case, as time progresses. A series of temperature and pressure contours showing this process for gas phase SiO$_2$ modeling can be seen in Figure 5.23 while wall pressure plots for steady and transient results are shown in Figure 5.24.

A 1/2 activation energy Chinitz model with gaseous phase SiO$_2$ was also run in order to force combustion, showing the evolution of the flame over time. Due to the greatly increased reaction rates, combustion starts as soon as oxygen reaches the fuel and occurs as quickly as they can mix. The recirculation zone seen in the steady-state predictions does not form until the main mass of air passes the injector and mixes with the fuel. Indeed, the growth of the recirculation zone seems to be completely driven by expansion of the fuel / air mixture due to heat release. It does not exist until combustion occurs and then grows larger as the initial mixture of fuel and air is consumed, before reducing in size as the mixing and heat-release rates equilibrate. The transient solution approaches essentially the same solution as was seen in the steady case as time progresses. Figure 5.25 shows a series of images showcasing the change in pressure and temperature of the solution over time and wall pressure results for both steady and transient cases can be seen in Figure 5.24.
Figure 5.23: Series of centerplane temperature (left) and pressure (right) results for transient case using the modified Chinitz model and an equivalence ratio of 1.1
Figure 5.24: Mach 7, $\phi = 1.1$ transient case: Comparison of injector-side wall pressure for steady-state and transient analysis
Figure 5.25: Series of centerplane temperature (left) and pressure (right) results for transient case using Chinitz model with 1/2 activation energies and an equivalence ratio of 1.1
5.2 Mach 10 Test Case

Results were also obtained for a Mach number of 10 with simulated flight and corresponding test conditions given in Table 4.1 and Table 4.2. Experimental tests at this condition were not slated to start until after publication of this thesis, so there is not yet any data available to allow for comparisons.

5.2.1 Tare Flow

As with the Mach 7 case, results were first obtained for the tare case without any fuel injection using both variations of Menter’s model. Again, the solutions obtained are very similar to each other. Inlet pressure and Mach number contours can be seen in Figure 5.26 for Menter’s BSL model; virtually no discernible difference could be seen with the SST case. Overall, the flow appears to be similar to the Mach 7 case; however, the greater flow enthalpy has allowed the flow to remain attached to the wall in the area between the low pressure region formed by the expansion wave at the transition between the forebody and isolator and the first of the reflected shock waves coming off the cowl.

Wall pressure results are plotted in Figure 5.27 for both BSL and SST cases for the centerplane of the injector-side wall. Again, the most discernible difference between the two models is the large pressure rise along the injector ramp. The BSL model again predicts much greater pressures along the length of the injector and now predicts a maximum pressure towards the center of the ramp followed by a small decrease in pressure towards the end of the ramp, while the SST model still predicts a maximum pressure at the end of the ramp. Without any experimental data in this region it is difficult to determine which result is more realistic. The BSL model also still predicts higher peak pressures throughout the rest of the engine, though the difference between the two models is even smaller than seen at the Mach 7 conditions. The reason the reduced difference is likely due to the lack of flow separation at the entrance to the isolator and the greater flow energy reducing the impact of the adverse pressure gradient at the shock wave / boundary layer interaction, as the primary difference between the BSL and SST model is in the modeling of the principal turbulent shear stress in this region. Even though the difference between the two models is not very significant, only the BSL model was chosen to be used for all subsequent runs at the Mach 10 condition. This is due to the slightly more accurate results of the BSL model over the SST model at the Mach 7 condition and due to recent work using the University of Virginia’s DMSJ engine suggesting that the BSL model predicts more accurate shock trains [10].
Figure 5.26: Inlet / isolator centerplane pressure (top) and Mach number (bottom) for Mach 10 tare case using Menter’s BSL model

Figure 5.27: Mach 10 tare case: centerplane, injector-side wall pressure comparison
5.2.2 Fuel / Air Mixing

Similarly to the Mach 7 case, fuel / air mixing results were generated for both the hydrogen and the silane - hydrogen fuels before allowing combustion to occur. Temperature and pressure contours in the injector and combustor region are given in Figure 5.28 and Figure 5.29 for the silane - hydrogen blend; there was virtually no difference between the results of the two fuels. It can immediately be seen that conditions are much warmer and at higher pressure than in the Mach 7 case, owing to the greater flow enthalpies. Temperatures range from 750 K to 1250 K in the highly mixed region between the fuel plume and core flow at the start of the combustor and are within the range of initial temperatures the Chinitz silane reaction mechanism was optimized for. Though pressures are still slightly lower than what the Chinitz model was optimized for, ranging from 30,000 Pa to 45,000 Pa, they are much closer than seen at the Mach 7 condition.

![Figure 5.28: Mach 10 silane - hydrogen / air mixing case: combustor centerplane temperature](image1)

![Figure 5.29: Mach 10 silane - hydrogen / air mixing case: combustor centerplane pressure](image2)

Nitrogen mass fractions can be seen in Figure 5.30 where the black lines represent levels of 75%, 85% and 95% of the free-stream nitrogen mass fraction. Compared to the Mach 7 case with an equivalence ratio of 0.8, mixing occurs slower with the entirety of the flow reaching its
75% mixing value by $x = 14.2h$ and the 85% value by $x = 25.0h$. This is due to the greater energy of the flow causing the fuel plume to be pushed against the injector-side wall to a greater extent, diminishing mixing from that direction.

Wall pressures along the centerplane of the injector-side wall are given in Figure 5.31 for both fuels along with the BSL model tare results. It can be seen that the addition of the fuels has resulted in a small increase in pressure over that of the tare case owing to the additional compression caused by the increased mass flow and the injection process. Looking back to centerplane pressure contours, Figure 5.29, a compression wave can be seen to be formed at the shear layer of second fuel “bubble” resulting from the Mach disk wave structure caused by the fuel being injected in an underexpanded state. This results in a second shock wave reflecting down the combustor, trailing the injector ramp induced shock wave. It is similar
to the shock caused by the injector-turned flow hitting the injector-side wall in the tare case, but occurs slightly upstream and results in a greater pressure rise, and it is what causes the largest differences in the wall pressure between the tare and mixing cases. A small difference in pressures between the two fuels can also be seen at a few locations owing to the greater molecular weight of the silane-hydrogen blend resulting in greater mass flow over that of pure hydrogen, but also a greater decrease in momentum of the flow.

5.2.3 Hydrogen / Air Combustion

Unlike in the Mach 7 test case, the combustion of pure hydrogen could be maintained at the Mach 10 conditions owing to the higher initial combustor temperatures and pressures, though it failed to self ignite. This can readily be seen in the OH mass fraction contours seen in Figure 5.32. OH is a radical both rapidly formed in the initial breakdown of the fuel and consumed in the creation of the saturated combustion products, making it useful for determining where combustion is actually taking place. This contour shows combustion starting in the warmer boundary layer along the injector-side wall near the injector, before slowly enveloping the rest of the fuel plume. However, this is a very slow process with it not completely surrounding the rest of the fuel plume until about 40% ($x = 23h$) of the way down the combustor. Even then, the greatest concentration still occurs in the boundary layer, even up until the point where the fuel leaves the combustor. This indicates the combustion process is occuring very slowly, and a significant quantity of the fuel is escaping the system. This greatly reduces the amount of heat release and pressure rise that can be achieved, decreasing the effectiveness of the engine.

![Figure 5.32: Mach 10 H$_2$ combustion case: combustor OH mass fraction](image)

Figure 5.32: Mach 10 H$_2$ combustion case: combustor OH mass fraction
Viewing temperatures contours, Figure 5.33, little heat release is seen, with the majority of it occurring along the boundary layer near the exit of the combustor. Wall pressure graphs for both the mixing and combusting case are given in Figure 5.34. This shows nearly no pressure rise occurring until about 20h downstream of the injector and only a relatively small pressure rise occurring further downstream. As the flow exits the combustor, only an increase in pressure of 25.7% is realized over that of the mixing case. It is likely that the combustor would need to be greatly increased in length in order to allow for complete combustion and achievement of a more significant pressure rise.
5.2.4 Silane - Hydrogen / Air Combustion

As mixing temperatures were within the range of initial temperatures the Chinitz model was optimized for and pressures were nearly within the range of optimized initial pressures, only the standard Chinitz model was examined at the Mach 10 test condition. While it was able to maintain combustion when started from a combusting solution, it was still unable to auto ignite. Viewing OH mass fraction contours, Figure 5.35, for both 100% gas phase and instantaneous formation into solid phase considerations of SiO\textsubscript{2}, it can be seen that combustion starts primarily in the warmer boundary layer near the injector, though a small amount is taking place along the fuel / air shear layer all the way up to the injector ramp. This very quickly spreads to envelope the rest of the fuel plume by $x \approx 8.5h$ for the gas phase SiO\textsubscript{2} consideration and $x \approx 5.5h$ for solid phase SiO\textsubscript{2}, far upstream of what was seen for the combustion of pure hydrogen. Both silane cases also react much more intensely than the pure hydrogen case, as evidenced by the much higher OH mass fractions throughout the reacting region. Comparing the two silane cases, the solid phase SiO\textsubscript{2} results in greater OH formation over that of the gas phase SiO\textsubscript{2} consideration and shows combustion occurring closer to the injector. This is due to the greater heat release caused by the more negative heat of formation of the solid phase increasing temperatures and, thus, reaction rates. This is clearly seen in the temperature contours in Figure 5.36 with temperatures being higher throughout the combustor when using solid phase SiO\textsubscript{2}. Compared to pure hydrogen, both silane cases show much higher temperatures, indicating greater heat release and more efficient combustion with more of the fuel reaching its fully oxidized state.

![Figure 5.35: Mach 10 SiH\textsubscript{4} combustion case: combustor OH mass fraction](image)

Wall pressure results for both combusting cases and the mixing case are given in Figure 5.37. It can be seen that both combusting cases give a much greater pressure rise over the mixing case than was seen using the pure hydrogen fuel resulting in pressures 52.8% higher than for
Figure 5.36: Mach 10 SiH₄ combustion case: combustor temperature

Figure 5.37: Mach 10 SiH₄ combustion case: centerplane, injector-side wall pressure comparison
the hydrogen fuel at the exit when using the solid phase consideration. This also indicates that the addition of silane greatly enhances combustion, allowing it to initiate sooner and driving it further to completion. Considering SiO\textsubscript{2} formation in its solid phase again results in a greater pressure rise over the gas phase consideration, as expected; however, this pressure rise is not nearly as substantial as seen at the Mach 7 test condition, only being 13.5% greater at the engine exit. It was seen in the Mach 7 case, that the impingement of the fuel plume into the core flow could have a greater effect on the combustor pressure near the injector than could be accounted for just by the heat release of combustion. In that case, even though most combustion occurred downstream, the relatively small amount of extra heat released near the injector by the solid phase over the gas phase caused the core flow to be pinched to a greater extent, driving the very large pressure difference between the two cases. This is much less of a factor at the Mach 10 condition owing to the lower equivalence ratio reducing the size of the fuel plume and due to the use of the standard Chinitz model. Since this model lacks the low temperature reaction pathway of the Britten model or the increased low temperature reaction rates of the modified model, it should lead to slower combustion in the cooler regions near the injector, pushing heat release even further downstream and diminishing the difference between the two phases near the injector.

As was seen in the Mach 7 case, the formation of SiO\textsubscript{2} is greatly dependent on its phase modeling. This is seen in SiO\textsubscript{2} mass fraction contours in Figure 5.38. In the gas phase consideration, it is seen that a significant quantity of SiO\textsubscript{2} is able to build up in the core of the fuel plume only in the initial combustion of the fuel near the injector. As temperature rises as the flow travels downstream, this SiO\textsubscript{2} is consumed due to the backward rate constant in SiO\textsubscript{2} forming reactions being calculated from an equilibrium constant in the Chinitz model.
This results in the release of an O atom, allowing for a greater formation of water and the unsaturated combustion product SiO. A small amount continues to form in the reacting region between the fuel plume and core flow, but none is able to survive in the fuel rich center of the plume. This demonstrates that even with the smaller equivalence ratio, mixing is still less than perfect and sufficient amounts of oxygen are unable to diffuse into the center of the fuel plume. When its solid phase is considered, significantly more SiO$_2$ is formed, and it continues to exist in within the fuel rich center of the fuel plume. Please note that the scales used on the two images are different. This was done in order to show better show the existence of SiO$_2$ throughout the combustor for both cases.
SUMMARY AND CONCLUSIONS

Computational results using RANS turbulence modeling were generated for a dual-mode scramjet engine operating in its hypersonic regime for two test conditions, simulated Mach 7 and Mach 10 flight, and were compared to experimental results obtained at NASA’s HYPULSE shock tunnel facility for both reacting and tare (no-injection) cases at the Mach 7 test conditions. Tare results indicated good agreement with experimental data in general, though there were some differences with peak pressures in the isolator and shock locations in the combustor. Using Menter’s BSL model gave slightly more accurate results than the SST model despite the presence of a large shock-induced separation region at the inlet to the isolator.

Combusting results were obtained using a fuel blend of 20% silane / 80% hydrogen, as pure hydrogen was unable to be ignited in the experiment due to the low static pressures and temperatures at the isolator exit. Reaction mechanisms by Jachimowski and McLain [17] and Chinitz [6] were unable to maintain combustion of the fuel. As both of these models were developed using high temperature and pressure shock tube data, they failed to reproduce the pyrophoric nature of silane at low temperatures. A reaction mechanism by Britten, Tong, and Westbrook [5] includes a separate low temperature reaction pathway but is far more computationally expensive. To keep computational costs low, modifications were first made to the Chinitz model in order to match low temperature ignition times generated by this model before the full BTW model was implemented. Both of these models achieved similar results and were able to sustain combustion, suggesting that the modification process can allow for some degree of accuracy in replicating the more expensive model, though it is far from ideal. However, they were still unable to self ignite, though, after ignition was forced, they indicated a flame sitting much closer to the injector than seen in the experiment. This illustrates the difficulty in accurately modeling flames lifted far from their injection point.

While all reactions take place in the gas phase, the saturated combustion product SiO$_2$ is
a solid at flame temperatures. To determine upper and lower bounds of the heat release that could be expected, SiO$_2$ has been modeled using both pure gas phase and pure solid phase thermodynamic data using the modified Chinitz model and both pure gas phase and a finite rate reaction condensing it from a gas to a solid using the BTW model. Solid phase modeling results indicate greater heat release and a very large increase in pressure over that of the gas phase results near the injector, a much greater increase than could be expected purely by the extra heat release. This is primarily attributed to the growth of a recirculation region at the base of the injector leading to a greater blockage of the core flow. The difference in pressure between results of the two phase modeling at the exit of the combustor is much more reasonable, and very good agreement with experimental pressure data in this region was achieved when using solid phase thermodynamic data. This suggests that even though the initial combustion of the fuel is not being modeled accurately, the reaction mechanisms are able to achieve an accurate equilibrium result by the end of the combustor. Finite rate condensation from gas to solid phase indicated an extremely rapid transition with virtually all of the SiO$_2$ existing in its solid phase, validating the instantaneous formation assumption.

Transient analysis indicated the presence of a significant amount of fuel upstream of the injector in the isolator, inlet, and forebody regions before testing starts. However, this was found to have no effect on the initial ignition of the fuel. Further analysis showed combusting results resulted in essentially the same solution as seen in the steady-state analysis, indicating that facility start-up transients do not need to be considered.

Computational results have also been obtained using a Mach 10 flight condition, though no experimental data is available to allow for comparisons yet. Mixing results indicate much warmer combustor temperatures and pressure, allowing for the standard Chinitz silane mechanism to maintain combustion. Combustion of the pure hydrogen fuel could also be obtained, but combustor temperature and pressure rise was not nearly as substantial as was seen with the silane - hydrogen blend fuel. This clearly demonstrated the usefulness of silane as a fuel additive in serving as an ignition and combustion aid.

More accurate results may be achieved using LES / RANS modeling, though it is unlikely this alone would enable better agreement with experimental data at the front half of the combustor in the Mach 7 combusting case. Instead, the low temperature pathway used by the BTW model needs to be completely reexamined so that it can self ignite at the cold Mach 7 conditions but also maintain a detached flame at the location seen in the experimental data. Using the BTW model for the Mach 10 condition should reveal the importance of its low temperature mechanism at much warmer conditions and could serve to test the accuracy of the Chinitz model until experimental data becomes available.
REFERENCES


## A.1 Jachimowski: Hydrogen / Air Mechanism

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*The rate coefficients are given in the form $k = AT^D e^{-E/RT}$; units are in seconds, moles, cubic centimeters, calories, and degrees Kelvin.

*Third body efficiencies for all ternolecular reactions are 2.5 for $M = H_2$, 16.0 for $M = H_2O$, 4.0 for $M = CO_2$, and 1.0 for all other M.
A.2 Jachimowski and McLain: Silane - Hydrogen / Air Mechanism

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<td>( \text{OH} + \text{SiH}_4 \rightarrow \text{H}_2 \text{O} + \text{SiH}_3 )</td>
<td>( 8.4 \times 10^{12} \text{ exp}(-100/RT) )</td>
</tr>
<tr>
<td>( \text{H} + \text{SiH}_3 \rightarrow \text{SiH}_2 + \text{H}_2 )</td>
<td>( 1.5 \times 10^{13} \text{ exp}(-2500/RT) )</td>
</tr>
<tr>
<td>( \text{O} + \text{SiH}_3 \rightarrow \text{SiH}_2 \text{O} + \text{H} )</td>
<td>( 1.3 \times 10^{14} \text{ exp}(-2000/RT) )</td>
</tr>
<tr>
<td>( \text{OH} + \text{SiH}_3 \rightarrow \text{SiH}_2 \text{O} + \text{H}_2 )</td>
<td>( 5.0 \times 10^{12} \text{ exp}(-2000/RT) )</td>
</tr>
<tr>
<td>( \text{SiH}_3 + \text{O}_2 \rightarrow \text{SiH}_2 \text{O} + \text{OH} )</td>
<td>( 8.6 \times 10^{14} \text{ exp}(-11400/RT) )</td>
</tr>
<tr>
<td>( \text{SiH}_2 + \text{O}_2 \rightarrow \text{HSiO} + \text{OH} )</td>
<td>( 1.0 \times 10^{14} \text{ exp}(-3700/RT) )</td>
</tr>
<tr>
<td>( \text{H} + \text{SiH}_2 \text{O} \rightarrow \text{H}_2 + \text{HSiO} )</td>
<td>( 3.3 \times 10^{14} \text{ exp}(-10500/RT) )</td>
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<tr>
<td>( \text{O} + \text{SiH}_2 \text{O} \rightarrow \text{OH} + \text{HSiO} )</td>
<td>( 1.8 \times 10^{13} \text{ exp}(-3080/RT) )</td>
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<tr>
<td>( \text{OH} + \text{SiH}_2 \text{O} \rightarrow \text{H}_2 \text{O} + \text{HSiO} )</td>
<td>( 7.5 \times 10^{12} \text{ exp}(-170/RT) )</td>
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<tr>
<td>( \text{H} + \text{HSiO} \rightarrow \text{H}_2 + \text{SiO} )</td>
<td>( 2.0 \times 10^{14} )</td>
</tr>
<tr>
<td>( \text{O} + \text{HSiO} \rightarrow \text{OH} + \text{SiO} )</td>
<td>( 1.0 \times 10^{14} )</td>
</tr>
<tr>
<td>( \text{OH} + \text{HSiO} \rightarrow \text{H}_2 \text{O} + \text{SiO} )</td>
<td>( 1.0 \times 10^{14} )</td>
</tr>
<tr>
<td>( \text{HSiO} + \text{M} \rightarrow \text{H}_2 + \text{SiO} + \text{M} )</td>
<td>( 5.0 \times 10^{14} \text{ exp}(-29000/RT) )</td>
</tr>
<tr>
<td>( \text{HSiO} + \text{O}_2 \rightarrow \text{SiO} + \text{HO}_2 )</td>
<td>( 3.0 \times 10^{12} \text{ exp}(-29000/RT) )</td>
</tr>
<tr>
<td>( \text{HSiO} + \text{HO}_2 \rightarrow \text{HSiO} + \text{H}_2 \text{O}_2 )</td>
<td>( 1.0 \times 10^{12} \text{ exp}(-8000/RT) )</td>
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<tr>
<td>( \text{SiO} + \text{O} + \text{M} \rightarrow \text{SiO}_2 + \text{M} )</td>
<td>( 2.5 \times 10^{15} \text{ exp}(-4370/RT) )</td>
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<tr>
<td>( \text{SiO} + \text{OH} \rightarrow \text{SiO}_2 + \text{H} )</td>
<td>( 4.0 \times 10^{12} \text{ exp}(-5700/RT) )</td>
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<tr>
<td>( \text{SiO} + \text{O}_2 \rightarrow \text{SiO}_2 + \text{O} )</td>
<td>( 1.0 \times 10^{13} \text{ exp}(-6500/RT) )</td>
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</tbody>
</table>

*The rate coefficient is defined by \( k = A \text{ exp}(-E/RT) \) where \( A \) is in \( s^{-1} \) for unimolecular reactions, \( \text{cm}^3/\text{mole} \cdot \text{s} \) for bimolecular reactions, and \( \text{cm}^6/\text{mole}^2 \cdot \text{s} \) for termolecular reactions. The activation energy \( E \) is in \( \text{cal/mole} \), \( R = 1.987 \text{ cal/mole} \cdot \text{K} \), and \( T \) is temperature in \( \text{K} \).

†Determined in this study.

‡M is a third-body molecule.
## TABLE II.- HYDROGEN REACTION MECHANISM

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate coefficient</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2 + \text{O}_2 \rightarrow \text{OH} + \text{OH}$</td>
<td>$1.7 \times 10^{13} \exp(-48100/RT)$</td>
<td>Jachimowski and Houghton 1971</td>
</tr>
<tr>
<td>$\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$</td>
<td>$1.2 \times 10^{17} \exp(-16600/RT)$</td>
<td>Schott 1973</td>
</tr>
<tr>
<td>$\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$</td>
<td>$2.1 \times 10^{14} \exp(-13750/RT)$</td>
<td>Schott 1973</td>
</tr>
<tr>
<td>$\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$</td>
<td>$3.2 \times 10^7 \text{T}^{1.8} \exp(-3030/RT)$</td>
<td>Gardiner et al. 1974</td>
</tr>
<tr>
<td>$\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}$</td>
<td>$5.5 \times 10^{13} \exp(-7000/RT)$</td>
<td>Gardiner et al. 1973</td>
</tr>
<tr>
<td>$\text{H} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O} + \text{M}$</td>
<td>$1.4 \times 10^{23} \text{T}^{-2.0}$</td>
<td>Baulch et al. 1972</td>
</tr>
<tr>
<td>$\text{M} = \text{H}_2$</td>
<td>$2.2 \times 10^{22} \text{T}^{-2.0}$</td>
<td>Baulch et al. 1972</td>
</tr>
<tr>
<td>$\text{M} = \text{H}_2$</td>
<td>$3.9 \times 10^{12} \text{T}^{-1.0}$</td>
<td>Baulch et al. 1972</td>
</tr>
<tr>
<td>$\text{M} = \text{H}_2\text{O}$</td>
<td>$6.5 \times 10^{17} \text{T}^{-1.0}$</td>
<td>Baulch et al. 1972</td>
</tr>
<tr>
<td>$\text{H} + \text{H}_2 + \text{M}$</td>
<td>$2.6 \times 10^{12} \text{T}^{-1.0}$</td>
<td>Baulch et al. 1972</td>
</tr>
<tr>
<td>$\text{M} = \text{H}_2\text{O}$</td>
<td>$3.9 \times 10^{12} \text{T}^{-1.0}$</td>
<td>Baulch et al. 1972</td>
</tr>
<tr>
<td>$\text{M} = \text{H}_2\text{O}$</td>
<td>$6.5 \times 10^{17} \text{T}^{-1.0}$</td>
<td>Baulch et al. 1972</td>
</tr>
<tr>
<td>$\text{H} + \text{O}_2 + \text{M} \rightarrow \text{H}_2\text{O}_2 + \text{M}$</td>
<td>$7.0 \times 10^{18} \text{T}^{-1.0}$</td>
<td>Slack 1977</td>
</tr>
<tr>
<td>$\text{M} = \text{H}_2\text{O}$</td>
<td>$4.4 \times 10^{19} \text{T}^{-1.0}$</td>
<td>Slack 1977</td>
</tr>
<tr>
<td>$\text{M} = \text{H}_2\text{O}$</td>
<td>$3.2 \times 10^{18} \text{T}^{-1.0}$</td>
<td>Slack 1977</td>
</tr>
<tr>
<td>$\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$</td>
<td>$5.0 \times 10^{13} \exp(-1000/RT)$</td>
<td>Lloyd 1974</td>
</tr>
<tr>
<td>$\text{H} + \text{HO}_2 \rightarrow \text{H}_2 + \text{O}_2$</td>
<td>$2.5 \times 10^{13} \exp(-700/RT)$</td>
<td>Lloyd 1974</td>
</tr>
<tr>
<td>$\text{H} + \text{HO}_2 \rightarrow \text{OH} + \text{OH}$</td>
<td>$2.0 \times 10^{14} \exp(-1900/RT)$</td>
<td>Lloyd 1974</td>
</tr>
<tr>
<td>$\text{O} + \text{HO}_2 \rightarrow \text{OH} + \text{O}_2$</td>
<td>$5.0 \times 10^{13} \exp(-1000/RT)$</td>
<td>Lloyd 1974</td>
</tr>
<tr>
<td>$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$</td>
<td>$2.0 \times 10^{12}$</td>
<td>Slack 1977</td>
</tr>
<tr>
<td>$\text{HO}_2 + \text{H}_2 \rightarrow \text{H}_2\text{O}_2 + \text{H}$</td>
<td>$3.0 \times 10^{11} \exp(-18700/RT)$</td>
<td>Slack 1977</td>
</tr>
<tr>
<td>$\text{OH} + \text{HO}_2 \rightarrow \text{HO}_2 + \text{H}_2\text{O}$</td>
<td>$1.0 \times 10^{13} \exp(-1800/RT)$</td>
<td>Baulch et al. 1972</td>
</tr>
<tr>
<td>$\text{M} + \text{H}_2\text{O}_2 \rightarrow \text{OH} + \text{OH} + \text{M}$</td>
<td>$1.2 \times 10^{17} \exp(-45500/RT)$</td>
<td>Baulch et al. 1972</td>
</tr>
</tbody>
</table>

*The rate coefficient is defined by $k = \text{A} \exp(-E/RT)$. The rate coefficient units are $\text{cm}^{-3} \text{s}^{-1}$ for unimolecular reactions, $\text{cm}^3$/mole-s for bimolecular reactions, and $\text{cm}^6$/mole$^2$-s for termolecular reactions. The activation energy $E$ is in cal/mole, $R = 1.987$ cal/mole$\cdot$K, $T$ is temperature in K, and $n$ is a temperature exponent.

$^1$M is a third-body molecule.
### A.3 Chinitz: Silane - Hydrogen / Air Mechanism

<table>
<thead>
<tr>
<th>Reaction</th>
<th>A</th>
<th>n</th>
<th>E</th>
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</thead>
<tbody>
<tr>
<td>SiH4 + SiH3</td>
<td>2 SiH3 + H</td>
<td>2.00E+17</td>
<td>0.0</td>
</tr>
<tr>
<td>SiH4 + O2</td>
<td>SiH3 + H20</td>
<td>2.00E+14</td>
<td>0.0</td>
</tr>
<tr>
<td>SiH4 + O</td>
<td>SiH3 + OH</td>
<td>2.88E+13</td>
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<tr>
<td>SiH4 + OH</td>
<td>SiH3 + H20</td>
<td>4.10E+12</td>
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<td>SiH4 + H2</td>
<td>SiH3 + H20</td>
<td>8.64E+12</td>
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<td>SiH4 + HO2</td>
<td>SiH3 + H202</td>
<td>3.00E+12</td>
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<tr>
<td>SiH3 + O2</td>
<td>SiH20 + OH</td>
<td>7.72E+14</td>
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<tr>
<td>SiH3 + O</td>
<td>SiH20 + H</td>
<td>1.37E+14</td>
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</tr>
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<td>SiH3 + OH</td>
<td>SiH20 + H2</td>
<td>5.00E+12</td>
<td>0.0</td>
</tr>
<tr>
<td>M + SiH20</td>
<td>HS10 + H</td>
<td>5.00E+16</td>
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<td>SiH20 + H</td>
<td>HS10 + H2</td>
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<td>SiH20 + O</td>
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<td>Si10 + H20</td>
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<td>SiH20 + O2</td>
<td>Si10 + HO2</td>
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<td>Si10 + H202</td>
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<tr>
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<td>H + S10</td>
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<td>HS10 + H</td>
<td>S10 + H2</td>
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</tr>
<tr>
<td>HS10 + O</td>
<td>S10 + OH</td>
<td>1.00E+14</td>
<td>0.0</td>
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<td>HS10 + OH</td>
<td>S10 + H20</td>
<td>1.00E+14</td>
<td>0.0</td>
</tr>
<tr>
<td>S10 + O2</td>
<td>S10 + H202</td>
<td>1.20E+14</td>
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</tr>
<tr>
<td>S10 + O</td>
<td>S10 + O2</td>
<td>1.00E+13</td>
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</tr>
<tr>
<td>S10 + OH</td>
<td>S10 + H</td>
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<td>S10 + O2 + M</td>
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<td>H2 + OH</td>
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<td>H202 + M</td>
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<td>M + H202</td>
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<td>O + H</td>
<td>OH + M</td>
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<td>H20 + O</td>
<td>OH + OH</td>
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<tr>
<td>H2 + OH</td>
<td>H20 + H</td>
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<tr>
<td>O2 + H</td>
<td>OH + O</td>
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<tr>
<td>H2 + O</td>
<td>OH + H</td>
<td>7.51E+13</td>
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</tr>
</tbody>
</table>

*The coefficients are for the rate coefficient in the forward direction written in the form \( k_f = A \eta^n \exp(-E/RT) \), where \( A \) is in cm³/mole·s for bimolecular reactions, and cm⁶/mole·s·s for termolecular reactions. The activation energy \( E \) is in cal/mole, \( R = 1.987 \) cal/mole·K, and \( T \) is the temperature in K. \( M \) is any third-body molecule. (Note that 2.00E+17 = 2.00 \times 10^{17}, etc.)*
A.4 Britten, Tong, and Westbrook: Silane - Hydrogen / Air Mechanism

Kinetic constants for SiH₄–O₂ reaction mechanism, in cal, cm²/mol, s units

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Ref.</th>
<th>Δf</th>
<th>nj</th>
<th>Eᵣ</th>
<th>Δf</th>
<th>nᵣ</th>
<th>Eᵣ</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>H₂O + M = H + OH + M</td>
<td>21</td>
<td>2.20e + 16</td>
<td>0</td>
<td>1.00e + 05</td>
<td>1.00e + 13</td>
<td>-2.0</td>
<td>0</td>
</tr>
<tr>
<td>R2</td>
<td>H₂O₂ + M = H + O₂ + M</td>
<td>21</td>
<td>2.74e + 15</td>
<td>0</td>
<td>4.00e + 04</td>
<td>1.00e + 15</td>
<td>-1.00e + 03</td>
<td>0</td>
</tr>
<tr>
<td>R3</td>
<td>OH + M = O + H + M</td>
<td>21</td>
<td>8.00e + 19</td>
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<td>1.00e + 05</td>
<td>1.00e + 16</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>R4</td>
<td>O₂ + M = O + O + M</td>
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<td>5.10e + 15</td>
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<td>1.15e + 05</td>
<td>4.70e + 15</td>
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</tr>
<tr>
<td>R5</td>
<td>H₂ + M = H + H + M</td>
<td>21</td>
<td>2.30e + 14</td>
<td>0</td>
<td>5.00e + 04</td>
<td>3.00e + 15</td>
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<tr>
<td>R6</td>
<td>O₂ + H₂ = OH + OH</td>
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<td>8.00e + 14</td>
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<td>4.00e + 04</td>
<td>2.70e + 13</td>
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<td>R7</td>
<td>HO₂ = O₂ + O</td>
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<td>5.00e + 13</td>
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<td>1.00e + 03</td>
<td>6.42e + 12</td>
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<tr>
<td>R8</td>
<td>H + O₂ = OH + H₂</td>
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<tr>
<td>R9</td>
<td>H₂ + O = OH + H</td>
<td>21</td>
<td>1.50e + 10</td>
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<td>5.00e + 03</td>
<td>8.30e + 04</td>
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<tr>
<td>R10</td>
<td>O + H₂O = OH + H₂</td>
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<td>1.85e + 04</td>
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</tr>
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<td>H + H₂O = OH + H₂</td>
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<td>9.50e + 13</td>
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<td>2.00e + 04</td>
<td>2.35e + 13</td>
<td>0</td>
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</tr>
<tr>
<td>R12</td>
<td>H₂O + M = O + OH + M</td>
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<td>5.10e + 21</td>
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<td>5.00e + 04</td>
<td>1.00e + 17</td>
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</tr>
<tr>
<td>R13</td>
<td>SH₂ + OH = SiH₂ + H₂O</td>
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<td>8.75e + 11</td>
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<td>9.50e + 01</td>
<td>5.50e + 12</td>
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</tr>
<tr>
<td>R14</td>
<td>SH₂ + O = SiH₂ + OH</td>
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<td>4.00e + 12</td>
<td>0</td>
<td>1.75e + 03</td>
<td>2.35e + 11</td>
<td>0</td>
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</tr>
<tr>
<td>R15</td>
<td>SiH₂ + H₂O = SiH₂ + H₂O</td>
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<td>1.05e + 04</td>
<td>4.65e + 11</td>
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<td></td>
</tr>
<tr>
<td>R16</td>
<td>SiH₂O₂ = SiH₂ + O₂</td>
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<td>-1.0</td>
<td>7.10e + 04</td>
<td>3.00e + 16</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>R17</td>
<td>H + HO₂ = OH + OH</td>
<td>21</td>
<td>2.50e + 14</td>
<td>0</td>
<td>1.50e + 03</td>
<td>1.25e + 13</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>R18</td>
<td>H + HO₂ = H₂ + O₂</td>
<td>21</td>
<td>2.50e + 13</td>
<td>0</td>
<td>7.00e + 02</td>
<td>5.50e + 13</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>R19</td>
<td>OH + HO₂ = HO₂ + O₂</td>
<td>21</td>
<td>5.00e + 13</td>
<td>0</td>
<td>1.00e + 03</td>
<td>6.33e + 14</td>
<td>0</td>
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<tr>
<td>R20</td>
<td>H₂O₂ + O = H₂O + HO</td>
<td>21</td>
<td>4.00e + 13</td>
<td>0</td>
<td>4.20e + 04</td>
<td>1.00e + 13</td>
<td>0</td>
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</tr>
<tr>
<td>R21</td>
<td>H₂O₂ = M = OH + OH + M</td>
<td>21</td>
<td>1.60e + 17</td>
<td>0</td>
<td>4.50e + 04</td>
<td>9.10e + 14</td>
<td>0</td>
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</tr>
<tr>
<td>R22</td>
<td>H₂O₂ + H₂ = H₂O + H₂</td>
<td>21</td>
<td>7.30e + 11</td>
<td>0</td>
<td>1.87e + 04</td>
<td>1.75e + 12</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>R23</td>
<td>SH₂ + O₂ = SO₂ + H₂</td>
<td>4</td>
<td>1.00e + 14</td>
<td>0</td>
<td>3.70e + 03</td>
<td>7.60e + 06</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>R24</td>
<td>SH₂O = H + SO₂ + H₂O</td>
<td>4</td>
<td>3.30e + 14</td>
<td>0</td>
<td>1.05e + 04</td>
<td>4.65e + 11</td>
<td>0</td>
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<tr>
<td>R25</td>
<td>SH₂O + HO₂ = SO₂ + H₂O</td>
<td>4</td>
<td>1.05e + 12</td>
<td>0</td>
<td>9.00e + 03</td>
<td>2.20e + 10</td>
<td>0</td>
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<tr>
<td>R26</td>
<td>SiH₂ = SiH₂ + H</td>
<td>15</td>
<td>5.00e + 12</td>
<td>0</td>
<td>5.20e + 04</td>
<td>7.10e + 07</td>
<td>0</td>
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<tr>
<td>R27</td>
<td>SiH₂ = SiH₂ + H</td>
<td>15</td>
<td>3.00e + 15</td>
<td>0</td>
<td>9.30e + 04</td>
<td>2.68e + 11</td>
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<td>R28</td>
<td>H₂O + M + H₂ = SO + M</td>
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<td>5.00e + 14</td>
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<td>H₂O + H + SO + H₂</td>
<td>4</td>
<td>2.00e + 14</td>
<td>0</td>
<td>0</td>
<td>1.15e + 15</td>
<td>9.00e + 04</td>
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<td>R30</td>
<td>H₂O + O + SO + OH</td>
<td>4</td>
<td>1.00e + 14</td>
<td>0</td>
<td>0</td>
<td>2.85e + 14</td>
<td>8.75e + 04</td>
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<tr>
<td>R31</td>
<td>H₂O + OH = SO₂ + H₂O</td>
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<td>0</td>
<td>0</td>
<td>2.85e + 15</td>
<td>1.45e + 05</td>
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<td>R32</td>
<td>H₂O + O₂ = SO₂ + H₂O</td>
<td>4</td>
<td>3.00e + 12</td>
<td>0</td>
<td>0</td>
<td>5.25e + 12</td>
<td>5.45e + 04</td>
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<tr>
<td>R33</td>
<td>SO₂ + O₂ = SO₃ + O</td>
<td>4</td>
<td>1.00e + 13</td>
<td>0</td>
<td>0.50e + 03</td>
<td>0</td>
<td>0</td>
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<tr>
<td>R34</td>
<td>SO₂ + OH = SO₃ + H</td>
<td>4</td>
<td>4.00e + 12</td>
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<td>5.70e + 03</td>
<td>0</td>
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<td>R35</td>
<td>SO₂ + M = SO₂ + M + O</td>
<td>4</td>
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<td>0</td>
<td>0</td>
<td>0</td>
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<td>R36</td>
<td>SiH₂O₂ = SiH₂O + OH</td>
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<td>6.00e + 14</td>
<td>0</td>
<td>4.00e + 04</td>
<td>0</td>
<td>0</td>
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<tr>
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<td>SiH₂ + M = SiH₂ + H</td>
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<td>2.50e + 03</td>
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<td>7.60e + 13</td>
<td>0</td>
<td>4.00e + 04</td>
<td>2.57e + 13</td>
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<td>R39</td>
<td>SiH₂ + O = SiH₂ + OH</td>
<td>4</td>
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<td>0</td>
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<td>R40</td>
<td>SiH₂ + SH₂O₂ = SiH₂ + SH₃OH</td>
<td>25</td>
<td>2.00e + 11</td>
<td>0</td>
<td>5.30e + 03</td>
<td>1.05e + 04</td>
<td>0</td>
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<tr>
<td>R41</td>
<td>SiH₂ + SiH₂O₂ = SiH₂ + SiH₃OH</td>
<td>25</td>
<td>1.10e + 13</td>
<td>0</td>
<td>1.50e + 04</td>
<td>7.45e + 11</td>
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<td>R42</td>
<td>SiH₂ + OH = SiH₂ + H₂O</td>
<td>25</td>
<td>1.30e + 13</td>
<td>0</td>
<td>0.50e + 03</td>
<td>3.50e + 10</td>
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<tr>
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<td>SiH₂O₂ = SiH₂O + H₂O</td>
<td>25</td>
<td>4.00e + 10</td>
<td>0</td>
<td>0</td>
<td>3.00e + 12</td>
<td>3.00e + 04</td>
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<td>SiH₂O₂ = Si = SiH₂O + OH</td>
<td>25</td>
<td>6.00e + 14</td>
<td>0</td>
<td>4.85e + 04</td>
<td>2.50e + 10</td>
<td>0</td>
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<tr>
<td>R45</td>
<td>SiH₂O₂ = H = SiH₂O₂ + H</td>
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<td>4.80e + 13</td>
<td>0</td>
<td>7.90e + 03</td>
<td>1.30e + 14</td>
<td>0</td>
<td>1.65e + 04</td>
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</tbody>
</table>
Table A.1: Gas phase to solid phase condensation of SiO\textsubscript{2} implemented in BTW reaction mechanism in cal, cm\textsuperscript{3}, mol, s units

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Ref.</th>
<th>$A_f$</th>
<th>$n_f$</th>
<th>$E_f$</th>
<th>$A'_b$</th>
<th>$n_b$</th>
<th>$E_b$</th>
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<tbody>
<tr>
<td>B46</td>
<td>SiH\textsubscript{3}O + H\textsubscript{2}O$\rightleftharpoons$Si\textsubscript{2}H\textsubscript{3}O + H\textsubscript{2}O</td>
<td>20</td>
<td>1.20e+11</td>
<td>0</td>
<td>9.71e+02</td>
<td>5.20e+12</td>
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<td>1.52e+04</td>
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<td>SiH\textsubscript{3}O + H\textsubscript{2}O$\rightleftharpoons$Si\textsubscript{2}H\textsubscript{3}O + H\textsubscript{2}O</td>
<td>20</td>
<td>1.50e+12</td>
<td>0</td>
<td>5.30e+03</td>
<td>2.50e+09</td>
<td>0</td>
<td>1.06e+04</td>
</tr>
<tr>
<td>B48</td>
<td>Si\textsubscript{2}H\textsubscript{3}O + O$\rightleftharpoons$Si\textsubscript{2}H\textsubscript{3}O + HO</td>
<td>20</td>
<td>1.00e+12</td>
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<td>4.50e+03</td>
<td>3.50e+13</td>
<td>0</td>
<td>3.22e+04</td>
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<td>B48</td>
<td>Si\textsubscript{2}H\textsubscript{3}O + H$\rightleftharpoons$Si\textsubscript{2}H\textsubscript{3}O + H\textsubscript{2}</td>
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<td>3.00e+13</td>
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<td>5.30e+03</td>
<td>4.10e+11</td>
<td>0</td>
<td>1.36e+04</td>
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<tr>
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<td>20</td>
<td>1.70e+12</td>
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<td>1.73e+03</td>
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<td>7.56e+03</td>
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<tr>
<td>B51</td>
<td>Si\textsubscript{2}H\textsubscript{3}O + OH$\rightleftharpoons$Si\textsubscript{2}H\textsubscript{3}O + H\textsubscript{2}O</td>
<td>20</td>
<td>4.00e+12</td>
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<td>1.50e+03</td>
<td>2.30e+11</td>
<td>0</td>
<td>2.56e+04</td>
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<tr>
<td>B52</td>
<td>Si\textsubscript{2}H\textsubscript{3}O + Si\textsubscript{2}H\textsubscript{3}O$\rightleftharpoons$Si\textsubscript{2}H\textsubscript{3}O + Si\textsubscript{2}H\textsubscript{3}O</td>
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<td>1.90e+11</td>
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<td>7.40e+03</td>
<td>1.50e+10</td>
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<td>1.36e+03</td>
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<td>Si\textsubscript{2}H\textsubscript{3}O + Si\textsubscript{2}H\textsubscript{3}O$\rightleftharpoons$Si\textsubscript{2}H\textsubscript{3}O + Si\textsubscript{2}H\textsubscript{3}O</td>
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<td>6.30e+12</td>
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<td>1.42e+04</td>
<td>1.00e+09</td>
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<td>1.06e+04</td>
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<td>B54</td>
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<td>6.30e+12</td>
<td>0</td>
<td>1.42e+04</td>
<td>1.00e+09</td>
<td>0</td>
<td>1.06e+04</td>
</tr>
<tr>
<td>B55</td>
<td>Si\textsubscript{2}H\textsubscript{3}O + O$\rightleftharpoons$Si\textsubscript{2}H\textsubscript{3}O + HO</td>
<td>20</td>
<td>6.30e+12</td>
<td>0</td>
<td>1.42e+04</td>
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<tr>
<td>B56</td>
<td>Si\textsubscript{2}H\textsubscript{3}O + O$\rightleftharpoons$H\textsubscript{2}S\textsubscript{2}O + HO</td>
<td>20</td>
<td>1.00e+11</td>
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<td>7.00e+03</td>
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<td>1.00e+11</td>
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<td>B58</td>
<td>H\textsubscript{2}O + Si\textsubscript{2}H\textsubscript{3}O$\rightleftharpoons$Si\textsubscript{2}H\textsubscript{3}O + H\textsubscript{2}O</td>
<td>27</td>
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<td>6.00e+09</td>
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<td>1.86e+04</td>
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<td>B65</td>
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<td>27</td>
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<tr>
<td>B66</td>
<td>HS\textsubscript{2}OOH$\rightleftharpoons$Si\textsubscript{2}H\textsubscript{3}O + H</td>
<td>27</td>
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<td>2.00e+04</td>
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</tbody>
</table>

*$_f$ forward rate.  
*$_r$ reverse rate.

Table A.1: Gas phase to solid phase condensation of SiO\textsubscript{2} implemented in BTW reaction mechanism in cal, cm\textsuperscript{3}, mol, s units

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$A_f$</th>
<th>$n_f$</th>
<th>$E_{a,f}$</th>
<th>$A'_b$</th>
<th>$n_b$</th>
<th>$E_{a,b}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO\textsubscript{2}(g) $\rightleftharpoons$ SiO\textsubscript{2}(s)</td>
<td>$1.00 \times 10^8$</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
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</tbody>
</table>
This appendix will cover how Chinitz’s 15 species, 45 reaction silane - hydrogen / air reaction model was modified to match ignition times of Britten, Tong, and Westbrook’s 25 species, 70 reaction model at low temperatures. Ignition time was defined as the amount of time it takes for the system to experience a temperature rise equal to 5% of the overall temperature rise experienced at its equilibrium state. Five key chain initiating and chain branching reactions were first identified that had the greatest effect on the start of silane ignition. A separate set of modified Arrhenius coefficients was developed for these reactions and these coefficients were then used to calculate a modified reaction rate constant. This rate constant was blended with the original, unmodified rate constant so that at low temperatures the modified constant would be used and at temperatures above 800 K, the lowest initial temperature the Chinitz model was optimized for, the original rate constant would be used, with a smooth transition inbetween. This was done using the following:

\[
\begin{align*}
    k_{f,i}^u &= A_i^u T^{n_i^u} \exp \left( -\frac{E_i^u}{R T} \right), \\
    k_{f,i}^m &= A_i^m T^{n_i^m} \exp \left( -\frac{E_i^m}{R T} \right) \\
    k_{f,i} &= \begin{cases} 
        k_{f,i}^u \tanh \left( \frac{T}{800} \right) + k_{f,i}^m \left( 1 - \tanh \left( \frac{T}{800} \right) \right), & \text{if } T < 800K \\
        k_{f,i}^u, & \text{if } T \geq 800K
    \end{cases}
\end{align*}
\] (B.1)

(B.2)

where the superscripts \( u \) and \( m \) refer to the original, unmodified coefficients and the new, modified coefficients. The modified Arrhenius coefficients were then determined using an exhaustive search method in order to match ignition times given in [5]. In order to account for the increased heat release of solid phase SiO\(_2\), the model was developed for gaseous phase SiO\(_2\) first and then slightly modified for solid phase SiO\(_2\) in order to maintain correct ignition times.

This process could not match the pressure dependence on the ignition times calculated with
Table B.1: Ignition times for the BTW model and the modified Chinitz model at a pressure of 20,000 Pa

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Britten model</th>
<th>Modified Chinitz model</th>
</tr>
</thead>
<tbody>
<tr>
<td>373 K</td>
<td>$1.52 \times 10^{-4}$ sec</td>
<td>$1.49 \times 10^{-4}$ sec</td>
</tr>
<tr>
<td>393 K</td>
<td>$1.35 \times 10^{-4}$ sec</td>
<td>$1.34 \times 10^{-4}$ sec</td>
</tr>
<tr>
<td>413 K</td>
<td>$7.93 \times 10^{-3}$ sec</td>
<td>$7.95 \times 10^{-3}$ sec</td>
</tr>
</tbody>
</table>

Table B.2: Reactions used to modify Chinitz reaction mechanism. Original Arrhenius coefficients listed above with modified coefficients below for each reaction.

<table>
<thead>
<tr>
<th>Reaction Number</th>
<th>Reaction</th>
<th>A</th>
<th>n</th>
<th>$E_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SiH$_4$ + M $\leftrightarrow$ SiH$_3$ + H + M</td>
<td>2.00E+17</td>
<td>0.0</td>
<td>59000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.20E+14</td>
<td>-2.5</td>
<td>20650</td>
</tr>
<tr>
<td>2</td>
<td>SiH$_4$ + SiH$_3$ $\leftrightarrow$ 2 SiH$_3$ + H</td>
<td>7.76E+11</td>
<td>0.0</td>
<td>6980</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9.70E+10</td>
<td>0.0</td>
<td>3490</td>
</tr>
<tr>
<td>3</td>
<td>SiH$_4$ + O$_2$ $\leftrightarrow$ SiH$_2$O + H$_2$O</td>
<td>2.00E+14</td>
<td>0.0</td>
<td>19600</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.06E+35</td>
<td>-7.5</td>
<td>14110</td>
</tr>
<tr>
<td>8</td>
<td>SiH$_3$ + O$_2$ $\leftrightarrow$ SiH$_2$O + OH</td>
<td>1.72E+14</td>
<td>0.0</td>
<td>11430</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.44E+12</td>
<td>0.0</td>
<td>5140</td>
</tr>
<tr>
<td>15</td>
<td>SiH$_2$O + O$_2$ $\leftrightarrow$ HSiO + HO$_2$</td>
<td>3.95E+14</td>
<td>0.0</td>
<td>29500</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9.88E+15</td>
<td>-2.0</td>
<td>13275</td>
</tr>
</tbody>
</table>

the BTW model at low temperature and pressure due the Chinitz model lacking an equivalent to the low temperature pathway used by the BTW model described in Section 2.3.2. However, very good agreement was obtained for a pressure of 20,000 Pa and a temperature range of 373 K to 413 K, conditions closely matching the mixing region between the fuel plume and core flow in the Mach 7 mixing case. Ignition times of the BTW mechanism and the resulting times of the new modified Chinitz mechanism are given in Table B.1. The modified reactions, with their original coefficients on the same line as the reaction and the new modified coefficients below, are given in Table B.2. While some of these modifications appear severe, they result in reasonable rate constants, as seen in Figure B.1.
Figure B.1: Modified reaction rates