An Experimental and Chemical Kinetics Study of the Combustion of Syngas and High Hydrogen Content Fuels

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Motivation

- Effective combustion of high hydrogen content (HHC) fuels resulting from gasification processes
- Meet/beat emissions standards set by natural gas-fired technologies

Strategic Challenges

- Compositional variation in HHC fuels
- High $\text{H}_2\text{O}/\text{CO}_2$ dilution levels
- Lean-premixed combustion stability limits: ignition, blowout, flashback, acoustic instability...
Challenges: An Example

Burning velocity dependence on pressure -- lean H₂/O₂

- Relevant combustion conditions pushing limits of experimental knowledge
- Kinetic models unable to provide *predictive* performance
Project Goals

• Obtain kinetic, ignition, and flame speed data of HHC fuels, also with H$_2$O/CO$_2$ dilution
• Development of validated high hydrogen syngas kinetic mechanism at pressures of gas turbine conditions
• Development of computationally efficient, reduced kinetic modeling algorithm
Approach

HHC Fuel Kinetic Model:
Global & speciated combustion targets
Accurate emissions predictions $\rightarrow \text{NO}_x$

(Princeton)

MTS Model:
Computational Speed-up

(Ju)

HPLFR Speciation Experiments
(Dryer)

Laminar Flame Experiments
(Ju)

Ignition Delay Experiments
(Santoro)
1. Progress of $\text{H}_2$ Kinetic Model Development
H₂ Kinetic Submodel Development

- Burke et al. (2011) updates to H₂/O₂ kinetic model In press, about to appear online at Int. J. Chem. Kinet. DOI:10.1002/kin.20603
- Manuscript and model available at:
  http://www.princeton.edu/mae/people/faculty/dryer/homepage/kinetic_models/h2-o2-model-update/

- Developed, in large part, to address discrepancies of model predictions with laminar flame experiments at high pressure, low flame temperature conditions similar to lean-premix applications → HO₂ chemistry of increasing importance
- **Ten** recent (1999-present) H₂/O₂ kinetic models/submodels compared against broad range of validation targets in supplemental materials to the publication
- Rate coefficients supported by experiments and *kinetically accurate* computational theory
Addressing the Gap Between Model Predictions and Experiments

- H₂/O₂/He, He:O₂ = 7
- H₂/O₂/He, He:O₂ = 11.5
- H₂/O₂/Ar
Effect of Pressure on Kinetics

\[ \text{H} + \text{O}_2 \xrightarrow{+M} \text{HO}_2 \]

(R1) lower pressures and higher temperatures

(R2) higher pressures and lower temperatures

\[ +\text{H} \quad +\text{OH} \quad +\text{O} \quad +\text{HO}_2 \]

\[ \text{OH} + \text{OH} \quad \text{H}_2\text{O} + \text{O}_2 \quad \text{O}_2 + \text{OH} \quad \text{H}_2\text{O}_2 + \text{O}_2 \]

\[ \text{H}_2 + \text{O}_2 \]

- R1/R2 competition still controls pressure dependence
- New branching and termination reactions become important

Additional $\text{H}_2$ Model Validation Examples: Species Evolution & Ignition Delay Time

- **OH evolution**
  - $1880\text{K}, 1.74\text{ atm}$

- **H$_2$O and OH evolution**
  - $1398\text{K}, 1.91\text{ atm}$

- **Ignition Delay**
H₂ model is foundational . . .

- Predictive performance across a broad range of existing and emerging validation data
  - Global targets – ignition delay, laminar burning rate
  - Speciated targets – shock tubes, flow reactors, flames
    - Stable species and radicals
  - Diluents He, Ar, N₂, (H₂O, CO₂)
  - Tested at lean-premixed applications conditions

BUT . . .

- Model considers reactions of HₓOᵧ species only
- Validation likewise only for the HₓOᵧ system (some global CO₂ dilution effects considered)
- Altered sensitivities for CO/HC mixed into fuel
- Third body reactions of increasing importance (CO₂, H₂O)
- Presently lacks chemistry of NOₓ & other trace species
Important CO/Hydrogen Oxidation Reactions at High Pressures or with Product Dilution

1. (R1) $H + O_2(+M) = HO_2(+M)$, $M = CO_2, H_2O$
2. (R2) $H + OH + M = H_2O + M$
3. (R3) $O + H + M = OH + M$
4. (R4) $H + H + M = H_2 + M$
5. (R5) $H + O_2 = OH + O$
6. (R6) $O + H_2 = OH + H$
7. (R7) $OH + H_2 = H_2O + H$
8. (R8) $HO_2 + H = H_2O + O$
9. (R9) $HO_2 + H = OH + OH$
10. (R10) $HO_2 + OH = H_2O_2 + O_2$
11. (R11) $HO_2 + HO_2 = H_2O_2 + O_2$
12. (R12) $CO + OH = CO_2 + H$, HOCO??
13. (R13) $HCO + H = CO + H_2$
14. (R14) $H + CO + M = HCO + M$
15. (R15) $O + OH + M = HO_2 + M$
16. (R16) $HCO + O_2 = CO + HO_2$
17. (R17) $CO + O + M = CO_2 + M$
18. (R18) $CO + HO_2 = CO_2 + OH$

BLUE – updated in $H_2$ submodel
RED – Present focus of CO submodel revisions

Additional small hydrocarbon oxidation coupling with these kinetics!!

See Paper A-26 | ESSCI Fall Technical Meeting | University of Connecticut | 11OCT, 2011
2a. Rate Coefficient Determination for 3-body Reaction

\[ \text{H} + \text{O}_2 + \text{CO}_2 \rightarrow \text{HO}_2 + \text{CO}_2 \]
Rate Coefficients for \( H + O_2 + CO_2 \rightarrow HO_2 + CO_2 \) Determined in a New High Pressure Laminar Flow Reactor

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Motivation
Some fundamental cases – modeling simulations

- replacing Ar with 10% CO₂ in a mixture of stoichiometric H₂/O₂ in Ar bath increases experimental ignition delays ~15-30% near 1 atm, 900-1050 K¹
- Kinetic modeling for ε_CO₂/Ar = 4.5 shows similar suppression of global reactivity due to 10% CO₂ substitution
- Increasing pressure exacerbates the effect of title reaction on lean syngas laminar mass burning rates – no fuel dilution by CO₂ necessary!
- Varying rate coefficient of title reaction by ~20% leads to ~7% change in predicted mass burning rate at 25 atm!

¹Brabbs & Robertson (1987)
Take-Away Points

1. Rate coefficient for \( H + O_2 + CO_2 \rightarrow HO_2 + CO_2 \) is not particularly well determined
   - Frequently determined by modeling experiments that have high sensitivity to this rate.

2. Uncertainty in this rate coefficient due to kinetic model choice has not been well quantified previously

3. Present flow reactor determination of \( H + O_2 + CO_2 \rightarrow HO_2 + CO_2 \) not dependent on extraction from complex kinetic models
**Experimental Apparatus**

**Schematic/Sketch of HPLFR = High Pressure Laminar Flow Reactor**

**Along the reactor duct**

- Premixed Reactants
- \( t = \frac{z}{U_{plug}} \leftrightarrow \frac{dX}{dt} = kX \)

**Duct materials:** SS347 or quartz
Experimental Approach

- Ashmore & Tyler (1962) and Mueller (1998) show that rate coefficients for $\text{H}+\text{O}_2+\text{M} \rightarrow \text{HO}_2+\text{M}$ can be determined from NO$_x$-perturbed H$_2$/O$_2$ system at conditions below explosion limit:

$$
\begin{align*}
\text{H}+\text{O}_2+\text{M} & \rightarrow \text{HO}_2+\text{M} \quad (\text{R1}_M) \\
\text{HO}_2+\text{NO} & \rightarrow \text{OH}+\text{NO}_2 \quad (\text{R2}) \\
\text{NO}_2+\text{H} & \rightarrow \text{OH}+\text{NO} \quad (\text{R3}) \\
\text{OH}+\text{H}_2 & \rightarrow \text{H}+\text{H}_2\text{O} \quad (\text{R4})
\end{align*}
$$

- At these conditions, $k_{1M} = k_3[\text{NO}_2]/[\text{O}_2]$, with little influence from other reactions

- Measurement of [NO$_2$] and [O$_2$], and relatively well-known value (±18\%)$^1$ of $k_3$ are sufficient to determine $k_{1M}$

$^1$Su et al. (2002) [Argonne]
Excellent agreement using HPLFR & experimental approach to measure $k_{1\text{Ar}}$, very good agreement for $k_{1\text{N}_2}$
Present recommendation for
\[ \text{H} + \text{O}_2 + \text{CO}_2 \rightarrow \text{HO}_2 + \text{CO}_2 \]

- Present data evaluation supports \( \varepsilon_{\text{CO}_2/\text{N}_2} = 3.0 \), if using Burke et al. model for \( \text{H} + \text{O}_2 + \text{N}_2 \) reaction.
- Additional HPLFR data forthcoming. Reinterpretation of present error bars due to fall-off?

![Graph showing reaction rates and error bars for different temperature ranges.](graph.png)
Take-Away Points

0. Carbon dioxide is an ubiquitous combustion gas, either as a fuel diluent or combustion product. The reaction $H + O_2 + CO_2 \rightarrow HO_2 + CO_2$ (R1) can exert significant influence on combustion systems, and hence is an important reaction to study (✓ - motivated above)

1. Rate coefficient for $H + O_2 + CO_2 \rightarrow HO_2 + CO_2$ is not particularly well determined

2. Uncertainty in this rate coefficient due to kinetic model choice has not been previously well quantified

3. Present flow reactor determination of $H + O_2 + CO_2 \rightarrow HO_2 + CO_2$ not dependent on extraction from complex kinetic models

4. CO/H2 syngas oxidation model nearing completion (not shown)

Future Work

5. Additional experiments to finalize Collisional rate coefficient for CO$_2$, H$_2$O

6. Move to HHC speciation experiments to generate validation data for modeling
2a. Studies of Near-Limit Flame Chemistry of HHC and Small Hydrocarbon Fuels
Motivation

Source: Burke, Chaos, Ju, Dryer, and Klippenstein, *International Journal of Chemical Kinetics*, Accepted for publication
HO$_2$ chemistry increases in importance at advanced combustion conditions.

![Graph showing the bimolecular rate coefficient as a function of temperature and pressure]

- H+O$_2$+M=HO$_2$+M
  - M = Ar
- H$_2$O
- 1 atm
- 5 atm
- 25 atm

Temperature (T, K) ranges from 2000 to 500, and the bimolecular rate coefficient (mol/cm$^3$.s) spans from $10^9$ to $10^{12}$. The graph illustrates the decrease in rate coefficient as temperature increases, with different lines representing various pressures.
HO$_2$ chemistry increases in importance at advanced combustion conditions

- HO$_2$ paths are active at high P’s and T’s
  - R1/R2 competition still controls pressure dependence, along with competition among HO$_2$ paths
- HO$_2$ paths and the branching ratio will be affected by hydrocarbons and H$_2$O/CO$_2$ dilution
Predictive ability of present kinetic models varies widely!


Objectives

1. Measure mass burning rates of HHC and small hydrocarbons at near-limit conditions, and including H$_2$O and CO$_2$ diluents

2. Identify controlling reactions and paths

3. Validate and develop kinetic models
Experimental Apparatus

- Mercury Lamp
- 100 μm pinhole
- Oven
- Fan
- Electrodes
- Heater
- Thermocouples
- Liquid injection
- Vaporization chamber
- Gaseous Delivery
- To vacuum pump
- Knife Edge
- High speed camera
- To vacuum pump
- Heated tubes
- Thermocouple
- Thermocouple
## New HHC & Hydrocarbon Burning Rates Measured

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Flame Temperature</th>
<th>Equivalence Ratio</th>
<th>Pressure Range</th>
<th>Stoichiometric flame temperature in air</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂/CO</td>
<td>1600 K</td>
<td></td>
<td>1-25 atm</td>
<td>2377</td>
</tr>
<tr>
<td>H₂/C₂H₄</td>
<td></td>
<td>0.7</td>
<td></td>
<td>2376</td>
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<tr>
<td>H₂/C₂H₆</td>
<td></td>
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<td>2330</td>
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<tr>
<td>C₂H₄</td>
<td>1800 K</td>
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<td>2370</td>
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<tr>
<td>C₂H₆</td>
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<td></td>
<td></td>
<td>2260</td>
</tr>
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</table>

- Mixed fuels contain 90% H₂
New HHC Fuel Burning Rates

- Negative pressure dependence at high pressure due to importance of HO$_2$ chemistry
HHC Fuels Modeling Results

Sensitive Reactions for HHC systems

- Sensitive C-containing reactions:
  - CO+OH=CO₂+H
  - CH₃+H(+M)=CH₄(+M)
  - CH₃+HO₂=CH₃O+OH

- Most sensitive reactions are in H₂ model
Effect of $\text{H}_2$ submodel update

- $\text{H}_2/\text{CH}_4/\text{O}_2/\text{He}$, $\phi=0.7$, $T_f \sim 1600\text{K}$
- $\text{H}_2/\text{CH}_4 = 100/0$
- $\text{H}_2/\text{CH}_4 = 90/10$

- $\text{H}_2/\text{CH}_4/O_2/\text{He}$, $\phi=0.7$, $T_f \sim 1600\text{K}$
- $\text{H}_2/\text{CH}_4 = 100/0$
- $\text{H}_2/\text{CH}_4 = 90/10$

- $\text{H}_2/\text{CO} = 90/10$
- $\text{H}_2/\text{C}_2\text{H}_4 = 90/10$
- $\text{H}_2/\text{C}_2\text{H}_6 = 90/10$
Effect of $\text{H}_2$ submodel update

- At 20 atm, predictions span a factor of 4.6
- With the substituted Burke et al. $\text{H}_2$ model, they span a factor of 1.4
Effect of Water Dilution on $\text{H}_2$ flames

- $\text{H}_2/\text{O}_2/\text{He}/\text{H}_2\text{O}$, $\phi=0.85$
- $T_u=393\text{K}$, $T_f=1600\text{K}$
- Water becomes a stronger inhibitor at elevated pressure (modeling results)
- Shift in pressure at max burning rate

Model: Burke, Chaos, Ju, Dryer, and Klippenstein, *Int. Journ. of Chem. Kinet.*, Accepted for publication
Effect of Water Dilution on CO/H₂ flames

H₂/CO/O₂/He/H₂O, φ=0.85 T_u=393K, T_f=1600K

Water Dilution Affects Radical Pool

Model: Burke, Chaos, Ju, Dryer, and Klippenstein, *Int. Journ. of Chem. Kinet.*, Accepted for publication
Water Dilution Affects Radical Pool

This is inhibitive – there are more steps to an H radical.

\[ \text{H}_2\text{O} + \text{O} = 2\text{OH} \quad \text{vs} \quad \text{H}_2 + \text{O} = \text{H} + \text{OH} \]

At high pressure, \( \text{HO}_2 \) reactions become important. Water addition reduces branching from \( \text{HO}_2 \).

\[ \text{HO}_2 + \text{OH} = \text{H}_2\text{O} + \text{O}_2 \quad \text{vs} \quad \text{HO}_2 + \text{H} = 2\text{OH} \]

\[ \text{HO}_2 + \text{H} = \text{H}_2 + \text{O}_2 \]
Summary

• Present measurements add to burning rate database at near-limit conditions
  – Higher Pressures
  – Lower Flame Temperatures
  – Hydrocarbon Addition
  – Water as a Diluent

• Illuminate important reactions at these limits
  – HCO consumption
  – CH$_3$ consumption
  – H$_2$O+O=2OH
  – HO$_2$ reactions

• Contribute to larger efforts to create an accurate HHC fuel model
High-Pressure High-Temperature Flow Reactor Studies
Flow Reactor Details

- The variable-length test section (maximum length of 2.13 m (7 ft)) has a circular cross section (diameter of 43 mm (1.7 in.)).
- The test section is instrumented with pressure transducers and an axial array of thermocouples to determine the conditions at which autoignition occurs.
- For the present studies, air is supplied from two blowdown tanks at a maximum flow rate of approximately 0.45 kg/s (1 lbm/s) at a maximum temperature of ≈850 K (1070°F).
- Maximum pressure of 30 atm.
High-Pressure High-Temperature Autoignition Flow Reactor
High-Pressure High Temperature Flow Reactor

Injector  Removable sections  Test section Nozzle

Flow direction

High-pressure high-temperature flow reactor

Bottom half of clam shell heater
Flow Reactor Design

- Instrumented test section before nozzle
- Sonic nozzle and water quenching to isolate test section from afterburner
- Injector design
  - Venturi design for rapid mixing with minimal recirculation zones
  - 7 venturis with 3 fuel injection holes just upstream of throat

- $Re\# \ (Max) = 5 \times 10^5$ to $3 \times 10^6$
Array of thermocouples located 0.2 inches from the wall that provides for detection of the autoignition event in the flow reactor tube
Detection of an Ignition Event

\[ \tau = \frac{L}{v} \text{ for all these events} \]

Detector \((TC, PD)\)

Tube Length, \(L\)

Velocity, \(v\)
Detection of an Ignition Event

\[ \tau = \frac{L_i}{v} \text{ for these events where } i = 1, 2, \text{ and } 3 \]

Multiple Detectors (TC, PD)

\[ \tau = \frac{L_i}{v} \]

Velocity, \( v \)

Tube Length, \( L \)
Summary of Results

• The ignition delay time varies significantly for similar or even identical conditions.
• For a specific pressure and temperature, ignition will occur, but may be erratic in terms of repeatability.
• For the same pressure, ignition will be observed at temperatures where ignition was not observed for a higher temperature.
• Results from the axially distributed thermocouples show the ignition events occur at different locations in the flow tube for all velocities and pressures studied.
## Previous Tabulated Data

<table>
<thead>
<tr>
<th>Fuel Type</th>
<th>φ</th>
<th>% H₂ in Fuel</th>
<th>P (atm.)</th>
<th>T (K) at ign. Loc</th>
<th>velocity (m/s)</th>
<th>t (ms)</th>
<th>tadj (ms) to 20 atm</th>
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<tr>
<td>(75% H₂/25% CO) Re=126000</td>
<td>0.98</td>
<td>74.3</td>
<td>9.6</td>
<td>748.2</td>
<td>8.9</td>
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<td>123.2</td>
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<td>771.2</td>
<td>4.4</td>
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Flow reactor length = 2.16 m
## Recent Results

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<tr>
<th></th>
<th>$\Phi$</th>
<th>% H$_2$O in Fuel</th>
<th>$P$ (atm.)</th>
<th>Calculated Mixture Temperature T(K)</th>
<th>velocity (m/s)</th>
<th>t (ms)</th>
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</thead>
<tbody>
<tr>
<td><strong>(100% H$_2$)</strong>&lt;br&gt;Re=176000</td>
<td>0.46</td>
<td>5.8</td>
<td>21.1</td>
<td>712</td>
<td>15.4</td>
<td>34</td>
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<td>0.46</td>
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<td>20.7</td>
<td>714</td>
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<td></td>
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<td>19.4</td>
<td>663</td>
<td>15.4</td>
<td>no ignition</td>
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<td><strong>(H$_2$ + 0.08% toluene)</strong>&lt;br&gt;Re=176000</td>
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<td>5.5</td>
<td>21.0</td>
<td>707</td>
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<td>20.3</td>
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<td>15.7</td>
<td>6</td>
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</tbody>
</table>

Flow reactor length = 2.16 m Residence time 140 ms
Ignition Delay Time vs. Temperature

- 75% H2-25%CO - air 10 atm
- H2-air 23 atm
- H2-air 20 atm
- H2-air-toluene 20 atm
Axial Location vs. Nominalized Velocity

- Nominalized velocity on the y-axis
- Axial Position in Flow Tube on the x-axis

- Data points for 4.3 m/s 23 atm represented by blue diamonds
- Data points for 8.6 m/s 10 atm represented by red squares
- Data points for 15.5 (Tol) m/s 20 atm represented by green triangles
- Data points for 15.5 m/s 20 atm represented by purple crosses
# Study of H$_2$-O$_2$ Autoignition by Beerer and McDonnel


<table>
<thead>
<tr>
<th>Pressure (atm)</th>
<th>Equivalence ratio</th>
<th>Ignition Temperature (K)</th>
<th>Residence Time, $\tau$ (ms)</th>
<th>Flow Velocity, $v$ (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.4</td>
<td>0.31</td>
<td>778</td>
<td>451</td>
</tr>
<tr>
<td>2</td>
<td>5.8</td>
<td>0.37</td>
<td>780</td>
<td>178</td>
</tr>
</tbody>
</table>

$\tau_1/\tau_2 = 2.53$  \quad  v_2/v_1 = 2.54
Possible Phenomena Responsible for Observations

• Problem with our apparatus. (used for successful study of autoignition for octane and heptane)

• Unusually sensitive chain branching effects due to the proximity to the 3\textsuperscript{rd} explosion limit. (Toluene)
  \[ \text{C}_6\text{H}_5\text{-CH}_3 + \text{H} \rightarrow \text{C}_6\text{H}_5\text{-CH}_2 + \text{H}_2 \]

• The effects of turbulent mixing.
  \[ \text{(Re}=63750 \text{ – 176,000)} \]

• Presence of wall reactions occurring at the stainless steel walls of the flow tube (?)
Recent Results From Princeton HPLFR

- M. Haas and F. Dryer recently ran the Princeton HPLFR using a SS flow tube at ~830K, 10 atm, for a 1%/2% H2/O2 in N2 diluent.
- FTIR quantification of water showed about 30% conversion of the H2 to ~3000 ppm H2O.
Experiment Methodology

\[ \Phi = \text{const} \]

\[ \text{Temperature} \]

\[ \text{Ignition} \]
Significant difference between model prediction and measurements of ignition delay time for temperatures between 900K – 625K (1150°F - 665°F)
Interpreting Experimental Ignition Delay Observations

- Chemical induction is very important for ignition delay time in the H₂-O₂ system at temperatures below 1000K and is very sensitive to chemical perturbations from any source, e.g., pre-ignition pressure increases (left).
- Use of constant U,V constraint to calculate predictions to test models leads of erroneous results and the volume as a function of time (VTIM) constraint is the proper one to use.
Summary

• Based on the data and analysis that we have done to date, the highly variable results we are observing for autoignition appear to be characteristic of the \( \text{H}_2 - \text{O}_2 \) system at high pressures \((P>5 \text{ atm})\) and low temperatures \((T>1000\text{K})\)
Future Work

• Repeat autoignition studies that will establish, if they exist, a set of results that bound the autoignition lower bound for the high-pressure, high temperature H$_2$-O$_2$ system.

• Use a silica insert to change the wall material to establish if wall reactions are catalyzed with stainless steel.
Questions???