Chemical kinetic modeling development and validation experiments for direct fired sCO2 combustor

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Note: This version of the presentation is approved for public release. Please contact subith@ucf.edu for further information.
Project/Task Summary

Task 1: Project Management

Tasks 2&3: Acquire kinetics and ignition data in highly CO₂ diluted mixtures with shock tube experiments

Task 4: Refine and validate a chemical kinetic mechanism for Supercritical Carbon Dioxide (sCO₂) Mixtures

Task 5: Develop a CFD Code that utilizes mechanism for sCO₂ combustors
Motivation

• Current state-of-the-art, such as GRI-3.0 Mechanism, has only been validated for pressures up to 10 atm

• Mechanisms have not been developed for CO$_2$ diluted mixtures

• Updated mechanism will allow for accurate combustor modeling with multi-step combustion using a validated mechanism

• Current CFD combustion models do not consider non-ideal effects

Effects of Increasing Pressure. Equilibrium calculation for CH$_4$/O$_2$/CO$_2$ at $\phi = 1$. Figure adapted from Strakey, 2014, sCO$_2$ symposium
Motivation

Current state-of-the-art differ in their predictions even at atmospheric pressure

- GRI 3.0 is still a widely used mechanism created 15 years ago
- Aramco Mech 1.3 is a recent well-validated mechanism
Motivation

Effect of CO+OH→CO2+H and third-body collision efficiency of CO2 on ignition times
Existing High-Pressure Methane Ignition Data

CH₄/O₂/N₂/Ar ignition delay time measurements. The higher pressure data exhibit a significantly weaker variation with temperature (smaller activation energy) than the lower pressure, higher temperature mixtures

JPP, 1999, 15(1), 82-91
Tasks 2&3: Experimentation

Experiments will be performed in two different shock tube facilities for Methane Oxidation diluted with CO₂

Experiments will be performed pressures up to 300 bar for temperatures between 800 K and 2000 K and equivalence ratios of 0.7 to 1.2

Ignition delay times and key species time histories will be measured

Experiments will also be performed for selected mixtures of syngas
Combustion chemistry process

**MODEL**

**Reaction Mechanism Development**
1. Decomposition Pathways
2. Intermediate Species Sub-Mechanisms
3. Full Mechanisms
4. Reduced Mechanisms
5. Validation

**EXPERIMENT**

**Kinetic Targets (Shock Tubes)**
1. Ignition Time Measurements
2. Species Time-Histories
3. Direct Rate Measurements

**Fuel + O₂+CO₂**

- Initial Decomposition Products
- H-Abstraction & Oxidation Products
- Intermediate Species
  - OH, CH₃, C₂H₄, C₂H₂, H₂, CO, etc.
- Ignition
  - CO, CO₂, H₂O
Laser absorption spectroscopy

Beer - Lambert law

\[
\frac{I}{I_0} = \exp \left( -k_\lambda P_{\text{total}} X_{\text{species}} L \right)
\]

Spectral absorption coefficient

\[
k_\lambda = S(T) \cdot \Phi(T,P,X)
\]

S(T): line strength, \( \Phi(T,P,X) \): line shape
Tasks 2 & 3 Sample Results: Shock Tube
Reflected shock wave experiments: sidewall pressure profiles.
Reflected shock conditions: 1298K, 61.24atm, 50% CO2/50% argon mixture.
Ignition Delay Time Measurements

Ignition delay times measured from the arrival of reflected shockwave to rise of the pressure trace

Arrival of shockwave determined as midpoint of the second pressure rise (rise due to reflected shock)

Rise of OH Emissions measured as the intersection between the baseline and the tangent line drawn from maximum rise of OH
Methane Concentration Results

- Comparison of measured and simulated methane concentration for
  - Stoichiometric ignition of 3.5% CH\textsubscript{4} in Argon, 1600K

![Graph showing methane concentration results]
Methane Concentration Results

- Comparison of measured and simulated methane concentration for
  - Stoichiometric ignition of 3.5% CH$_4$ in Argon diluted with 30% CO$_2$, 1600K
Methane Ignition and Concentration Results

- Comparison of measured and simulated methane concentration for
  - Stoichiometric ignition of 3.5% CH₄ in argon/CO₂
  - GRI predictions are wrong for both ignition time and concentrations even at low pressures!!
Methane/O\textsubscript{2}/CO\textsubscript{2} Ignition: High-Speed Imaging for Accurate Ignition Determination
Methane/O2/CO2 Ignition: High-Speed Imaging Results

XCO2=0
Methane/O2/CO2 Ignition Imaging Results

CO2=85%

- Normalized Sidewall Emission
- Normalized Camera Emission
- Measured Pressure

$T_0 = 1839$ K

$P_0 = 0.993$ atm

$X_{CH4} = 0.05$

$X_{O2} = 0.10$

$X_{CO2} = 0.85$

- Methane Concentration
- Normalized Sidewall Emission

$t=166.7$ μs (1)  
$t=181.6$ μs (2)  
$t=196.5$ μs (3)  
$t=211.4$ μs (4)  
$t=226.3$ μs (5)  
$t=241.2$ μs (6)
2%CH₄/2%CO/5%O₂/85%CO₂ 12 atm
Syngas/O2/CO2 Ignition Delay Times

Syngas fuel is a mixture of CO and H₂
Syngas /O2/CO2 Ignition Delay Time Measurements

CO2=80%. Syngas=50% H2+ 50% CO
Syngas /O2/CO2 Ignition Delay Time Measurements
CO2=60%. Syngas=80% H2+ 20% CO
Task 4: Chemical Mechanism Development Summary

- Combustion kinetics model refinement/development

- Existing kinetic models are only valid at low pressures < 50 atm

- We will use multiscale simulations to extend their validity to above 300 bar by:
  1. Quantum Mechanic simulations of the activation enthalpies in gas vs. CO$_2$ environment
  2. Molecular Dynamic simulations of reaction processes
Combustion chemistry/kinetics

**Simplest fuel system:** Hydrogen/Oxygen

\[ 2H_2 + O_2 \rightarrow 2H_2O \]

- requires 19 reactions and 8 species to fully describe chemistry (not including NOx):
  - \[ H_2 + O_2 \rightarrow H + HO_2 \]
  - \[ H + O_2 \rightarrow OH + O \]
  - \[ OH + H_2 \rightarrow H_2O + H \]
  - \[ O + H_2 \rightarrow OH + H \]
  - \[ OH + OH \rightarrow O + H_2O \]
  - \[ O + HO_2 \rightarrow O_2 + OH \]
  - \[ H + HO_2 \rightarrow OH + OH \]
  - \[ OH + HO_2 \rightarrow H_2O + O_2 \]
  - \[ HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \]
  - \[ H_2O_2 + OH \rightarrow H_2O + HO_2 \]

**Larger fuels:**

- Natural gas in air (includes NO\textsubscript{x})
  - \# Reactions: 325
  - \# Species: 53

- A rate coefficient must be prescribed for each chemical reaction
  \[ k (T) = A \times \exp(-\frac{E_a}{RT}) \]
  - T: temperature, \( E_a \): activation energy, R: gas constant

- Rate coefficients can be measured using advanced laser diagnostics

- Models need to be reduced based on experience and intuition so they can be used with CFD
The important elementary steps in RD2010 mechanism of C0-C4 fuel combustion

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Reaction</th>
<th>A</th>
<th>n</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H₂O₂ → H₂O + O</td>
<td>3.55E+15</td>
<td>-0.406</td>
<td>1.66E+04</td>
<td>[7]</td>
</tr>
<tr>
<td>2</td>
<td>CO+OH → CO₂+H</td>
<td>2.20E+05</td>
<td>1.89</td>
<td>-1.16E+03</td>
<td>[7], A*1.24</td>
</tr>
<tr>
<td>3</td>
<td>HCO+M + H₂O → CO₂+H</td>
<td>4.75E+11</td>
<td>0.7</td>
<td>1.49E+04</td>
<td>[6]</td>
</tr>
<tr>
<td>4</td>
<td>H₂+O → H₂O + M</td>
<td>4.50E+22</td>
<td>-2</td>
<td>0.00E+00</td>
<td>[19]</td>
</tr>
<tr>
<td>5</td>
<td>C₄H₆a+H → C₄H₅a</td>
<td>2.06E+14</td>
<td>0</td>
<td>0.00E+00</td>
<td>[8]</td>
</tr>
<tr>
<td></td>
<td>Low pressure limit:</td>
<td>1.33E+60</td>
<td>-12</td>
<td>5.97E+03</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>CH₃+CH₃ → C₂H₆</td>
<td>9.21E+16</td>
<td>-1.17</td>
<td>6.36E+02</td>
<td>[7]</td>
</tr>
<tr>
<td></td>
<td>Low pressure limit:</td>
<td>1.14E+36</td>
<td>-5.246</td>
<td>1.71E+03</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Troe parameters:</td>
<td>0.02, 1.10E+03, 1.10E+03, 6.86E+03</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>CH₃+HO₂ → CH₃O+OH</td>
<td>1.00E+12</td>
<td>0.269</td>
<td>-6.88E+02</td>
<td>[7]</td>
</tr>
<tr>
<td>8</td>
<td>CH₄+H → CH₃+H₂</td>
<td>6.14E+05</td>
<td>2.5</td>
<td>9.59E+03</td>
<td>[7]</td>
</tr>
<tr>
<td>9</td>
<td>HO₂+HO₂ → H₂O₂ + O₂</td>
<td>4.20E+14</td>
<td>0</td>
<td>1.20E+04</td>
<td>[18]</td>
</tr>
<tr>
<td>10</td>
<td>CH₄+H₂O → CH₃+H₂O₂</td>
<td>1.13E+01</td>
<td>3.74</td>
<td>2.10E+04</td>
<td>[7]</td>
</tr>
<tr>
<td>11</td>
<td>CH₂O₂+CH₅ → CH₃O+CH₃O</td>
<td>5.08E+12</td>
<td>0</td>
<td>-1.41E+03</td>
<td>[7]</td>
</tr>
<tr>
<td>12</td>
<td>CH₃+OH → CH₃(S)+H₂O</td>
<td>4.51E+17</td>
<td>-1.34</td>
<td>1.42E+03</td>
<td>[7]</td>
</tr>
<tr>
<td>13</td>
<td>CH₃+O₂ → CH₃O+OH</td>
<td>2.64E+00</td>
<td>3.283</td>
<td>8.11E+03</td>
<td>[7]</td>
</tr>
<tr>
<td>14</td>
<td>CH₃+H → CH₃H+M</td>
<td>2.14E+15</td>
<td>-0.4</td>
<td>0.00E+00</td>
<td>[1]</td>
</tr>
<tr>
<td></td>
<td>Low pressure limit:</td>
<td>3.31E+30</td>
<td>2.11E+03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>CH₃+H₂ → C₂H₅</td>
<td>1.95E+12</td>
<td>0.454</td>
<td>1.82E+03</td>
<td>[7]</td>
</tr>
<tr>
<td></td>
<td>Low pressure limit:</td>
<td>2.16E+42</td>
<td>-7.62</td>
<td>6.97E+03</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Troe parameters:</td>
<td>0.975, 210, 984, 4.37E+03</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Collision efficiencies: CH₄ 2.0, CO 1.9, CO₂ 3.8, C₂H₆ 3.0, H₂O 6.0, H₂ 2.0, Ar 0.7.

• Five distinct steps along Reaction Coordinate:
  1. Reactants (R1,R2)
  2. Reactive complex (RC)
  3. Transition state (TS)
  4. Product complex (PC)
  5. Products (P1,P2)
• Two radicals may couple high spin or low spin; these result in reaction surfaces corresponding to two multiplicities.
• QST3 method will be used to locate TS.
• IRC method will be used to connect RC and PC.
Gas-Phase Heat release Reaction $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$

Pathways shown for gas phase
The supercritical solvent can modify predictions of this model in three ways:

- changing the ability to reach the equilibrium by the reactants and/or TS
- shifting this equilibrium, and
- changing probability of TS to convert to the products
Shifting the equilibrium between reactants and TS can be affected by two factors

Both factors will be studied using Quantum Chemistry methods:

• Changing reaction mechanism (CO₂ may be involved in TS structure)

• Products and TS may be stabilized by CO₂ to a different degree (thus, changing $\Delta H^\ast$)
Task 4 Sample Results: Quantum Mechanical Calculations
Elementary Reaction $\text{CO}+\text{OH}\rightarrow\text{CO}_2+\text{H}$
(results with covalent $\text{CO}_2$ addition: new mechanism discovered !!)

Figure 2. Relative energies (kcal/mol) of the reaction pathway shown on Scheme 1, with one covalently bound $\text{CO}_2$ molecule ($\text{trans-HOCO}$ + $\text{CO}_2$ system is chosen as the reference point).
Elementary Reaction $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$
(results with covalent CO$_2$ addition)
Elementary Reaction $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$
(results with spectator $\text{CO}_2$ molecule)

Figure 3. Relative energies (kcal/mol) of two of the reaction pathways shown shown on Scheme 2 (in black) and Scheme 3 (in red) with spectator $\text{CO}_2$ molecule (the trans-HOCO + $\text{CO}_2$ system is chosen as the reference point).
Elementary Reaction CO+OH→CO₂+H (results)

- CO₂ opens up new pathways and accelerates heat release
- Similar catalytic effects by CO₂ seen in other reactions (HO₂+HO₂ → H₂O₂ + O₂) but not in H₂CO + HO₂ → HCO + H₂O₂
Task 5: CFD development and implementation in OpenFOAM

- Real Gas Equations of State for sCO2
- Thermal properties for sCO₂ combustor
- CFD simulation status
- Next steps
Real Gas Equations of State for sCO2
For density and reaction rates
Introduction to Equation of States (EOS)

- EOS is a relation between Temperature, Pressure and Density of a system.

- Estimated operating conditions of sCO2 combustor:

Inlet

- Working fluid: CO₂
- Vary for 1200 K at outlet ~95% Vol.
- (CH₄/O₂)=0.5 → Fixed ratio
- T = 800 K; P = 200-300 bar

Outlet

- Working fluid: CO₂; H₂O
- T = 1200 K; P = 200-300 bar

Prediction of system state in this zone is crucial for modelling a sCO₂ combustor
Introduction to Equation of States

Ref: Joes O. Valderrama (2003)

Developed from Statistical Mechanics; Very complex.

1) Based on Helmholtz function.
2) Calculated for Pure fluids only.
3) Highly accurate.
4) REFPROP sCO2 properties.

Simple algebraic equations; not as accurate, but popular because they are quick to solve.

EoS’s are for single species, need relationships for mixture properties
Introduction to Equation of States

• **REFPROP**

  REFPROP is a program that uses equations for the thermodynamic and transport properties to calculate the state points of the fluid or mixture. These equations are the most accurate equations available world wide.

  → Most accurate EOS equations available, but limited pressure and temperature ranges.

  → No data is available for many combustion species.

  Example:
  Species that are common between REFPORP and GRI30 are only: H2O; H2; O2; CO; CO2; CH3OH; C3H4; CH4; C2H6; C3H8; C3H6

  → REFPROP is reported to be very time expensive for sCO2 simulations. (Mark Anderson et. al., 2016)
Introduction to Equation of States

- van der Waals Equation of state:

\[ p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \]

- \( b \) corrects for the volume available for random molecule movement
- \( a \) reduces kinetic energy due to intermolecular forces
- If first term dominates, \( Z > 1 \) and rho less than ideal gas rho.
- If second term dominates, \( Z < 1 \) and rho greater than ideal gas rho.
- van der Waals has poor accuracy, but is instructive.
Introduction to Equation of States

- **Peng-Robinson Equation of state:**

  \[
  p = \frac{RT}{V_m - b} - \frac{a\alpha}{[Vm(Vm + b) + b(Vm - b)]}
  \]

  Where,

  \[
  a = \frac{0.45724 \, R^2 \, T_c^2}{P_c}
  \]

  \[
  b = \frac{0.07780 \, R \, T_c}{P_c}
  \]

  It can also be represented in the form of a cubic equation:

  \[
  Z^3 - (1 - B)Z^2 + Z(A - 2B - 3B^2) - (AB - B^2 - B^3) = 0
  \]

  Where, \( Z = \frac{PV}{RT} \)

  \[
  A = \frac{0.45724 \, \alpha \, Pr}{Tr^2}
  \]

  \[
  B = \frac{0.07780 \, Pr}{Tr}
  \]

  \[
  \alpha = [1 + (0.37464 + 1.54226 \, \omega - 0.2699 \, \omega^2)(1 - Tr^{0.5})]^2
  \]

  \[
  Pr = \frac{P}{P_c}
  \]

  \[
  Tr = \frac{T}{T_c}
  \]

  \( \omega \) – Acentric factor
EOS suitable for sCO2 Combustor Simulations

- RK (Redlick-Kwong), SRK (Soave-Redlick-Kwong) and PR (Peng-Robinson) models are compared against the REFPORP for sCO2.

Note: REFPROP data for CO2 is available 1100 K only.
EOS suitable for sCO2 Combustor Simulations

- RK, SRK and PR models are compared against the REFPROP for sCH4

Note: REFPROP data for CH4 is available 625 K only.
EOS suitable for sCO2 Combustor Simulations

- RK, SRK and PR models are compared against the REFPORP for sO2

→ None of the models are predicting the sO2 behavior. Possible reasons for this deviation is under investigation.
→ ‘O2’ is second largest concentration in the sCO2 combustor.
• PR models are compared against the REFPORP mixtures properties at the Inlet of sCO2 Combustor

Note: The percentage differences are averaged over pressures between 30-480 bar at every temperature.
EOS suitable for sCO2 Combustor Simulations

- PR models are compared against the REFPORP mixtures properties at the Outlet of sCO2 Combustor
Thermal properties for sCO$_2$ combustor
EOS suitable for sCO2 Combustor Simulations

- Compressibility factor \( Z \) in Real gases

\[ dZ/dP \] may allow a simple model for \( Z \)

- ‘\( Z \)’ is related to many thermodynamic relations of Real gases.

Example:

<table>
<thead>
<tr>
<th>Property</th>
<th>Definition</th>
<th>Ideal Gas Case</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressibility factor</td>
<td>( Z = f(T, p) )</td>
<td>( Z = 1 )</td>
</tr>
</tbody>
</table>
| Isothermal compressibility | \( \beta_T = \frac{1}{\nu} \frac{\partial \nu}{\partial \rho} \) \( T \) \( = \frac{1}{\rho} \frac{\partial \rho}{\partial \rho} \) \( T \) \( \) \( = \frac{1}{p} \) \( \) \( \frac{\partial \rho}{\partial \rho} \) \( T \) \( = \frac{1}{p} \) \( \) \( \frac{\partial \rho}{\partial \rho} \) \( T \) \( = \frac{1}{p} \) \( \) \( \frac{\partial \rho}{\partial \rho} \) \( T \) \( = \frac{1}{p} \) \( \) \( \frac{\partial \rho}{\partial \rho} \) \( T \) \( = \frac{1}{p} \) \( \) \( \frac{\partial \rho}{\partial \rho} \) \( T \) \( = \frac{1}{p} \) \( \) \( \frac{\partial \rho}{\partial \rho} \) \( T \) \( = \frac{1}{p} \) \( \)
| Isochoric compressibility | \( \tilde{\beta}_p = \frac{1}{\nu} \frac{\partial \nu}{\partial \rho} \) \( T \) \( = \frac{1}{p} \) \( \) \( \frac{\partial \rho}{\partial \rho} \) \( T \) \( = \frac{1}{p} \) \( \)

More thermal properties for sCO$_2$ combustor

Compressibility factor ‘Z’ under various operating conditions:

<table>
<thead>
<tr>
<th>Operating Condition</th>
<th>What it explains?</th>
<th>Initial molar mixture and Temperature (K) (CH$_4$/O$_2$/CO$_2$/$T$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OP1</td>
<td>Reference Mixture</td>
<td>1/2/24/1000</td>
</tr>
<tr>
<td>OP2</td>
<td>Inlet [CO$_2$] increases</td>
<td>1/2/40/1000</td>
</tr>
<tr>
<td>OP3</td>
<td>Inlet [CH$_4$+O$_2$] increases</td>
<td>2/4/24/1000</td>
</tr>
<tr>
<td>OP4</td>
<td>Inlet temperature decreases</td>
<td>1/2/24/800</td>
</tr>
</tbody>
</table>
More thermal properties for sCO$_2$ combustor

Specific heats and ratio of specific heats:

\[ c = \frac{d\left(\frac{E}{\rho_i V}\right)}{dT} \]

‘Z’ is more than one, therefore ratio of specific heats greater than Ideal assumption.

- The $c_p$ ranges from 1.331-1.381, $c_v$ ranges from 1.111-1.187 and $\gamma$ ranges from 1.2-1.164 across the sCO$_2$ combustor.
• Repulsive forces also result in increasing speed of sound by a factor \( \left( \frac{\gamma}{n_sZ} \right)^{1/2} \).
CFD simulation status
Present CFD simulation status:
Validation of supercritical N2 jet (In progress)
(R. Branam and W. Mayer, 2002)

- Further validations with RANS and LES simulations are under progress.
• 4 journal papers and several conference presentations in 2016

• Acknowledgement: DE-FE0025260 (Dr. Seth Lawson as program manager)

• Thank you, Questions?