Combustion and Fluid Property Experimental Investigation for Improved Design of Supercritical CO$_2$ Power Cycle Components

PI: Prof. Subith Vasu

Associate Professor
UCF, Orlando, FL

DE-FE0025260

UTSR Meeting Virtual, 11/19/2020
Contact: subith@ucf.edu
Ph: 407-823-3468
Supercritical CO₂ Cycles

- High-pressure, closed or open Brayton Cycle
- CO₂ is used as the working fluid above the critical point
- High overall cycle efficiency

Size comparison of various turbines (~20 time size reduction compared to steam cycles)
Significant reduction of compressor work due to high fluid density close to the critical point,
Introduction to sCO$_2$ Power Cycles

- Possibility of wide application.

What is challenging?

“Typical” sCO$_2$ Cycle Conditions

<table>
<thead>
<tr>
<th>Application</th>
<th>Organization</th>
<th>Motivation</th>
<th>Size [MWe]</th>
<th>Temperature [°C]</th>
<th>Pressure [bar]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nuclear</td>
<td>DOE-NE</td>
<td>Efficiency, Size</td>
<td>300 - 1000</td>
<td>400 - 800</td>
<td>350</td>
</tr>
<tr>
<td>Fossil Fuel</td>
<td>DOE-FE</td>
<td>Efficiency, Water</td>
<td>500 - 1000</td>
<td>550 - 1200</td>
<td>150 - 350</td>
</tr>
<tr>
<td>Solar Power</td>
<td>DOE-EE</td>
<td>Efficiency, Reduction</td>
<td>10 - 100</td>
<td>500 - 800</td>
<td>350</td>
</tr>
<tr>
<td>Concentrated</td>
<td>DOE-NNSA</td>
<td>Efficiency, Water</td>
<td>10, 100</td>
<td>400 - 800</td>
<td>350</td>
</tr>
<tr>
<td>Shipboard Propulsion</td>
<td>CNO</td>
<td>Size, Efficiency</td>
<td>&lt; 1, 1, 10</td>
<td>230 - 650</td>
<td>150 - 350</td>
</tr>
<tr>
<td>Shipboard House Power</td>
<td>DOE-EE</td>
<td>Size, Efficiency</td>
<td>&lt; 1, 1, 10</td>
<td>230 - 650</td>
<td>15 - 350</td>
</tr>
<tr>
<td>Waste Heat Recovery</td>
<td>DOE-EE</td>
<td>Simple Cycles</td>
<td>1, 10, 100</td>
<td>15 - 350</td>
<td>150</td>
</tr>
<tr>
<td>Geothermal</td>
<td>DOE-EERE</td>
<td>Efficiency, Working fluid</td>
<td>1, 10, 50</td>
<td>100 - 300</td>
<td>120</td>
</tr>
</tbody>
</table>

Source: Pictures are taken from SWRI tutorials

- At these high operating pressures, simulation tools are very important because the experiments at these operating conditions are expensive, time consuming and dangerous.
Direct-fired Cycle: The Allam Cycle

- It is the direct-fired sCO$_2$ cycle.


300 bar and 95% CO$_2$ dilution by mass
NET Power’s Allam Cycle Demo Plant

- First successful test fire → May 2018
- Target for 300 MW commercial plant → 2021

Knowledge gaps before we started

- Existing 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 CO₂ diluted mixtures
- Updated/new mechanism will allow for accurate combustor modeling with multi-step combustion using a validated mechanism
- CFD combustion models need to consider non-ideal effects
  - Thermodynamics and kinetics are unknown!!
  - Fundamental work can shed light into this challenge

Effects of Increasing Pressure. Equilibrium calculation for CH₄/O₂/CO₂ at \( \phi = 1 \). Figure adapted from Strakey, 2014, sCO₂ symposium
Strategy successfully applied to Direct-fired Supercritical CO$_2$ Cycles: 300bar pressure CH$_4$/O$_2$, natural gas/O$_2$ mixtures

UTSR Project Impact:
- Understanding the reacting processes at 300bar require new facilities
- Vasu Lab published 26 journal papers
- > 40 conference papers at ASME Turbo Expo, sCO2 symposium, AIAA Meetings, Combustion Institute Meetings
- Prof. Vasu provided Tutorials at Turbo Expo, CelarWater Celan Energy Conference

Burn Fuels in CO$_2$ Environment

Fuel + O$_2$ → CO$_2$ + H$_2$O

300 bar pressure (similar to newer methane rocket engines SpaceX, Blue Origin)

Everything we have done so far is the first in the world! Thanks to the UTSR program

Industry/Government Sponsors and Collaborators

Vasu Lab helped NET Power’s Allam Cycle Demo Plant
Selected Examples from Our Work
Combustion chemistry/kinetics are different at high pressure

1 bar

300 bar

(Strakey, SCO2 symposium 2018, NETL)
Ignition Results in CH₄ Under SCO₂ Conditions: 77.5% CO₂ addition

With CO₂ addition there is some pressure rise (7.5% fuel) after ignition → but not as bad as the ones without CO₂.
Chemical Mechanism Development Summary

• Combustion kinetics model refinement/development

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

• We used multi-scale simulations to extend their validity to mixtures up to 300 bar by:
  1. Quantum Mechanic simulations of the activation enthalpies in gas vs. CO₂ environment
  2. Molecular Dynamic simulations of reaction processes
Molecular Dynamic Study: CO + OH → CO$_2$ + H

(results)

OVERALL REACTION: \( \cdot\text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H} \cdot \)  

(R1, \( k_1 \))

Actually goes through these 3 reactions including HOCO intermediate

\( \cdot\text{OH} + \text{CO} \rightarrow \text{HOCO} \cdot \)  \hspace{1cm} (R2, \( k_2 \))

\( \text{HOCO} \cdot \rightarrow \cdot\text{OH} + \text{CO} \)  \hspace{1cm} (R2r, \( k_{-2} \))

\( \text{HOCO} \cdot \rightarrow \text{CO}_2 + \text{H} \cdot \)  \hspace{1cm} (R3, \( k_3 \))

\[
k_1 = \frac{k_2 k_3}{k_{-2} + k_3}
\]
Molecular Dynamic Study: \( \text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H} \)

(results)

QM / MM model was used.
MM layer look like small tubes, QM layer – particle with balls
QM: MNDO; MM: force field CHARMM27
Molecular Dynamic Study: CO+OH→CO$_2$+H (results)

- CO$_2$ molecules are among the most efficient to accelerate heat release reaction with pressure
- mixed quantum mechanics/molecular mechanics (QM/MM) theory level and molecular dynamics (MD) approach
UCF’s $\text{SCO}_2$ Combustion Mechanism Performance

Mixture: 3.91% CH4, 9.92% O2, 86.77% CO2
Pressure: ~300 bar

- UCF 1.1 is performing better for this lean mixture compared to Aramco 2.0. Performance is significantly improved.

- Average deviation between UCF 1.1 detailed mechanism and 34-species mechanism is 0.25%.
Syngas /O₂/CO₂ Ignition Delay Time Measurements: Comparisons with Modeling

CO₂=85%

12 Literature kinetic mechanisms tested

All mechanisms overpredict data at high pressure!
Performance of sCO$_2$ Mechanism Developed by UCF: Summary

High pressure Ignition Delay Times in Methane:

- The UCF 1.1 mechanism
  → better than Aramco 2.0
  → has important reaction rates calculated by molecular level simulations.

UCF’s HiPER-STAR Facility (for Allam cycle)

*High Pressure Extended Range Shock Tube for Advanced Research*

**Capabilities**

- High-Pressure Combustion and Autoignition Measurements of Fuels including sCO$_2$ conditions for Allam Cycle-Both syngas and natural gas.
- Toxic impurities NOx, SOx, H$_2$S,
- Hydrogen or ammonia combustion with impurities
- Coal-derived fuels

**Up to 1000 bar** sCO$_2$ shock tube with capabilities to include natural gas and real syngas and impurities (e.g., Nitrogen oxides)

**Unique facility in the world** where all types of syngas mixtures can be tested for Allam cycle conditions
CFD Simulation is performed with the premixed CMC in the OpenFOAM RANS CFD code.

The current PCMC-OpenFOAM model is capable of using large mechanisms. The current simulation uses 493 species and 2,714 reactions.

Stoichiometric CH4/O2 with 95% by mass CO2.

Reactor network modeling

- Therefore, this work mainly focuses on reducing the domain of design considerations for sCO2 combustor development with simple 0-D and 1-D modeling.

- Extensively used by the gas turbine community.
Ongoing Work ➔ (Some of the materials are retracted as they are not yet publicly releasable)
Figure 1: temperature profiles predicted by LESLIE with mixture-averaged diffusion and with constant Lewis number = 1 at different time instants (Masi et al., 2013)

MD Simulations for Transport Properties

• Molecular dynamics simulations are performed by open-source LAMMPS (large-scale atomic/molecular massively parallel simulator) package.

• Some preliminary result for sCO$_2$ diffusion

<table>
<thead>
<tr>
<th>NPT</th>
<th>32 CO$_2$</th>
<th>(&lt;E&gt;)</th>
<th>(&lt;T&gt;)</th>
<th>(&lt;V&gt;)</th>
<th>(&lt;P&gt;)</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 ns</td>
<td>kcal</td>
<td>Kelvin</td>
<td>Å$^3$</td>
<td>atm</td>
<td>$10^{-8}$ m$^2$/s</td>
<td></td>
</tr>
<tr>
<td>1,000 K</td>
<td>-1888.65</td>
<td>999.266</td>
<td>20145.8</td>
<td>99.7942</td>
<td>24.2</td>
<td></td>
</tr>
<tr>
<td>1,000 K</td>
<td>-1863.83</td>
<td>1001.17</td>
<td>14498.9</td>
<td>206.885</td>
<td>17.6</td>
<td></td>
</tr>
<tr>
<td>1,000 K</td>
<td>-1846.55</td>
<td>998.28</td>
<td>12044.1</td>
<td>298.9</td>
<td>14.3</td>
<td></td>
</tr>
</tbody>
</table>
**sCO2 Flame Test Rig -670bar (ignition experiments, flame development, flame speed, flow visualization)**

First measurements of Temperature Distribution using Laser-Induced Fluorescence (LIF) in SCO₂ flows conducted near 80bar, *Suhyeon Park, Subith Vasu, et al. Optics Letters*
Students and postdocs

**Graduate Students**

1) Owen Pryor  
(Ph.D. 2018, now at Southwest Research Inst. -SwRI)

2) Raghu Kancherla  
Ph.D. 2019, UCF postdoc

3) Samuel Barak  
Ph.D. 2019, UCF, Siemens, Boeing

**Post docs**

1) Dr. Chun-Hung Wang, Northland

2) Dr. Sergey Panteleev  
(Lead Engineer, Center of Metrology of Nizhny Novgorod, Russia))

3) Dr. Batikan Koroglu  
(Research staff, LLNL)

**Undergraduate Students**

1) Elizabeth Wait  
(now at Los Alamos)  
5 journal papers as an undergraduate
• Acknowledgement: DE-FE0025260
• Dr. Matt Adams as program manager
• Dr. Seth Lawson (previous program manager)
• Rich Dennis, Rin Burke