Investigation of Autoignition and Combustion Stability of High Pressure Supercritical Carbon Dioxide Oxy-combustion

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UTSR Project: DE-FE0025174   PM: Seth Lawson

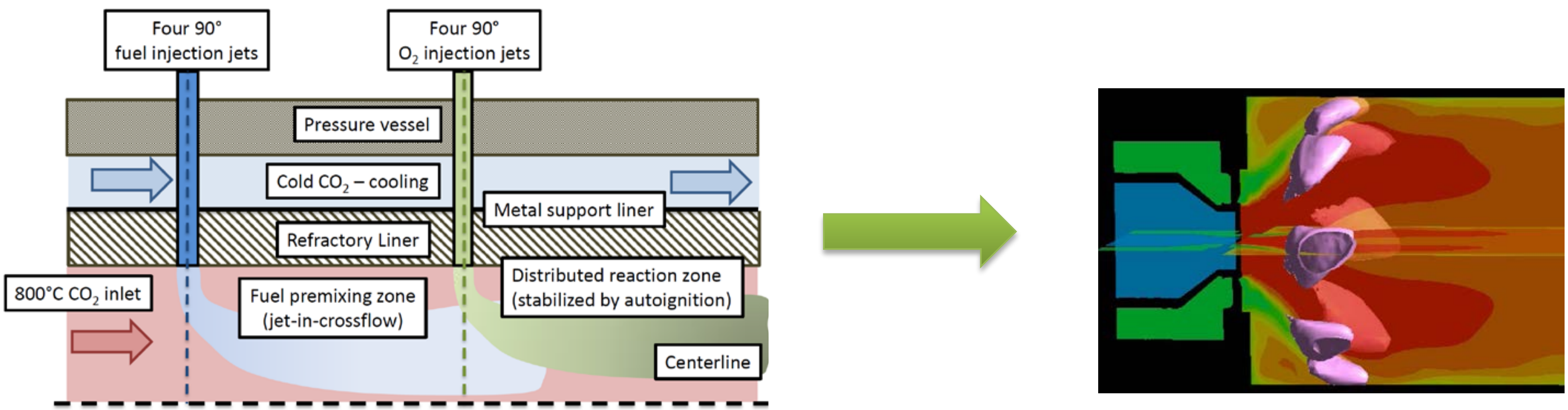
2018 UTSR Project Review Meeting

Overview of the Scientific Problem

- What fundamental combustion properties/knowledge we need in order to design combustor for sCO_2 oxy-combustion?
  - Kinetics and dynamics

Fundamental chemical kinetics
and
flame dynamics at relevant conditions

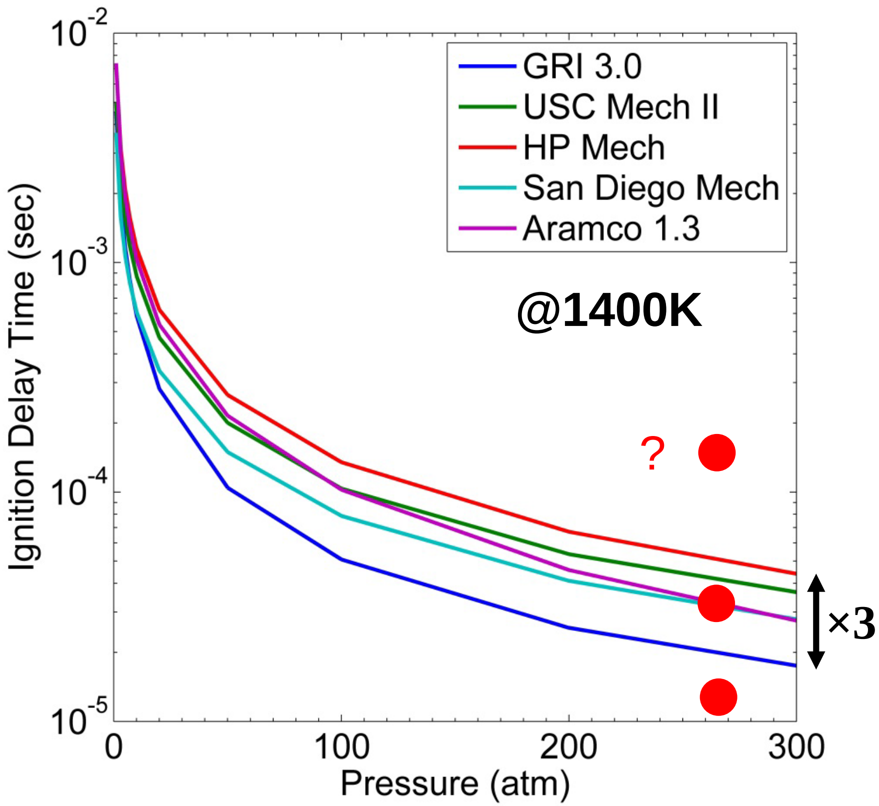
Conceptual combustors



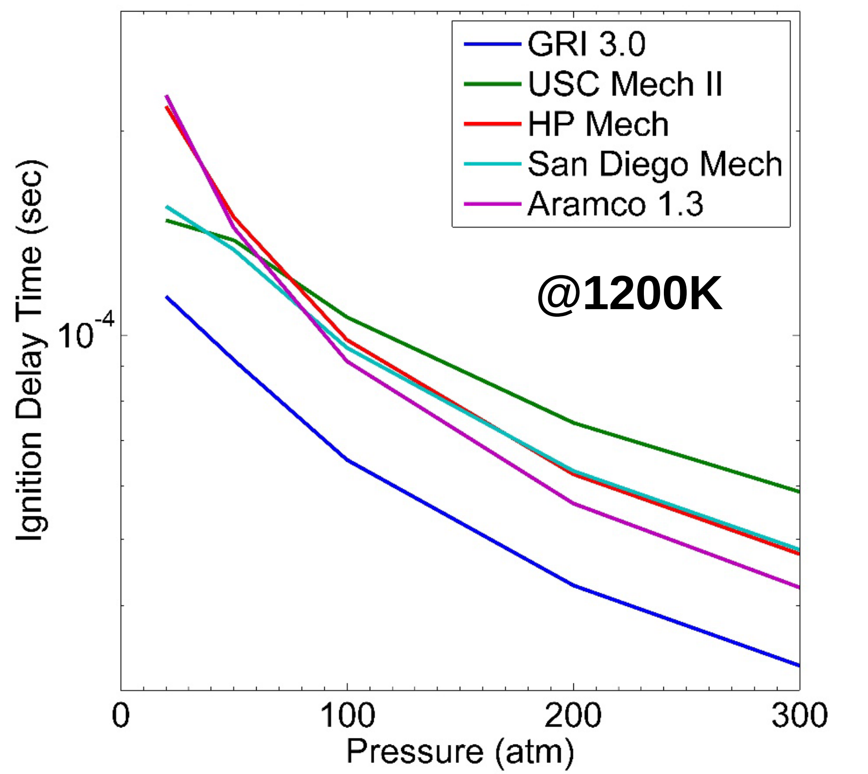
A. McClung et al. 2015 UTSR workshop
J.Delimont et al. 2017 UTSR workshop

Kinetic Challenges for sCO_2-fuel-O_2 Mixtures

Deviation increases with pressure: knowledge gap
Kinetic models must be validated at regime of interest



$CH_4/O_2/CO_2$ (9.5%:19%:71.48%)



$H_2/CO/O_2/CO_2$ (14.8%:14.8%:14.8%:55.6%)

We know the answer now

Overview of the Scientific Questions and Proposed Work

- What is the fundamental kinetic properties?
  - Experimental investigation of chemical kinetics for sCO_2 Oxy-combustion (Task 1&2: Ranjan & Sun)

So what?

- How can we use the kinetic model to design combustors?
  - Development of a compact and optimized chemical kinetic mechanism for sCO_2 Oxy-combustion (Task 3: Sun)

So what?

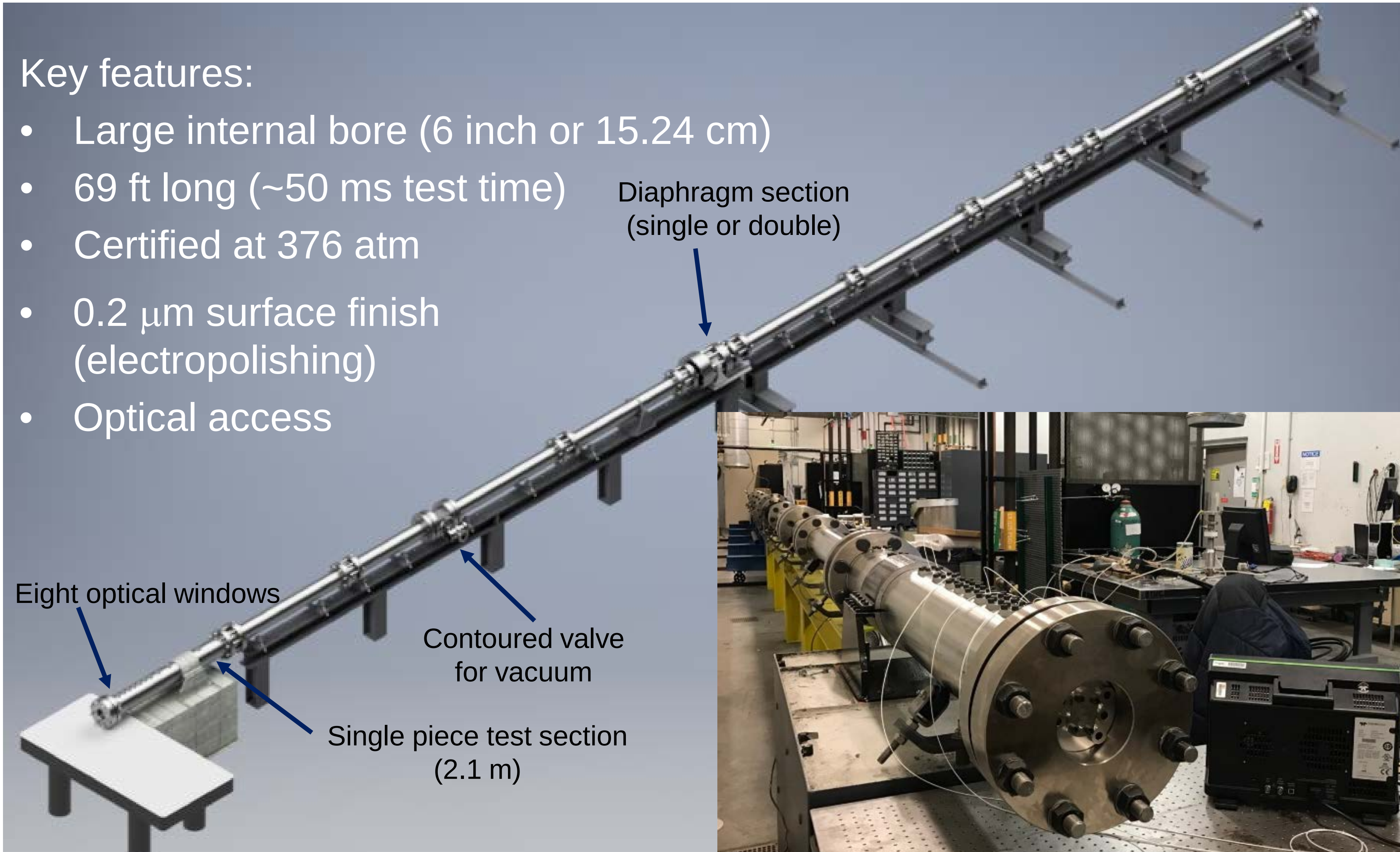
- What is the combustor dynamics at this new condition?
  - theoretical and numerical investigation of combustion instability for sCO_2 Oxy-combustion (Task 4&5: Lieuwen, Menon)

- What is the new emission property?
  - At new operating conditions, should we worry about things we didn't need before? (Task 6: Sun)

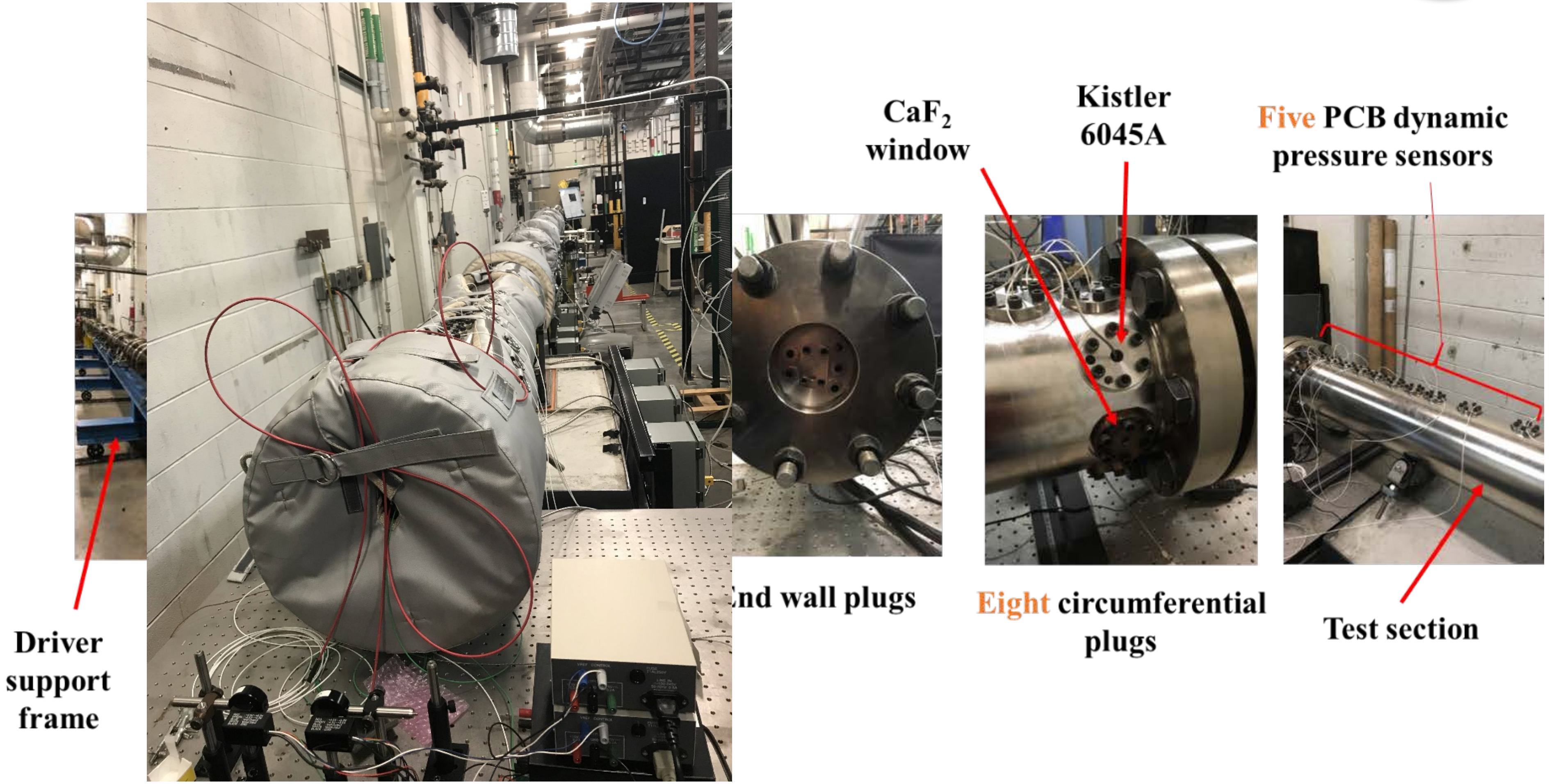
Task 1: Development of a High Pressure Shock Tube

Key features:

- Large internal bore (6 inch or 15.24 cm)
- 69 ft long (~50 ms test time)
- Certified at 376 atm
- 0.2 μm surface finish (electropolishing)
- Optical access



Task 1: Development of a High Pressure Shock Tube

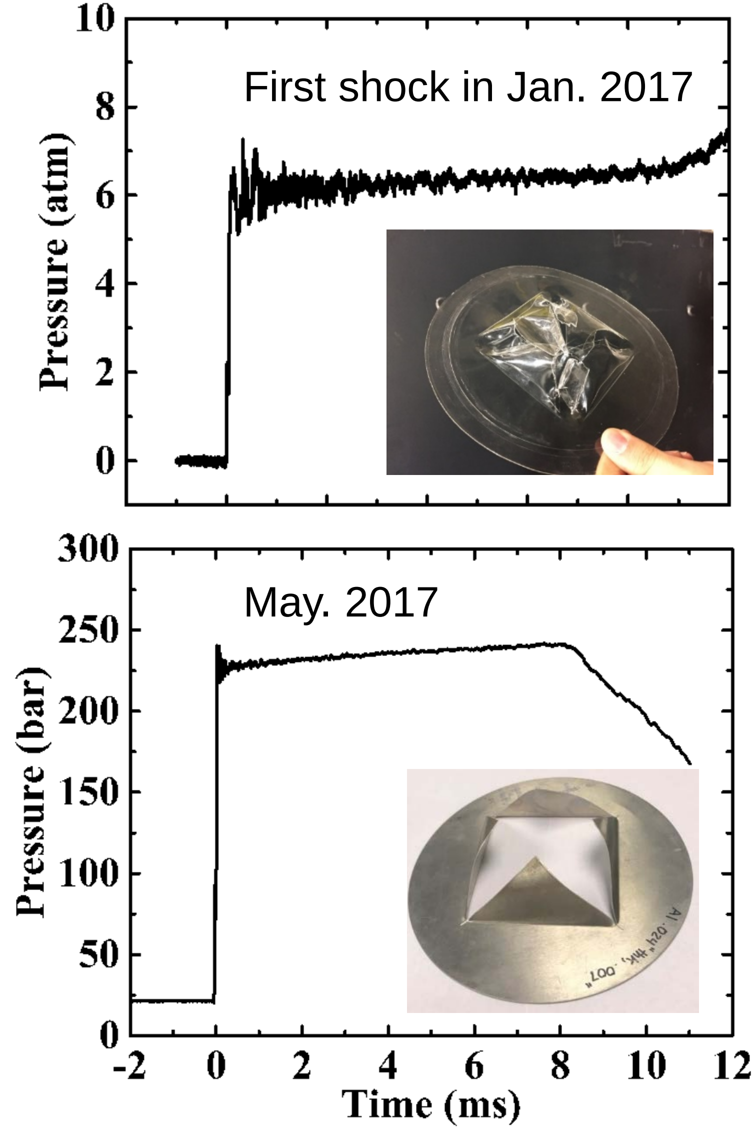


- **Driven section** vacuumed down to 1×10^{-6} Torr using an Agilent IDP-15 Dry Scroll pump and Agilent TwisTorr 304 FS AG turbo pump

Task 1: Development of a High Pressure Shock Tube

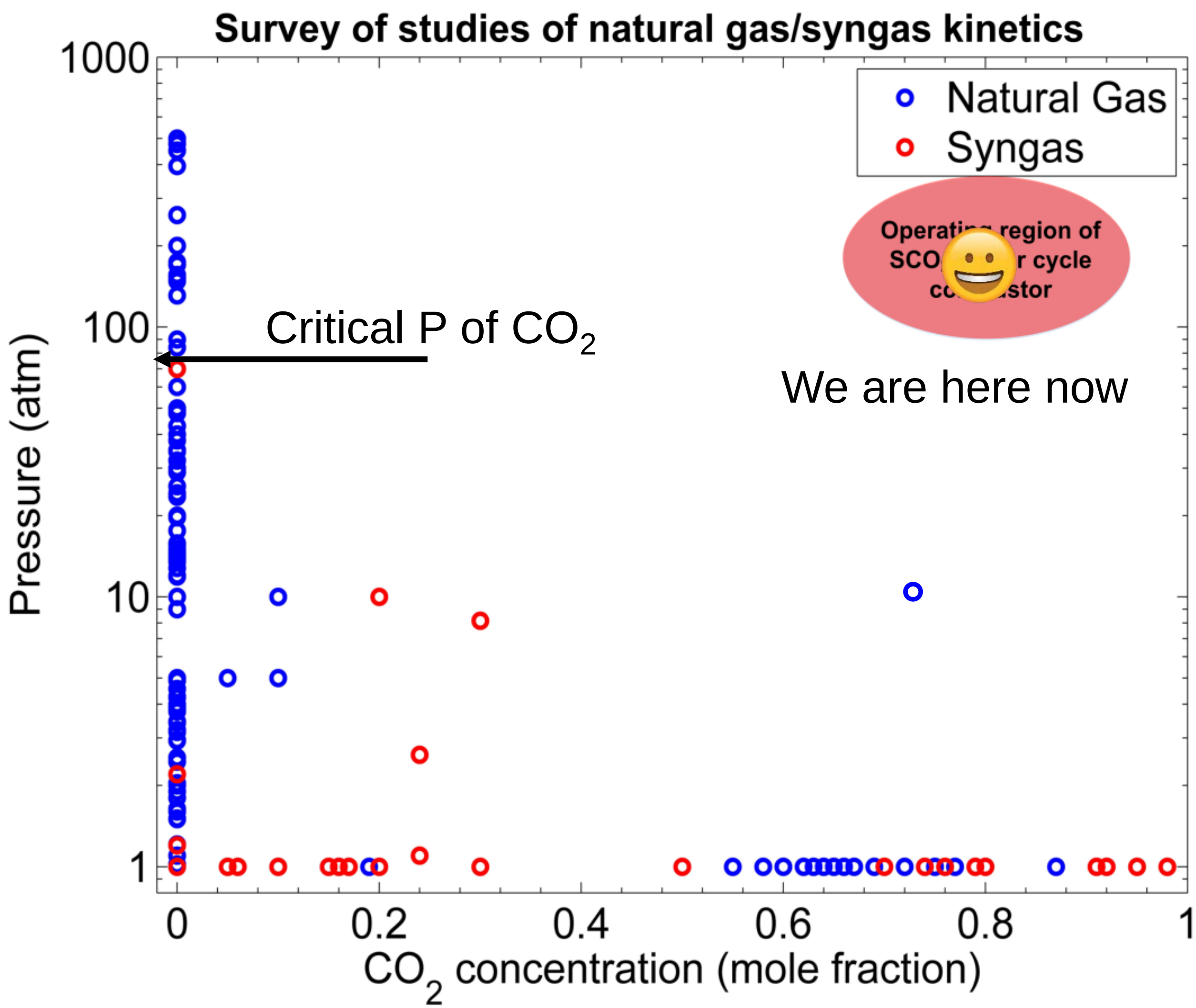
March 2016

October 2016



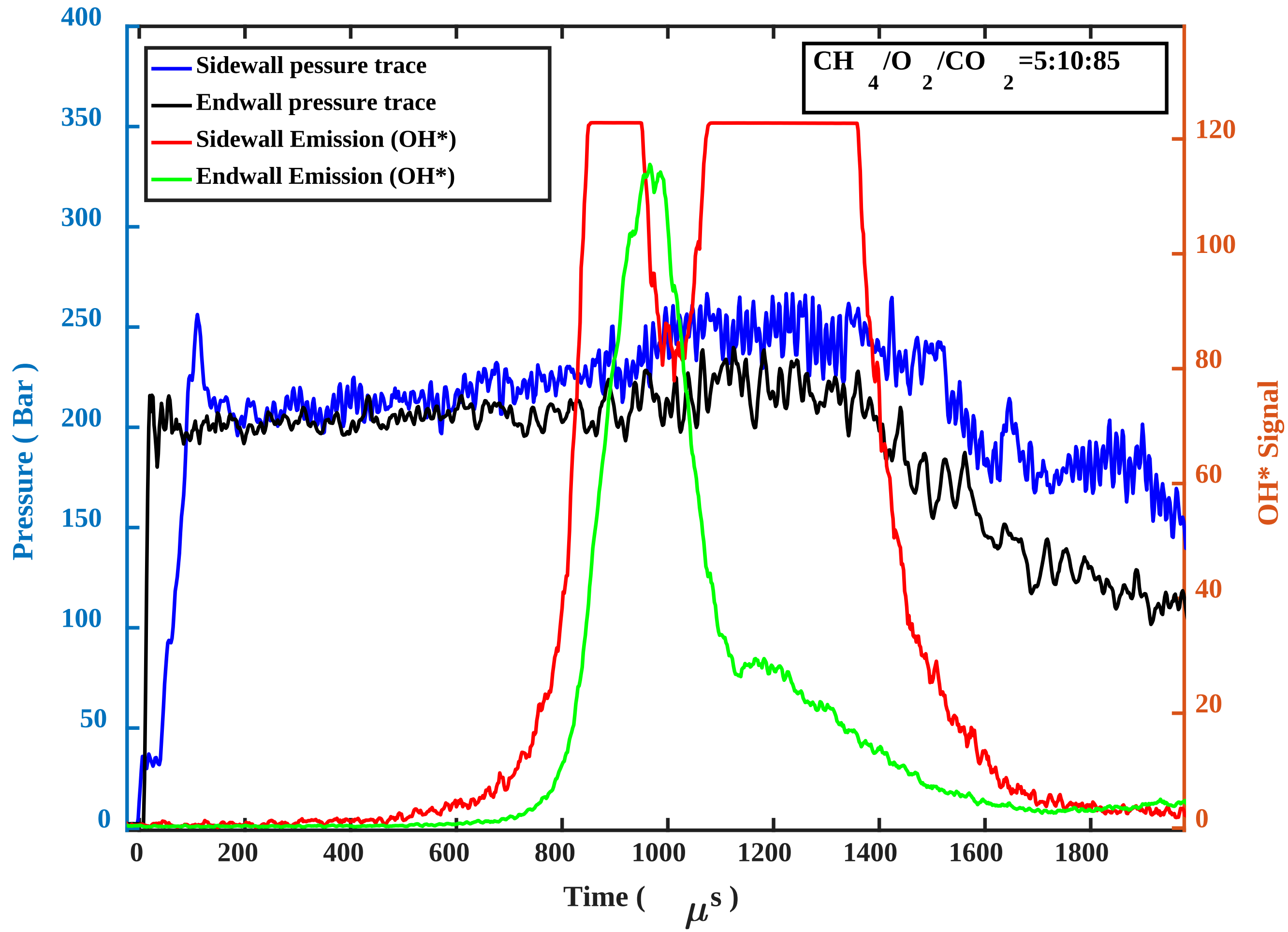
Task 2: Investigation of Natural Gas and Syngas Autoignition in sCO_2 Environment

- No study before in region of interest
- A new regime to explore!
- CO_2 has negligible chemical effect
  - Based on 1 to 15 atm results and simulation using GRI 3.0 and Aramco 1.3
  - GT 17 atm expt. Agreed with Aramco 1.3 using same mixture with Hargis et al.



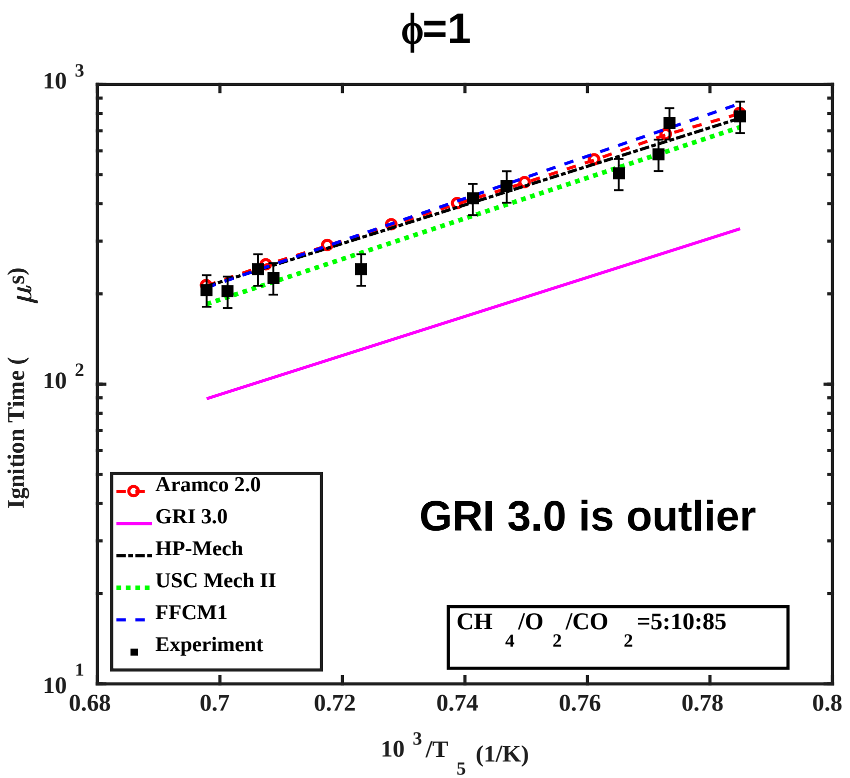
e.g.:
J.W. Hargis, E.L. Petersen, Energy & Fuels, (29) 2015
S. Vasu, D.F. Davidson, R.K. Hanson, Energy & Fuels, (25) 2011

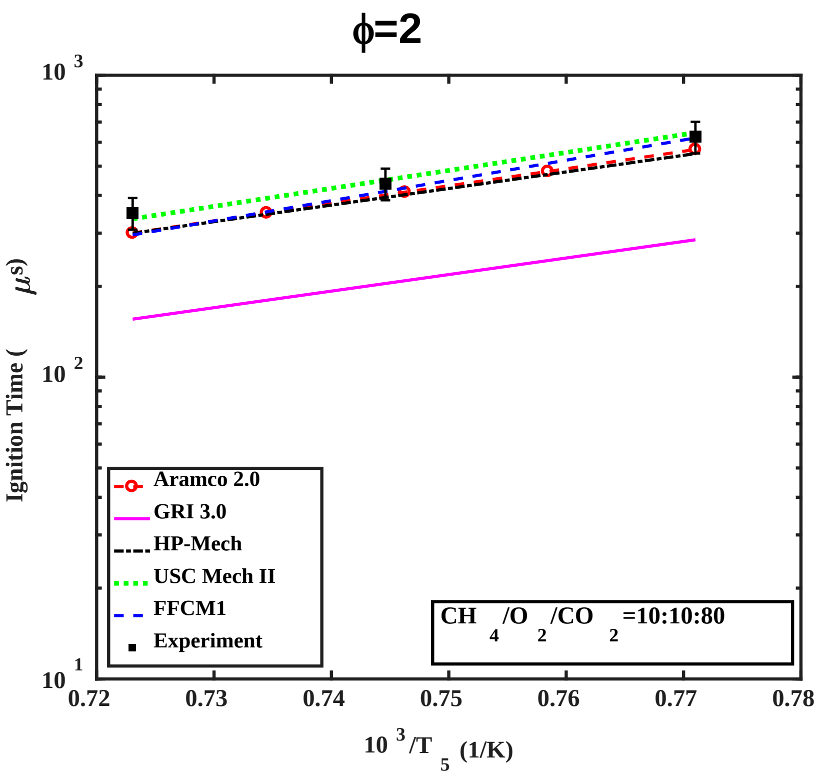
Pressure Traces in $CH_4/O_2/CO_2$ at 200 bar



Autoignition Delays at sCO_2 condition

- **Pressure: 100±5 bar**, and **temperature range of 1274 to 1433 K**

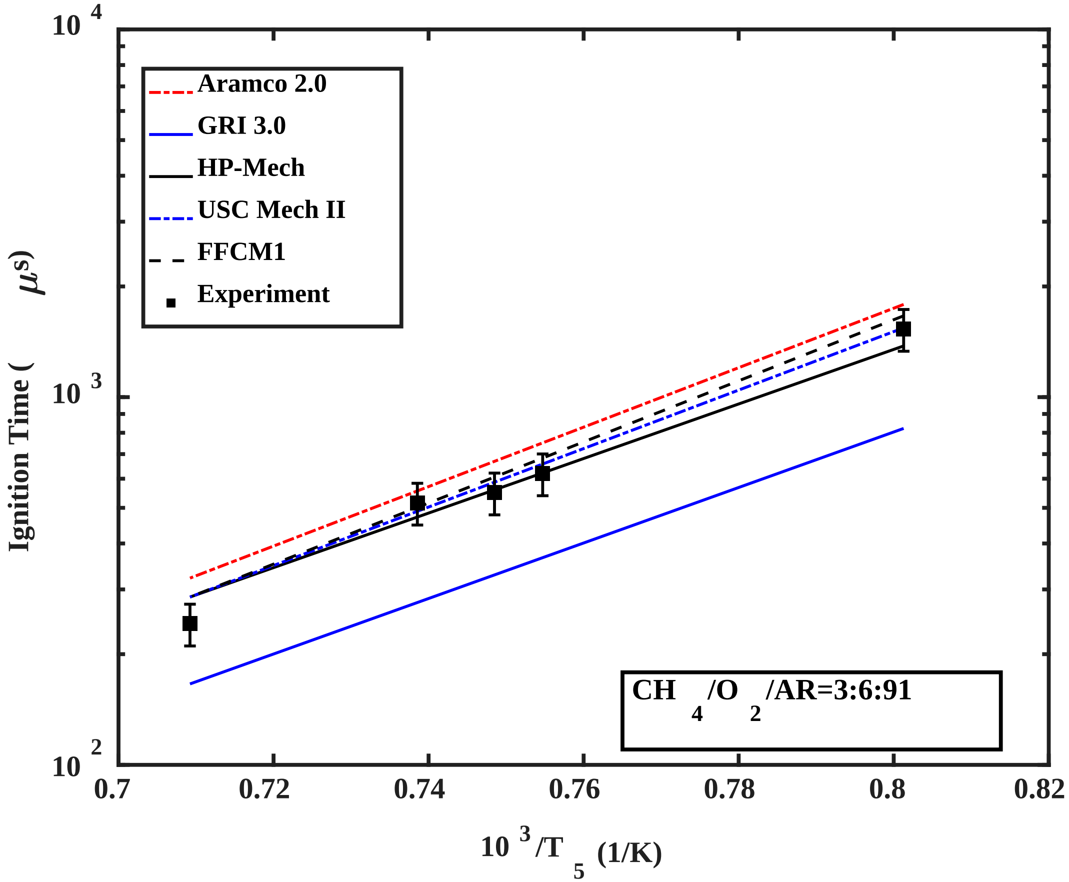




Simulation results from Aramco 2.0, USC Mech II and HP-Mech are close to each other, however GRI 3.0 predicts a significantly shorter autoignition delay, having approximately a **factor of 3 difference**

Autoignition Delays of CH_4 in Ar

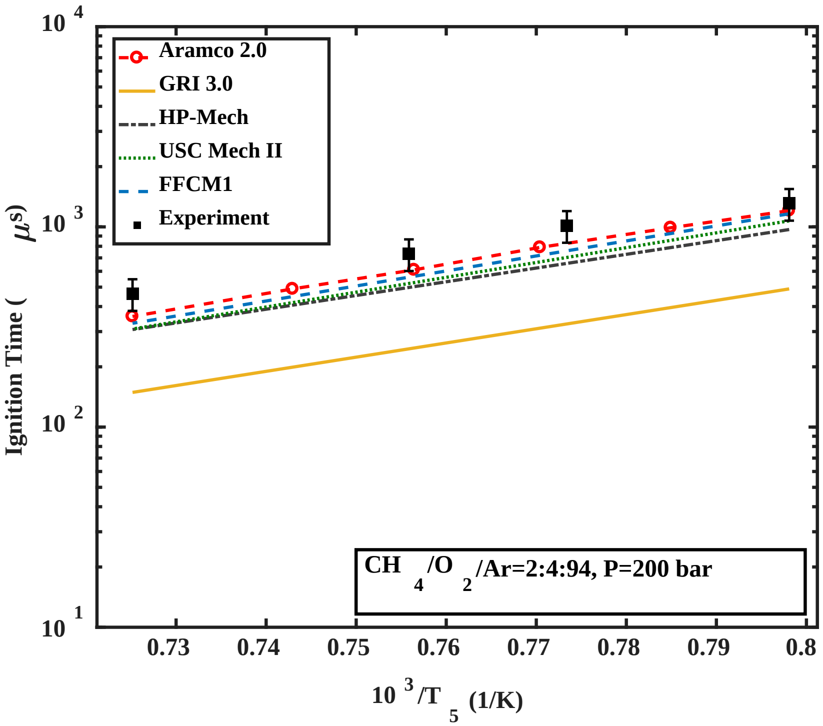
- **Pressure: 95±3 bar**, and **temperature range of 1248 to 1410 K**

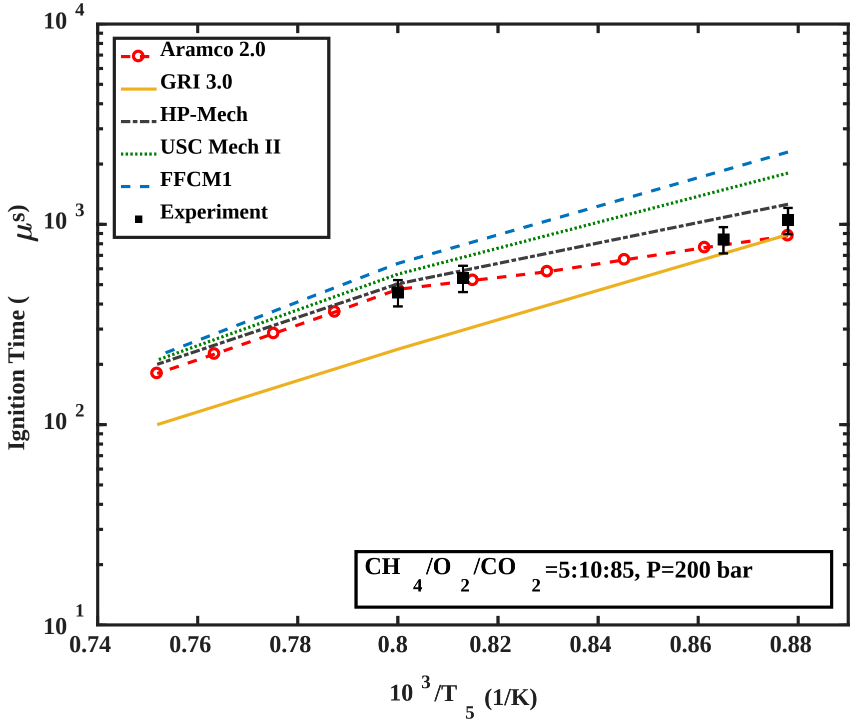


No chemical effect from diluent is observed

Autoignition Delays of CH_4 in CO_2 and Ar

- **Pressure: 200±5 bar**, and **temperature range of 1137 to 1380 K**





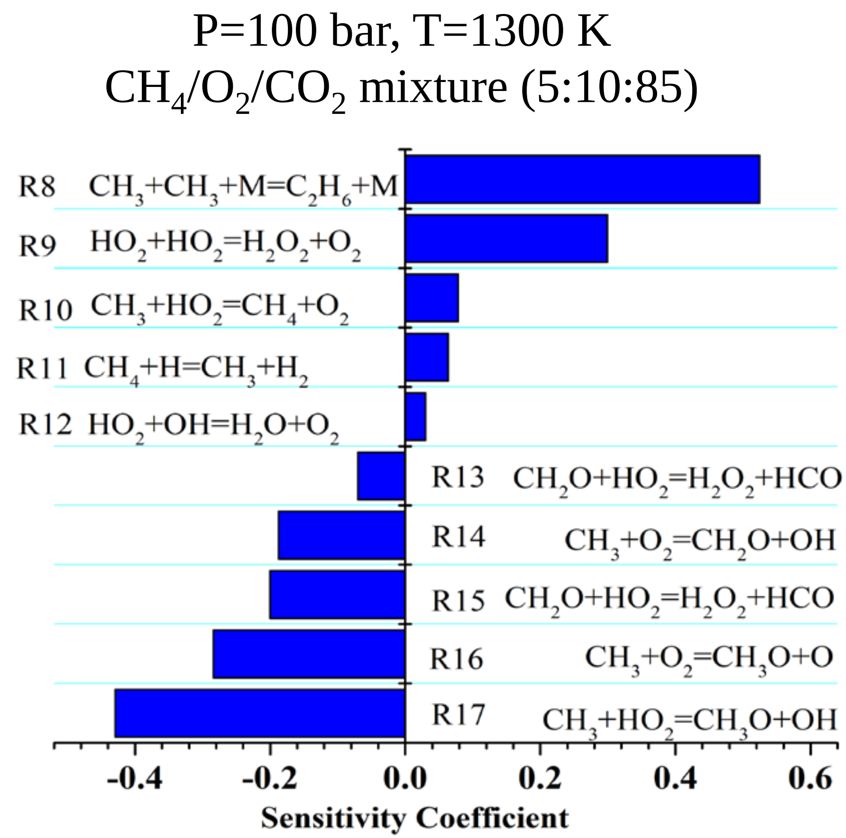
Temperature further distinguishes different kinetic models
- High T kinetics is much simpler than low T kinetics

Chemical Analysis

- Sensitivity Analysis: perturbing reaction rate constant of each reaction, see the response of autoignition delay

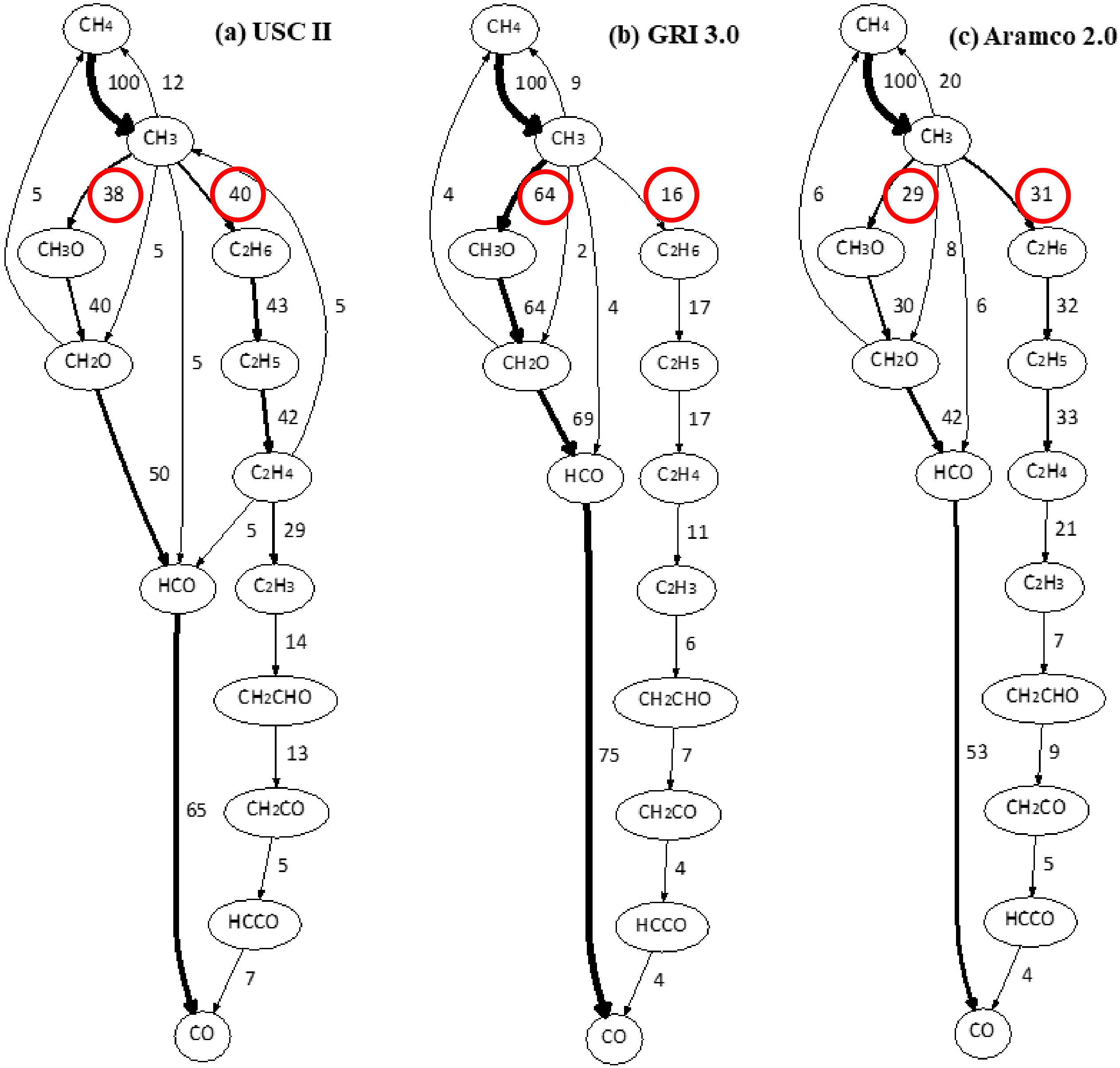
- CH_3+CH_3+M=C_2H_6+M becomes to be the most dominant one at high P condition

- Different from low pressure conditions, H+O_2=O+OH is the sixth most dominant reaction to enhance ignition



- The **third body efficiency** of CO_2 was investigated by simply doubling its value, which has a negligible effect on autoignition, consistent with previous work from 1-15 atm
    - J.W. Hargis, E.L. Petersen, Energy & Fuels, (29) 2015
    - S. Vasu, D.F. Davidson, R.K. Hanson, Energy & Fuels, (25) 2011

CH_4 Reaction Pathway Analysis

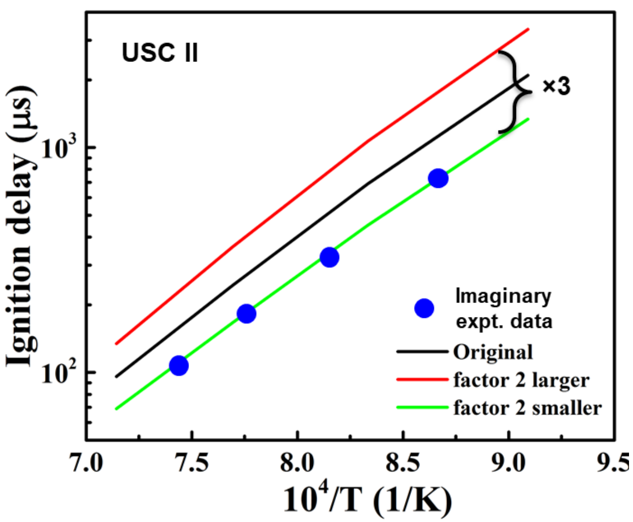


P=100 bar, T=1300 K

$CH_4/O_2/CO_2$ (5:10:85)

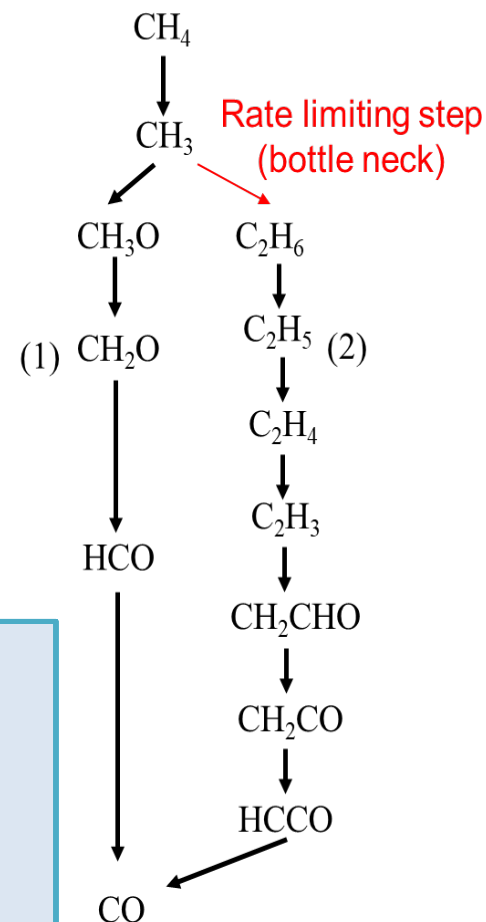
CH_4 Reaction Pathway Analysis

- Two reaction pathways
  - (1) CH_3 oxidation to CH_3O
  - (2) CH_3 recombination to C_2H_6
- Autoignition determined by **ratio of (1)/(2)**
- Ratio of (1)/(2): USC II: 0.94; Aramco: 0.95; GRI: 4
- First target for mechanism optimization



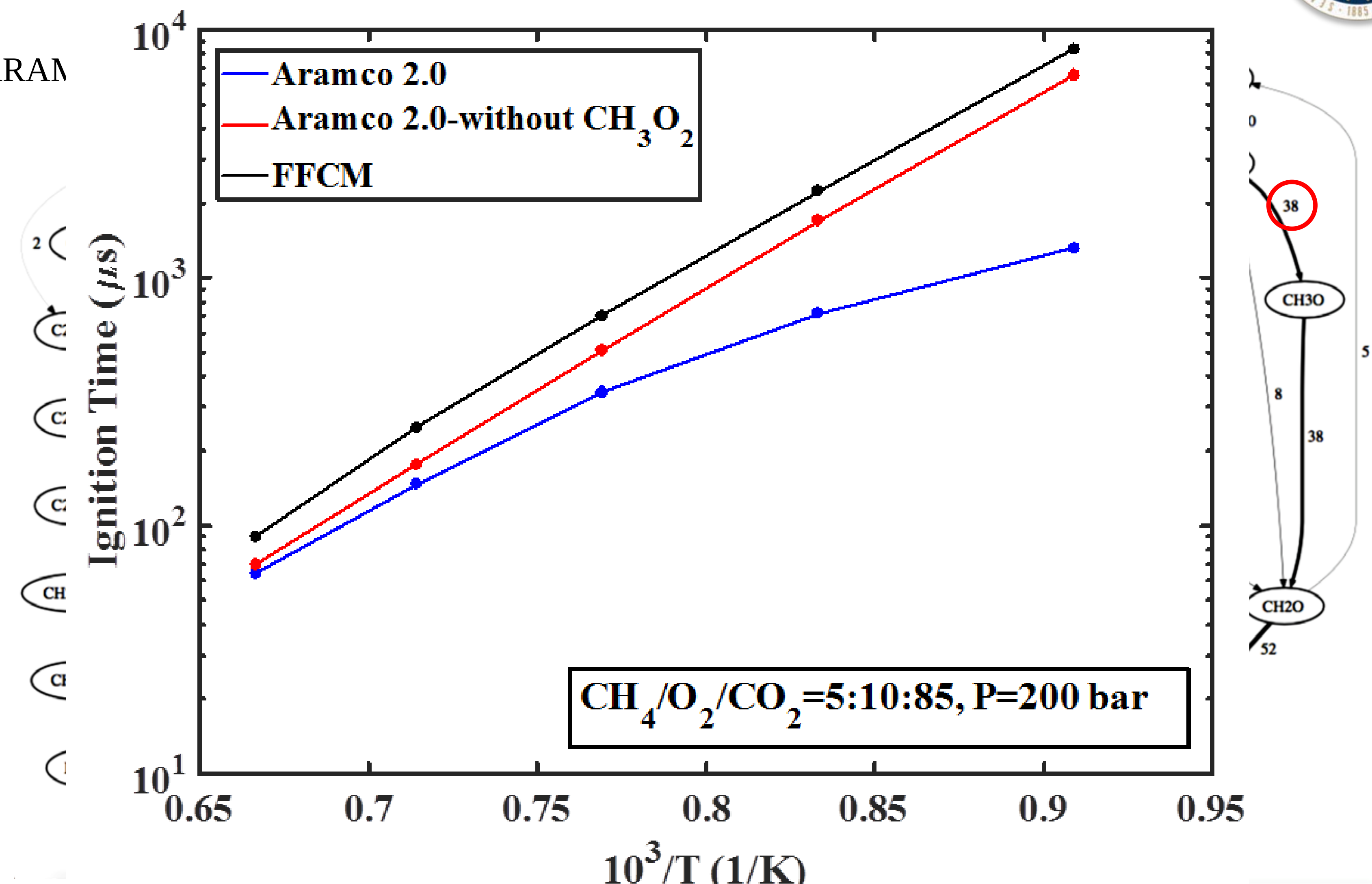
The rate constant of
CH_3+CH_3=C_2H_6
Determines τ_{ig}

It is already optimized



CH_4 Reaction Pathway Analysis

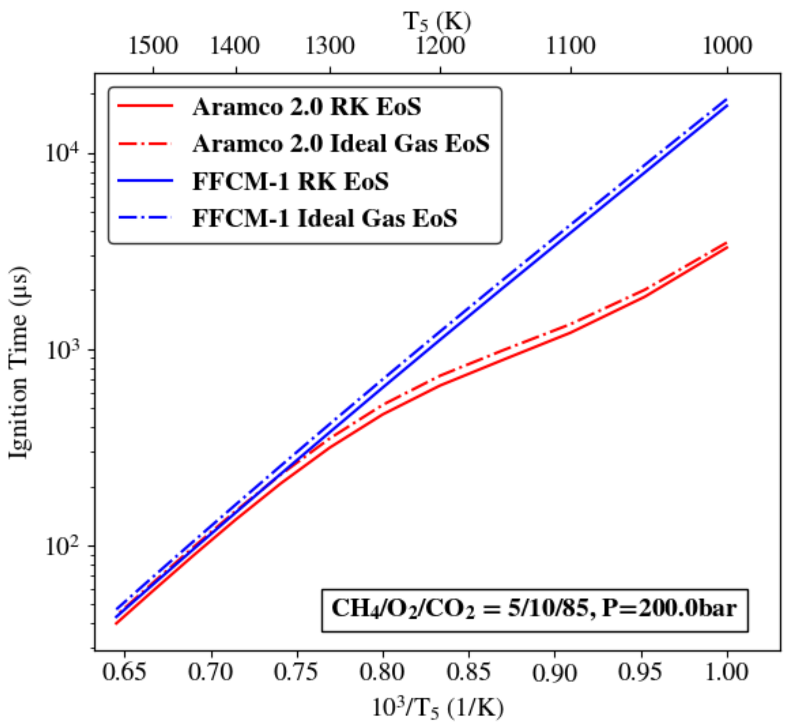
ARAM



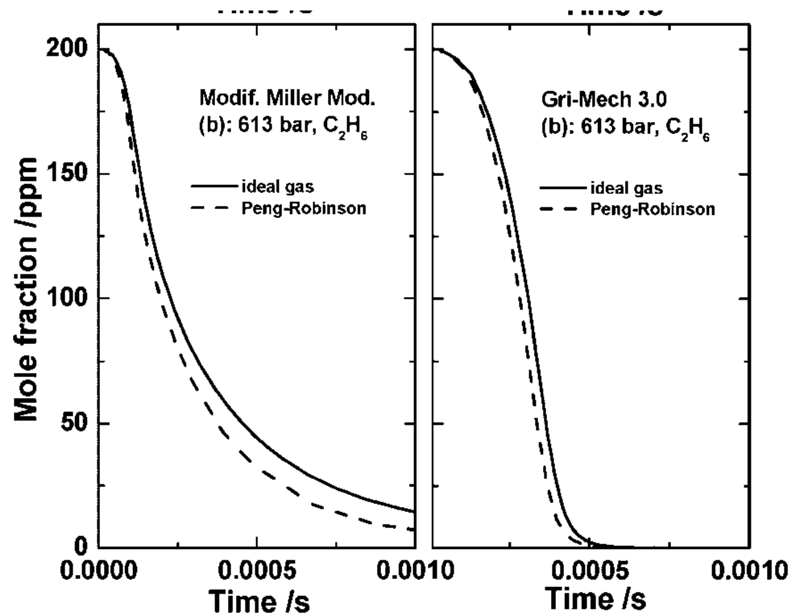
CH_3O_2 is NOT included in FFCM

Does Real Gas Effect Matter?

- Not here, but it depends…..



Real gas impacts on ethane profile
$C_2H_6/O_2/Ar$ @ 1300 K



Tang et al., IJCK 2006

- At high T (away from critical T), real gas behaves like ideal gas
- At low T (close to critical T), real gas effect is important

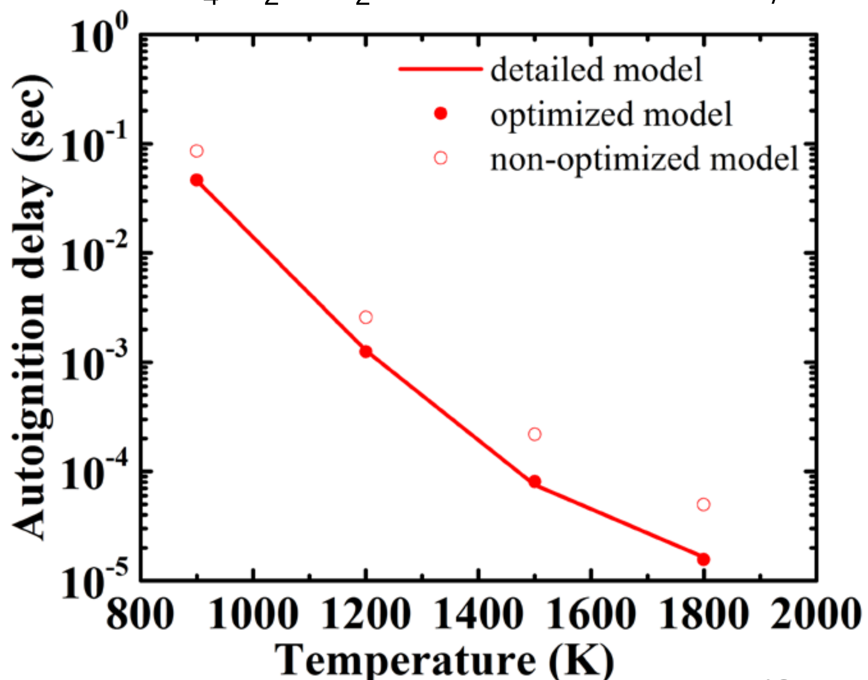
Task 3: Development of a Compact and Optimized Chemical Kinetic Model for sCO_2 Oxy-combustion

- USC II (111 species), Aramco 2.0 (493 species) can't be used in CFD
- 1st step is model reduction
  - GPS (http://sun.gatech.edu/download.htm)
  - Chem-RC (http://engine.princeton.edu/)

- A 27 species reduced mechanism[1] for natural gas and syngas is developed from USC II (still too large for CFD)

- A new 13 species model was developed with optimization
  - Covers 900 K to 1800 K, 100 atm to 300 atm
  - Max 12% deviation

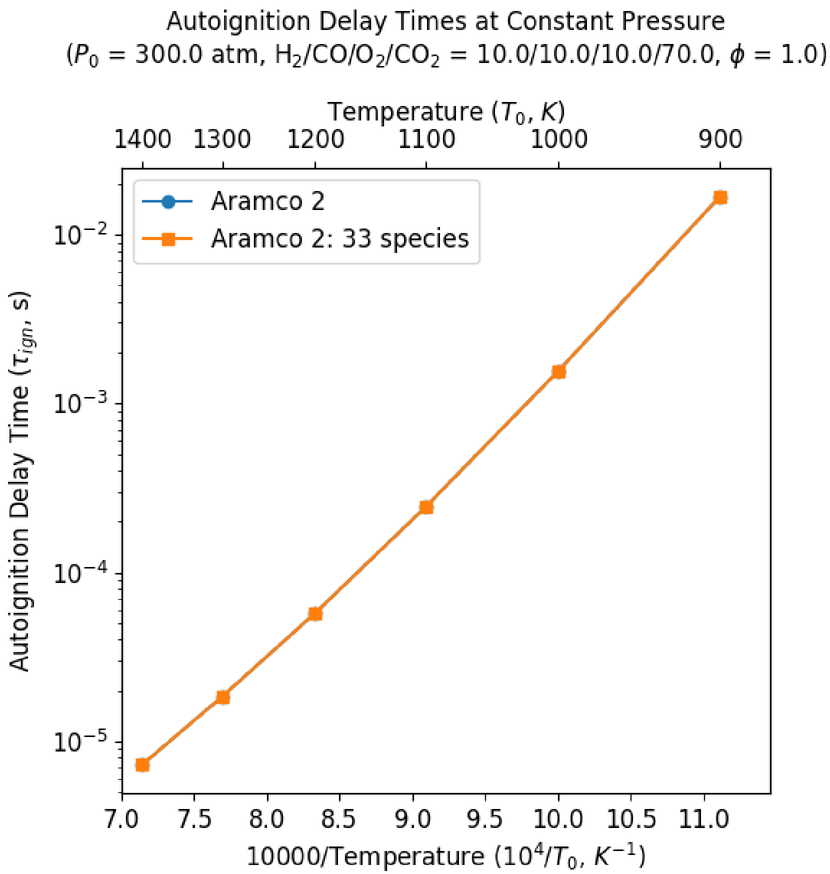
$CH_4/O_2/CO_2$=0.031/0.062/0.907 ϕ=1

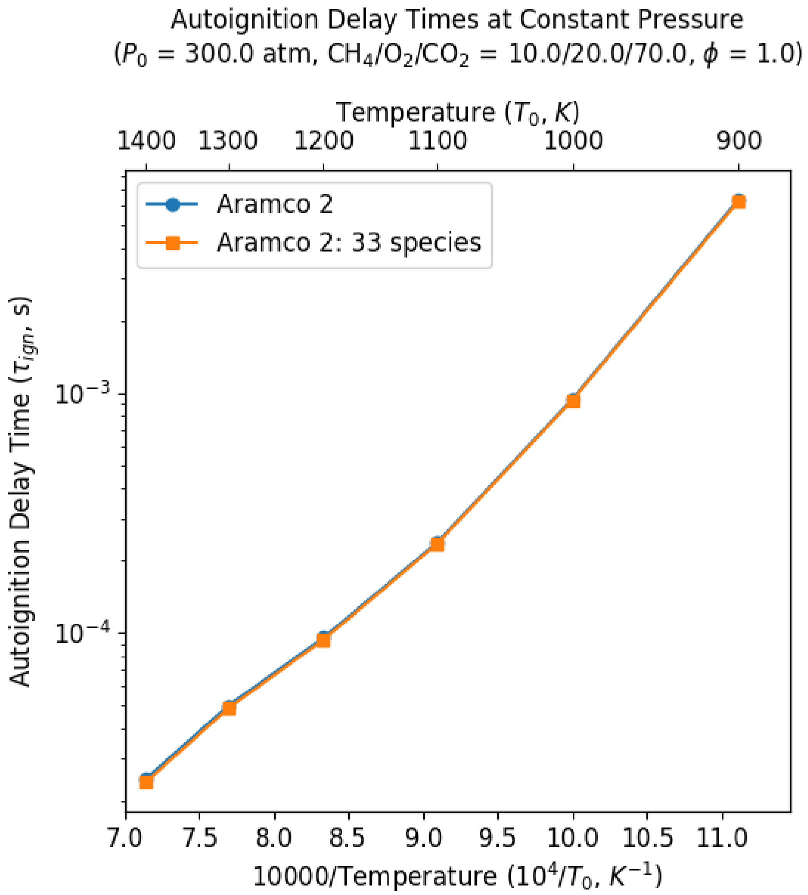


1. S. Coogan, X. Gao, W. Sun, Evaluation of Kinetic Mechanisms for Direct Fired Supercritical Oxy-Combustion of Natural Gas, TurboExpo 2016

Task 3: Development of a Compact and Optimized Chemical Kinetic Model for sCO_2 Oxy-combustion

- A 33 species reduced kinetic model for natural gas and syngas is developed using Aramco 2.0 (493 species)
  - Number of species is condition dependent: covers 900 K to 1800 K, 150 atm to 300 atm
  - Max 10% deviation



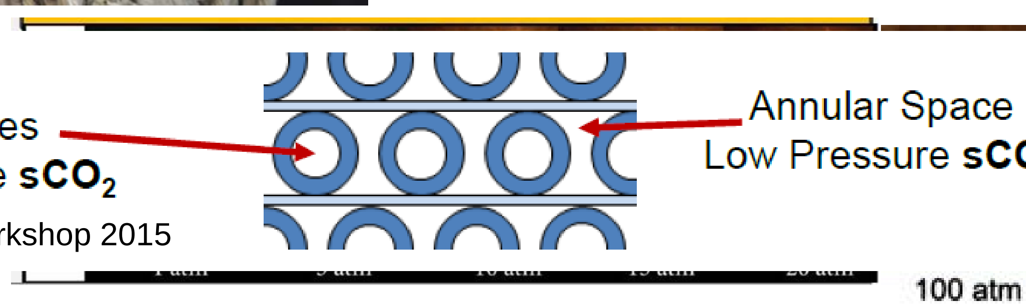


Task 6: Emission Properties of sCO_2 Oxy-combustion

- It seems pressure does not affect much in kinetics because model can predict ignition delays well
- Here comes the problem caused by pressure…

After 200

CH$_4$ diffusion flame

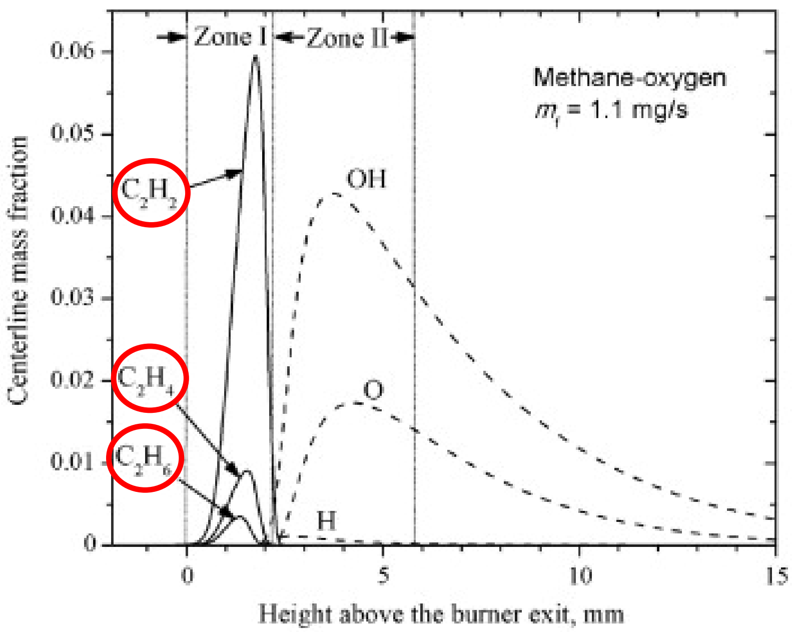


From Thar Energy, UTSR workshop 2015

Task 6: Emission Properties of sCO_2 Oxy-combustion

- Soot Formation Mechanism in High Pressure CH_4 Flame

CH_4/O_2 flame



Joo, Peter H., et al. *Combustion and Flame* 160.10 (2013): 1990-1998.

- Conclusion from our work:
- $CH_3+CH_3+M=C_2H_6+M$ becomes to be the dominant at high P condition

C_2H_6 → C_2H_4 → C_2H_2 → C_6 ring → soot

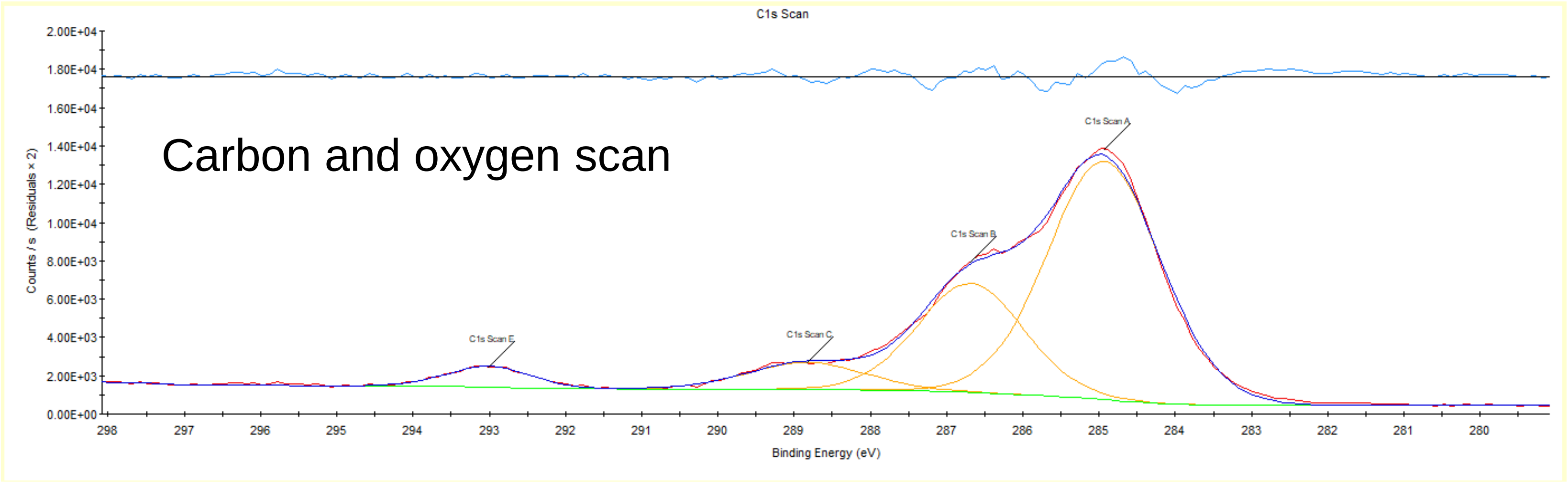
- Then C_2H_6 promotes soot formation

Task 6: Emission Properties of sCO_2 Oxy-combustion

- Analysis of deposits from shock tube experiments

Preliminary results:

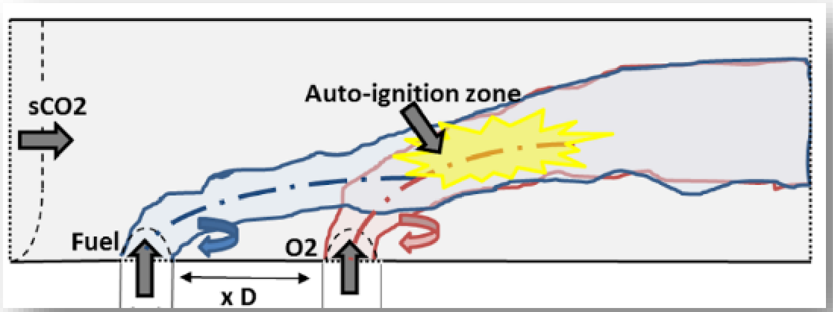
- Composition: C/O≈3/1 (typical value owing to partial oxidation)
- Chemical bond: C-C or C=C (~60%); C-O (~36%)



Recap of kinetic investigation

- GRI 3.0 fails at high pressure
  - It is compact and has NOx module included, but it does not work at high pressure (P>100 bar)
- Aramco 2.0 agrees with experiments very well through the temperature range of tests. HP-Mech works too.
- FFCM-1, USC II work well at high temperature region (T>~1200 K), but their predictions deviate with experiments when T<~1200 K because of the missing CH_3O_2 kinetics
- CO_2 has no chemical effect on <u>ignition</u> kinetics
- Significant particulate formation observed at high P, probably owing to partial oxidation (study ongoing)

Task 5: LES Studies of Supercritical Mixing and Combustion



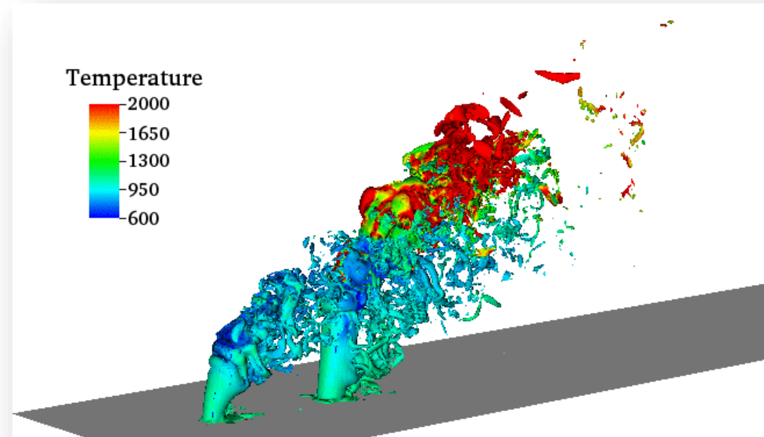
Baseline model
NOT actual design

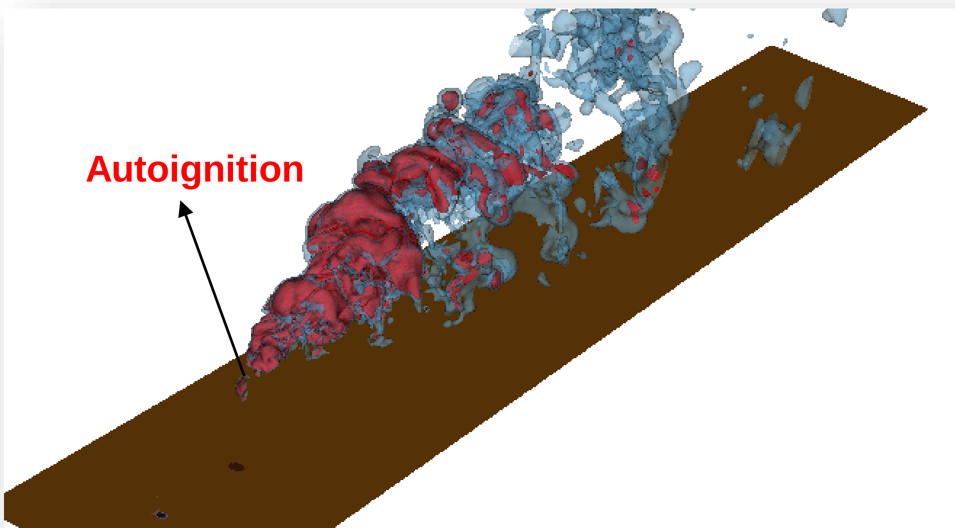
- Mixing and flame stability
- Systematic variation of design parameters
  - Momentum ratios for fuel and oxygen, flow rate, number of sets
  - Size, spacing, and locations of injectors
- Computational modeling may be more cost effective but include its own challenges
  - Kinetics
  - Turbulence-chemistry closure
  - Real gas effects

Task 5: LES Studies of Supercritical Mixing and Combustion

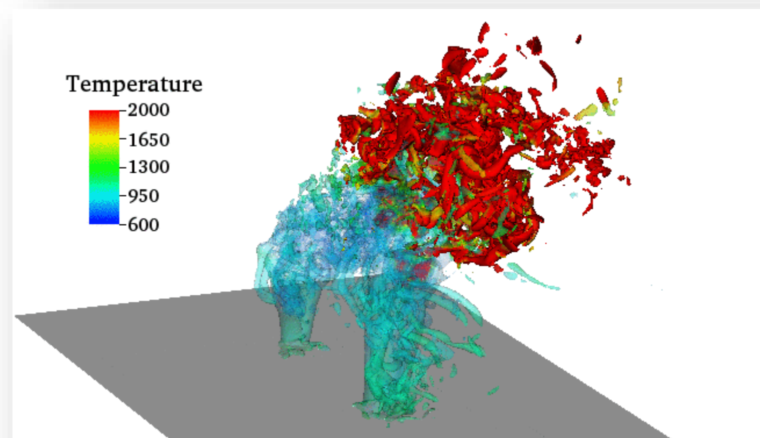
Instantaneous Reacting Flow Features

- Autoignition close to predicted location based on mixing
- Autoignition occurs slightly downstream of the oxidizer jet towards lean side
- Autoignition with lifted flame structure



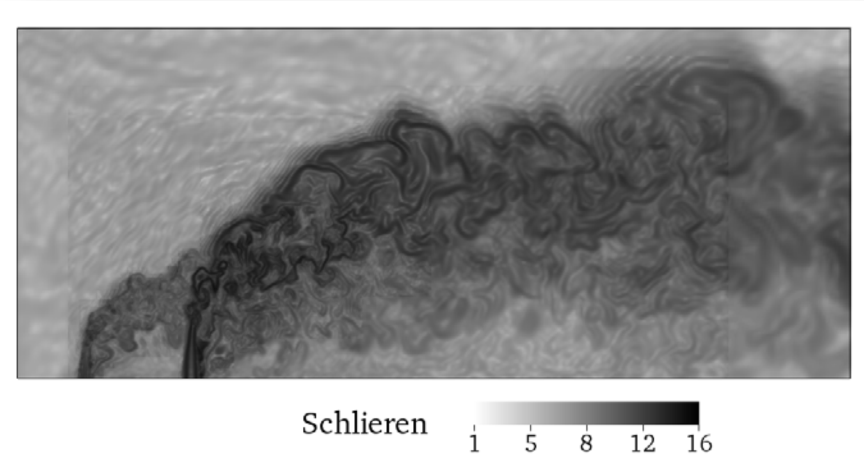


Temperature iso-surface (2100 K, 1500 K)

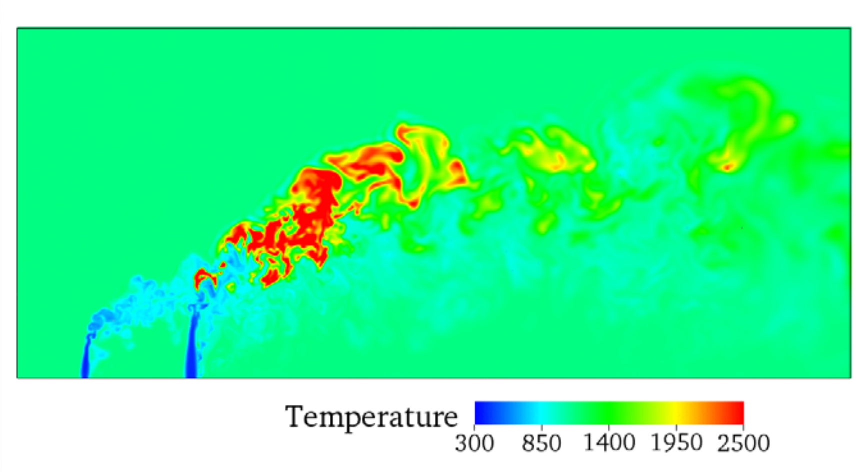


Vorticity magnitude colored by temperature

Instantaneous Reacting Flow Features



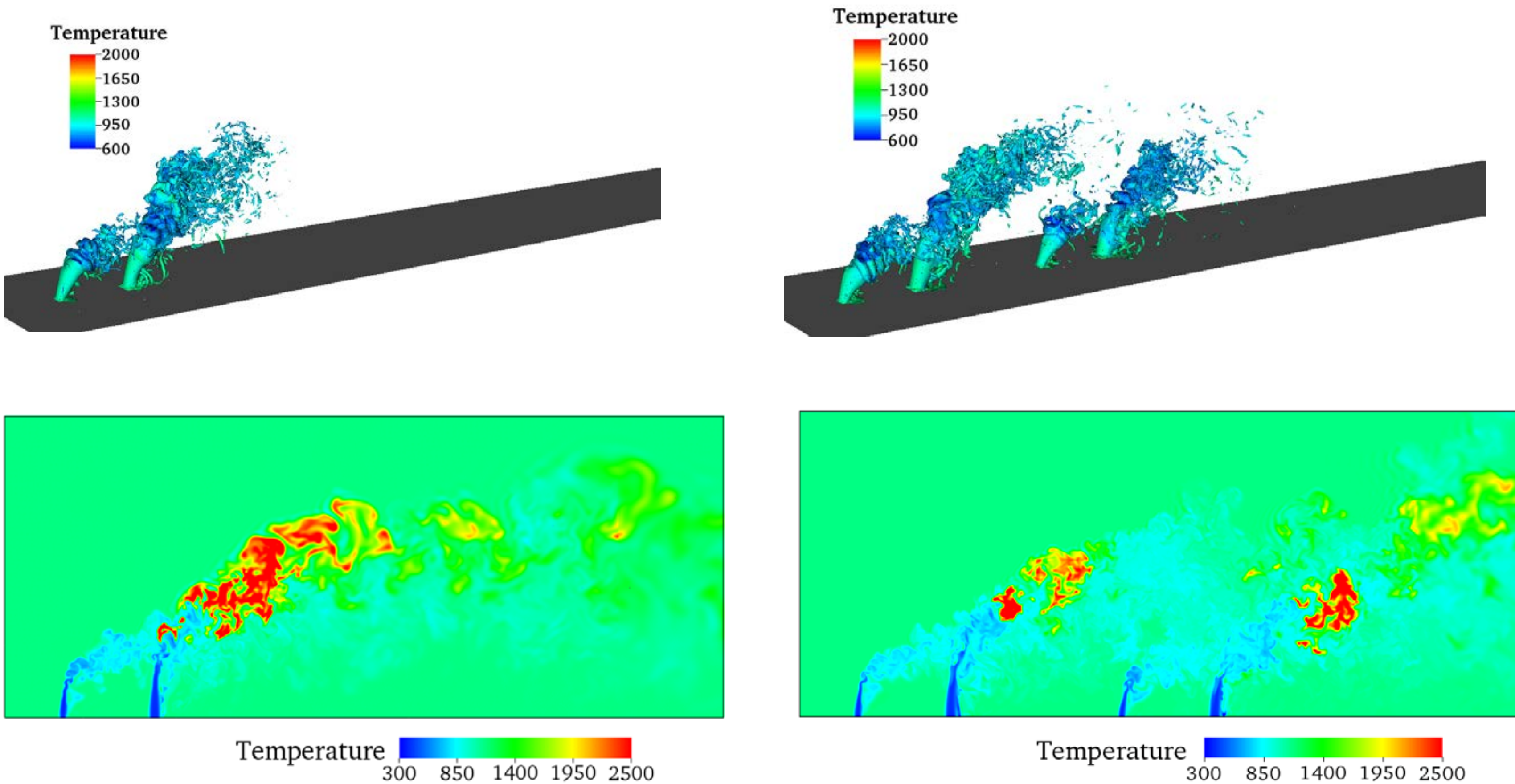
Schlieren



Temperature

- Large density gradient (Schlieren: log of density gradient)
- Mixing of fuel and oxidizer followed by ignition in lifted regions
- Autoignition in hot kernels where fuel mixes with oxidizer
  - Finite-size kernel but no continuous flame structure
- Autoignition sensitive to many parameters: mixing time, kinetics, local scalar dissipation rate, etc.

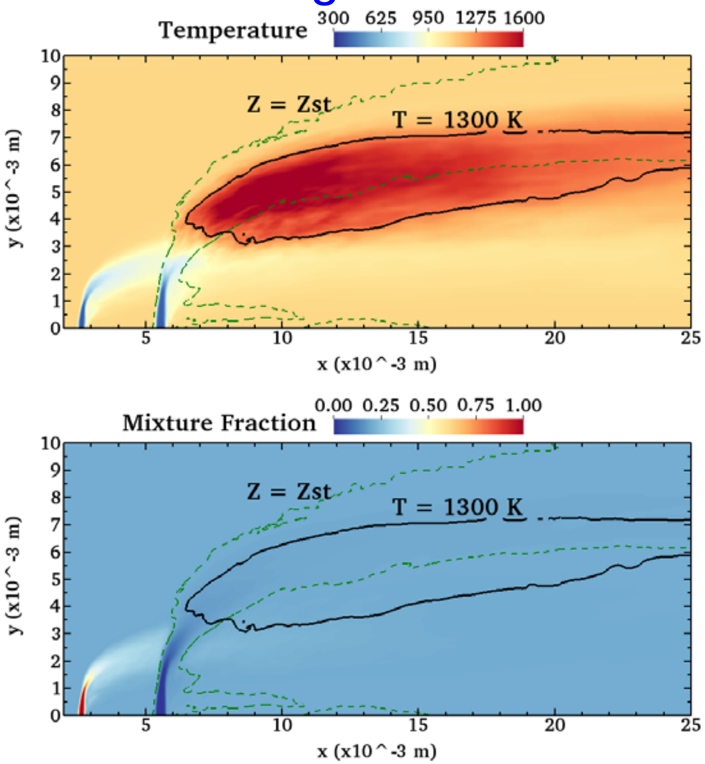
Autoignition and Blow out



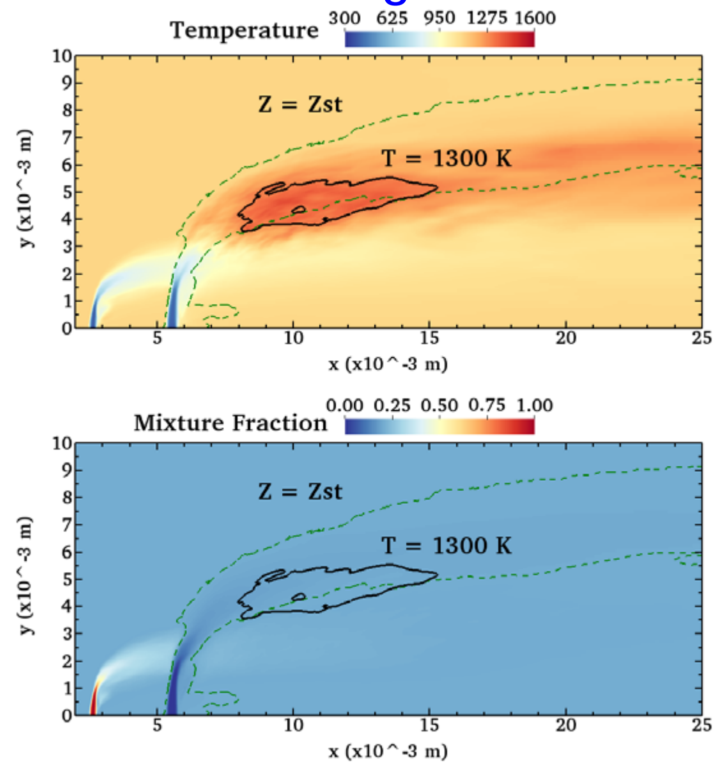
- Possible upstream influence of acoustic waves

Real Gas Effect

Real gas EOS



Perfect gas EOS



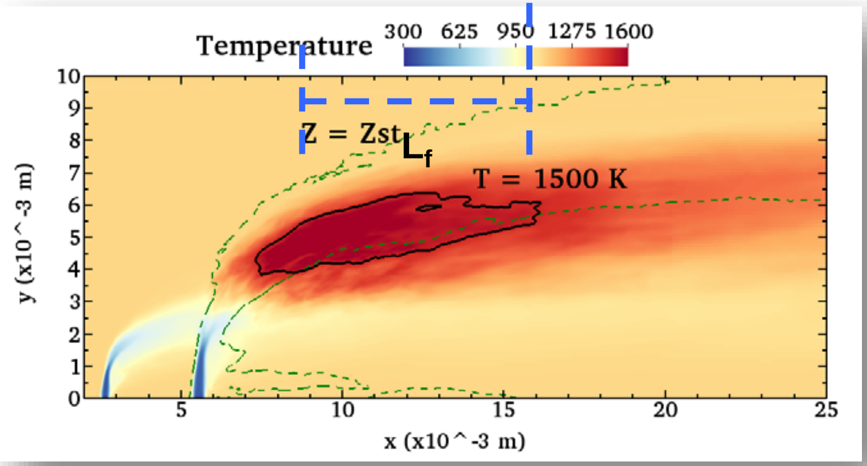
- Reduced jet penetration with perfect gas EOS in comparison to Peng Robinson EoS – clearly shows RG effects
- Heat release also decreased with perfect gas EOS

Flame Length and Combustion Efficiency

- **Combustion is not efficient**
- Combustion efficiency estimated as:

$$\eta = 100 \times \frac{\dot{m}_{f,in} - \dot{m}_{f,out}}{\dot{m}_{f,in}} \sim 49\%$$

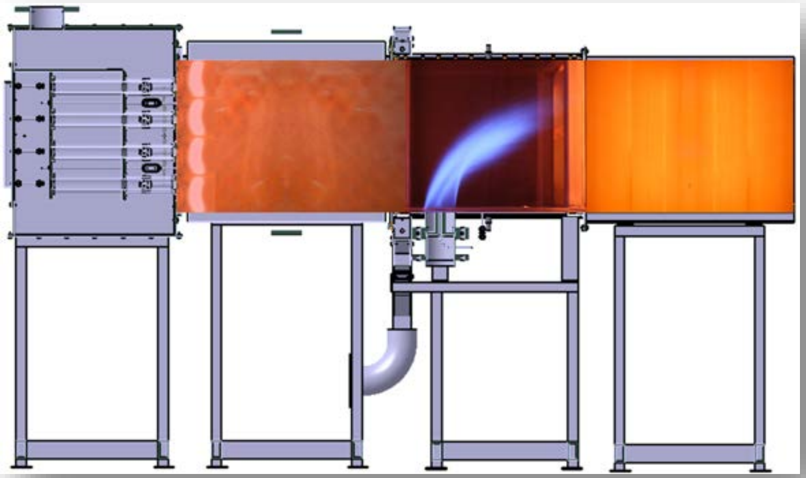
- Flame length, $L_f \sim 14.5\ D_{ox}$
  – estimated as intersection of $Z = Z_{st}$ and T = 1500 K
- η needs to be improved
  – Inflow realistic turbulence
  – Modify J and jet spacing
  – Mass flow rate changes
  – Jet-staging and distributed mixing
  – **Inflow swirling**
- Mixing is the key
- Use network modeling for rapid assessment



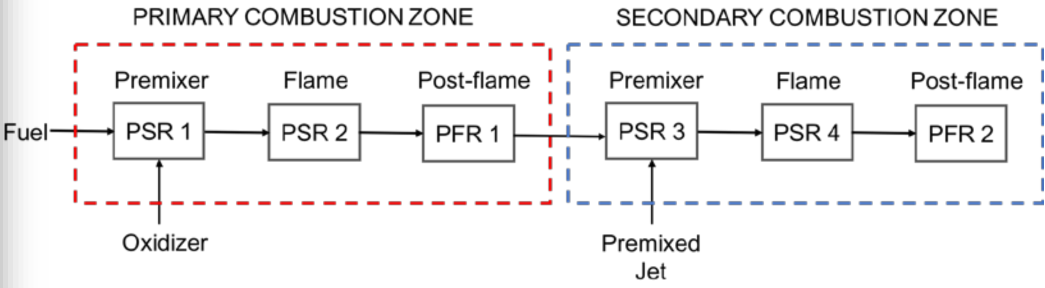
Temperature overlaid with stoichiometry line

Chemical Reactor Network (CRN) Modeling

- A viable computationally affordable alternative for parameter study



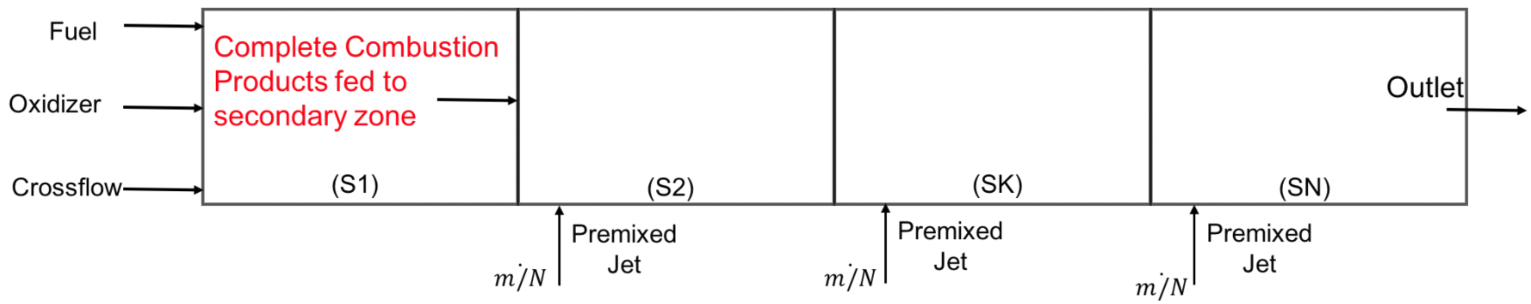
Axially staged premixed combustion device [Ahrens et al. (2014)]



CRN Model

- A two-stage premixed combustion device
  - where the fuel/air mixture is split across primary and secondary combustion zones
- Setup essentially is reacting jet in a hot crossflow
- CRN model: 2 PSRs and 1 PFR for each of the combustion zone

Effect of Staging on CO Emissions



Multi-staging

Number of jets	Outlet: T	Outlet: CO	Outlet: CO_2
1	3332.9 K	0.0091	0.279
2	2675.6 K	0.0078	0.227
3	2379.9 K	0.0011	0.190
4	2334.5 K	0.0010	0.151

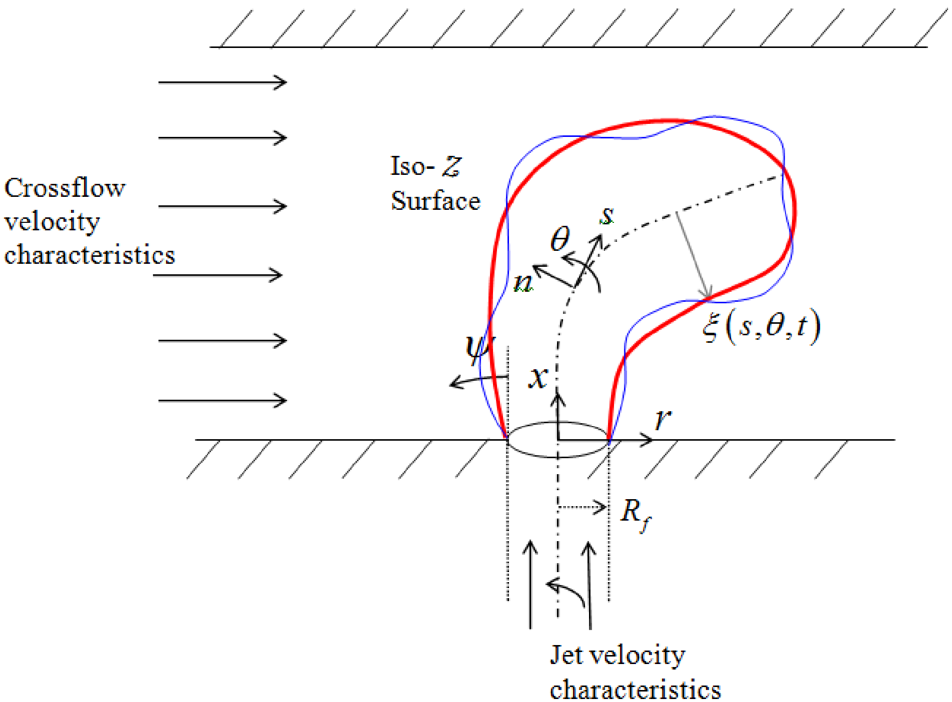
- Effect of number of stages on temperature and concentration of CO and CO_2 is examined
- With increase in number of stages, CO emission tends to reduce, which is consistent with experimental studies

Task 4: Analytical modeling of Supercritical Reacting Jets in Crossflow

- Analytical framework for reacting jets in cross-flow
  - connect flow dynamics to flame dynamics
  - Modeling explicit flame position dynamics
  - Modeling spatially integrated heat release dynamics as a function of flame position

- Understanding flow dynamics of a jet in cross-flow
  - provide key inputs to the velocity field used in the analytical model

CFD with large kinetics is pain…



Analytic model of jet in crossflow

Non-premixed Flame Position Dynamics

- Task outcome: PDE for flame position fluctuations & solution
- Wrinkle convection
  - Flow based convection of flame "wrinkles"
- Reactive nature of wrinkle generation
  - From diffusion based physics that drives the mean flame position
- Local flow fluctuations serve as source of "wrinkles" (RHS)

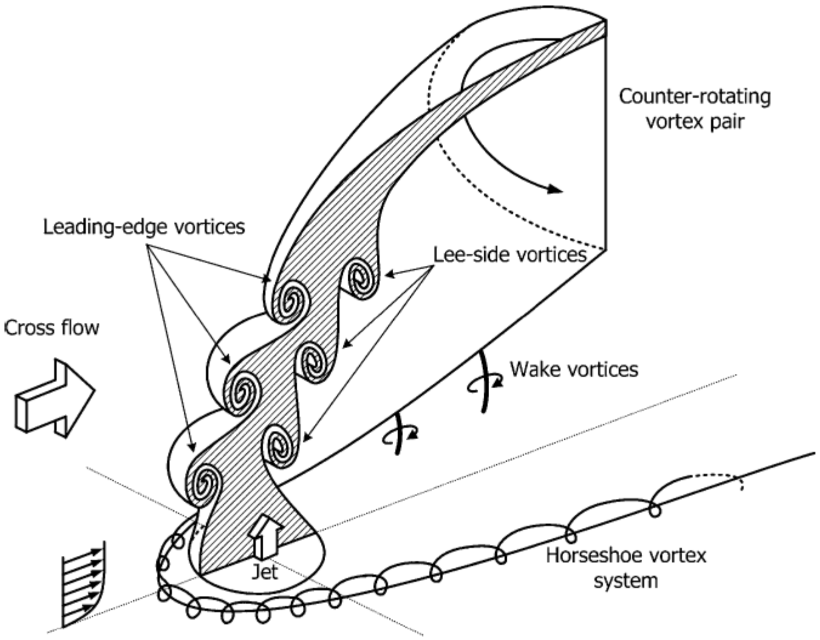
$$\frac{\partial \xi_{1,n}}{\partial t} + u_{x,0}\frac{\partial \xi_{1,n}}{\partial x} - u_{x,0}\left(\frac{d^2\xi_0}{dx^2}\Bigg/\left\{\frac{d\xi_0}{dx}\left(1+\left(\frac{d\xi_0}{dx}\right)^2\right)\right\}\right)\xi_{1,n} = -u_{x,1}\left(\frac{d\xi_0}{dx}\Bigg/\sqrt{\left(1+\left(\frac{d\xi_0}{dx}\right)^2\right)}\right)$$

$$\xi_{1,n}(x,t) = \int_0^t u_{n,1}(x,t')\,dt' - \int_0^{t-\frac{x}{u_{x,0}}} u_{n,1}(0,t')\,dt'$$

- Governing Physics in solution
  - Time history of local disturbances
  - Disturbances convected from inlet
- Allows comparative analysis with premixed flames for both laminar and turbulent framework

Understanding JICF from Measurements

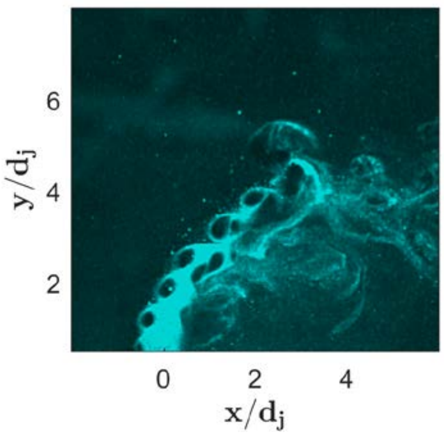
- Focus: Shear layer vortices (SLV)
  - leading-edge and lee-side
  - SLV behavior contributes to near-field and pre flame entrainment and mixing
  - SLV rollup and distort to form the CVP, major topological feature which governs mixing
- Use measured data from JICF experiments to characterize SLV
  - Stereo PIV flow measurements
  - OH-PLIF flame measurements
  - Compare reacting and non-reacting cases for JICF SLV behavior



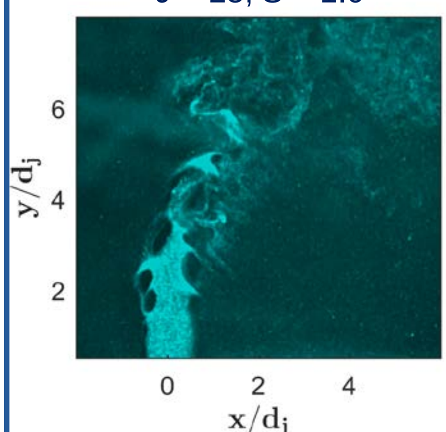
JICF Stability – Representative Results

Non-reacting cases

J = 5, S= 1.0



J = 25, S = 1.0



Globally unstable behavior

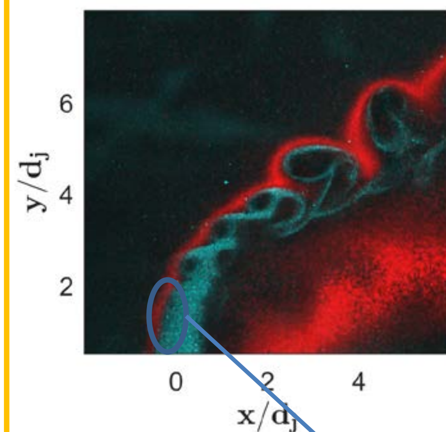
- Global jet oscillations
- SLV formed near jet exit

Convectively unstable behavior

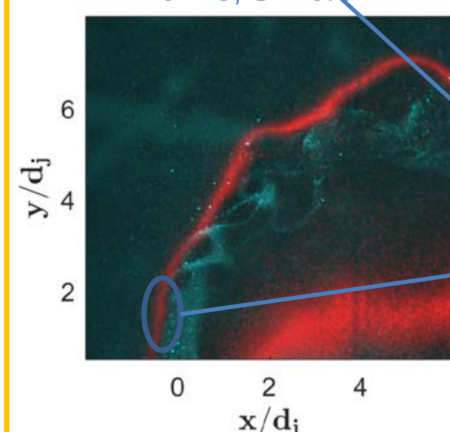
- Suppressed SLV formation
- Vortex growth/pairing

Reacting cases

J = 5, S = 1.0



J = 5, S = 0.4



Factors that govern SLV behavior:

- Jet momentum flux ratio, $J = \frac{\rho_j u_j^2}{\rho_\infty u_\infty^2}$
- Jet to crossflow density ratio, $S = \frac{\rho_j}{\rho_\infty}$

Reacting cases which should show globally unstable behavior based on S and J show convectively unstable SLV structure

Suppressed SLV behavior

Flame weakens mixing

Summary of Accomplishments

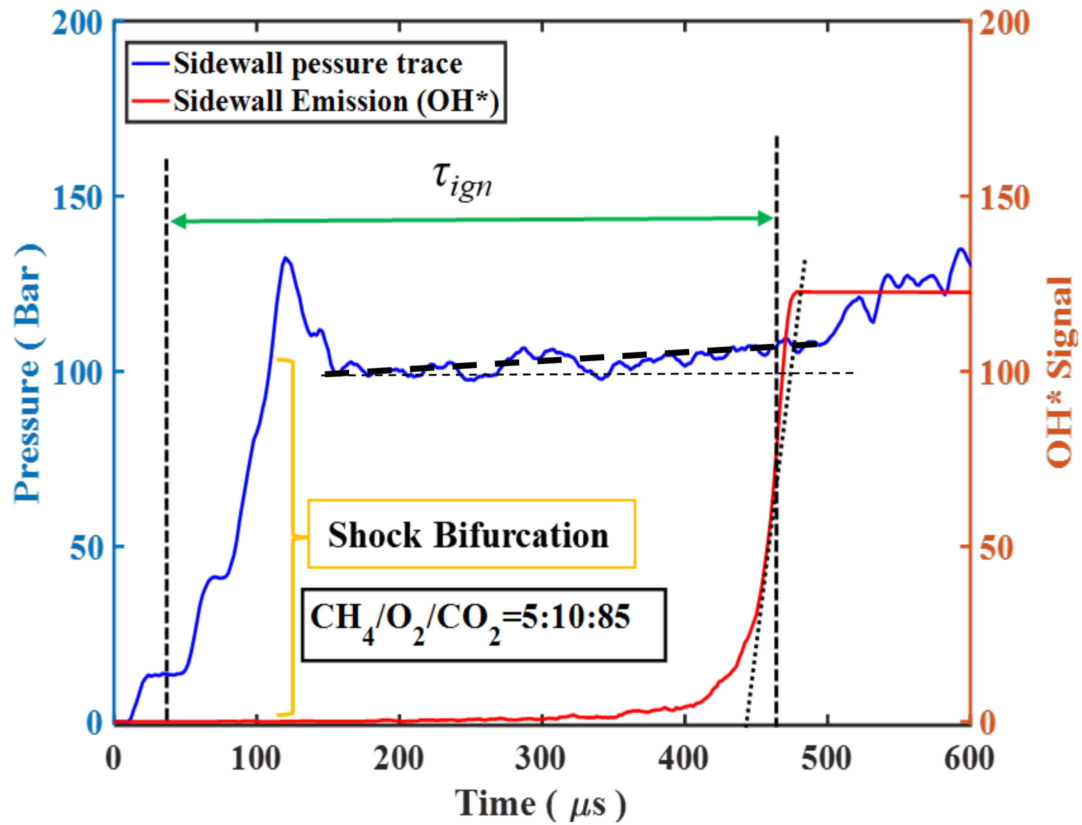
- High pressure shock tube developed and commissioned
- IDT measurements at relevant conditions validated kinetic models
- Reduced/optimized kinetic models developed and implemented in CFD
- Theoretical framework developed for JICF
- LES framework and investigation of JICF
- **Recommendation on combustor design:**
  - Mixing is critical and challenging: efficiency & emissions (watch out!)
  - Low T region is challenging both physically and chemically

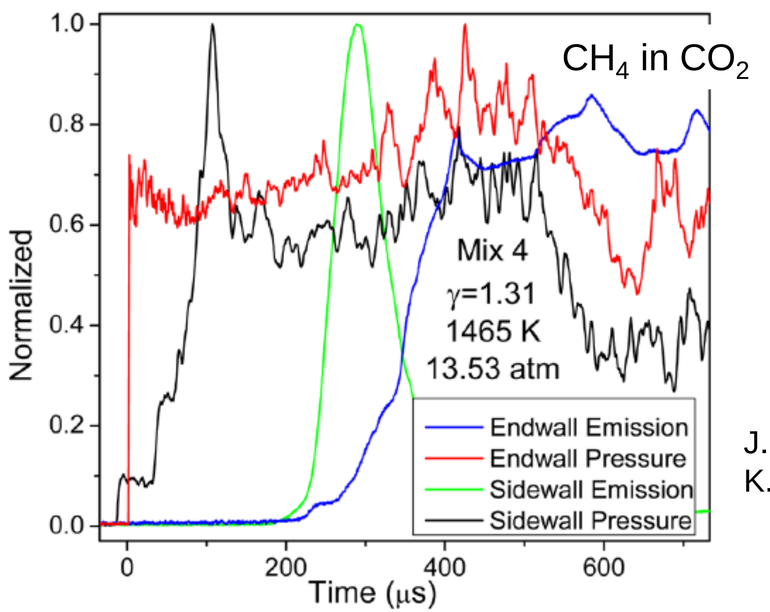
Thank you! & Questions?

Acknowledgement:
UTSR Project: DE-FE0025174; PM: Seth Lawson

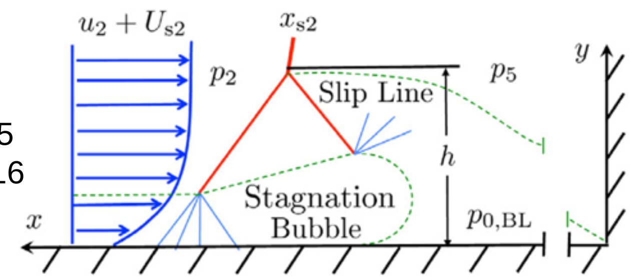
Challenges of Experiments at sCO_2 Condition

- Large C_p of CO_2
  - Strong shock needed for CO_2
- BL is much thicker with CO_2
  - Non-ideal effect
- **ID of shock tube must be large**
  - **150 mm**
  - **High experimental cost**





J. Hargis & E. Peterson, E&F, 2015
K. Grogan & M. Ihme, PROCI, 2016



Shock Tube Development
- mixture preparation system

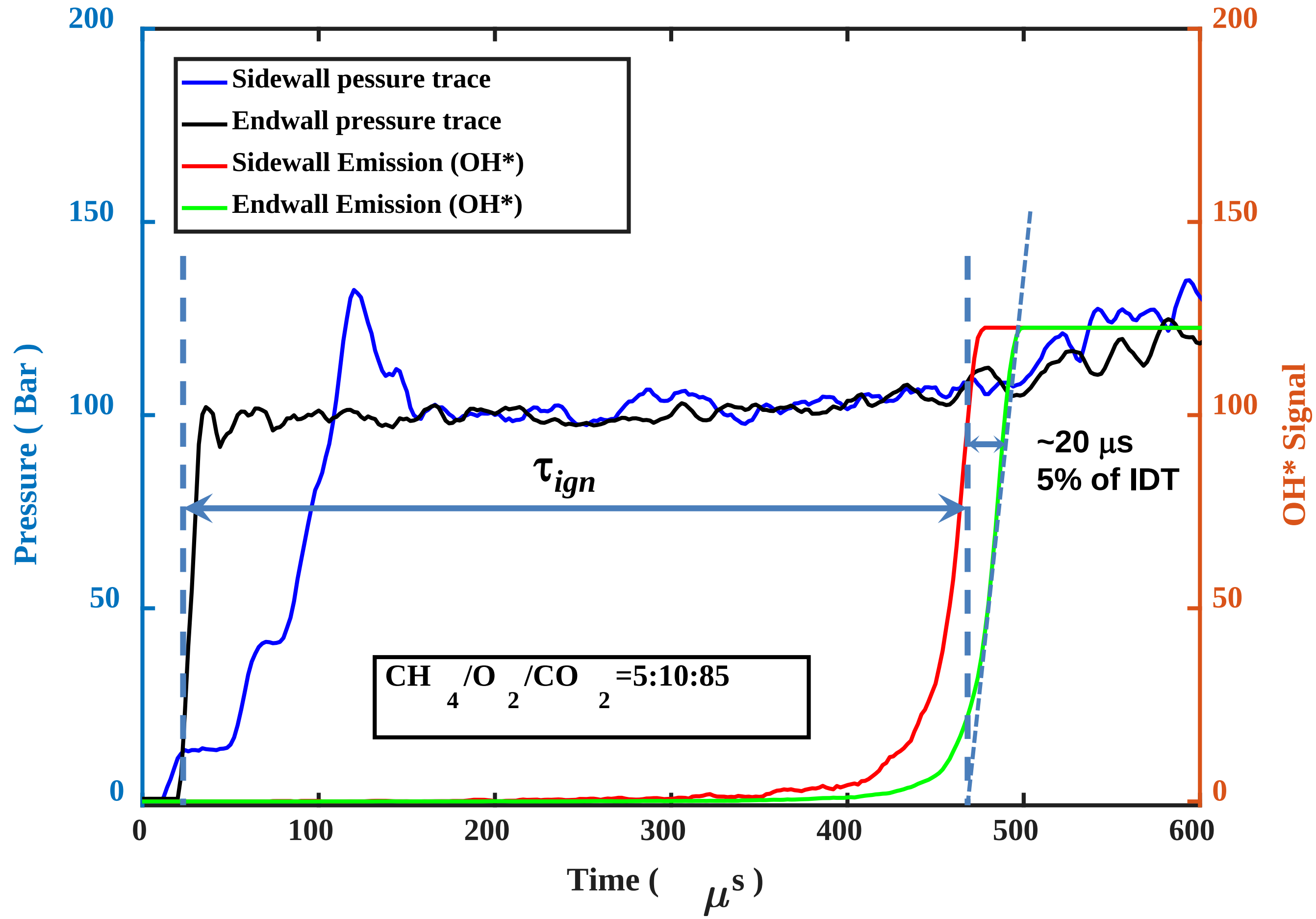
High accuracy Baratrons (**0.05%**) to measure partial pressure for mixture preparation

Turbo molecular pump

MicroGC to monitor compositions

Magnetic stir to promote mixing

Signal from End wall Needed



Simultaneous sidewall and end wall traces and emissions
Small difference between end wall and sidewall signals: “good chance” as quasi-homogeneous ignition event

https://web.stanford.edu/group/haiwanglab/FFCM1/download/mech-FFCM1

```
!
! FFCM-1
! H2/CO/C1 reaction model - Chemkin form - Draft v1.0c
! Release date: 05/31/3016.
!
! G. P. Smith, Y. Tao, and H. Wang, Foundational Fuel Chemistry Model Version 1.0 (FFCM-1),
! http://web.stanford.edu/group/haiwanglab/FFCM-1/index.html, 2016.
!
! Contact:
! Gregory P. Smith: gregory.smith@sri.com
! Hai Wang: haiwang@stanford.edu
!
ELEMENTS
O   H   C   N   AR HE
END
SPECIES
      AR                  HE                  N2                  H2
      H                   O                   O2                  OH
      H2O                 HO2                 H2O2                CO
      CO2                 C                   CH                  CH2
      CH2(S)              CH3                 CH4                 HCO
      CH2O                CH2OH               CH3O                CH3OH
      C2H                 C2H2                C2H3                C2H4
      C2H5                C2H6                HCCO                CH2CO
      CH2CHO              CH3CHO              CH3CO               H2CC
      OH*                 CH*
END
REACTIONS
H+O2<=>O+OH                                           9.841E+13    0.000    15310.00
```

Vapor-Liquid Equilibrium in Supercritical Mixtures

- Single species: the phase is uniquely defined by the equilibrium diagram
- Subcritical regime: jet exhibits atomization, droplets, and sharp gas/liquid interface
- Supercritical regime: Interface is diffused and no droplet formation
- Mixtures: VLE exists at interface for given (p, T) and composition z_i.
- JICF can have local VLE regions in
  - CH_4-CO_2, O_2-CO_2 interfaces
  - CH_4-O_2-CO_2-H_2O regions
- Critical properties of each component play a crucial role to determine VLE
- Need to include VLE effects to account for mixture effects