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

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Duration 3 years: 10/1/2015-9/30/2018

UTSR Meeting, Daytona Beach, FL, 11/1/2018

Distribution A: Approved for public release

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Direct-fired sCO_2 combustion

CO_2 is directly-fired based on the Brayton Cycle Concept

Typically highest pressures ranges from 200 - 300 bar at high pressures to just above the critical point

Ideal Oxy-fuel combustion

$CH_4 + O_2 + CO_2 \rightarrow CO_2 + H_2O$

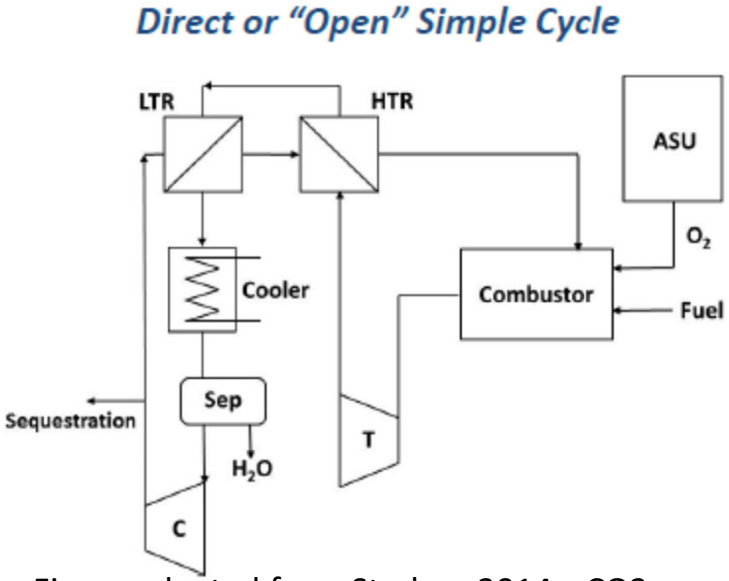


Figure adapted from Strakey, 2014, sCO2 symposium

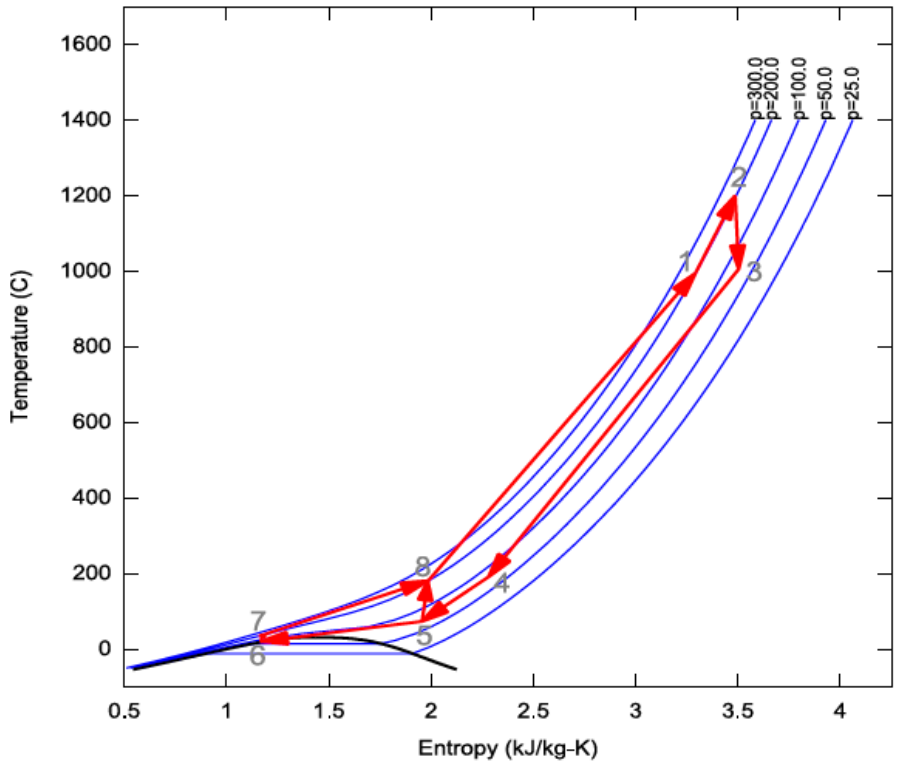
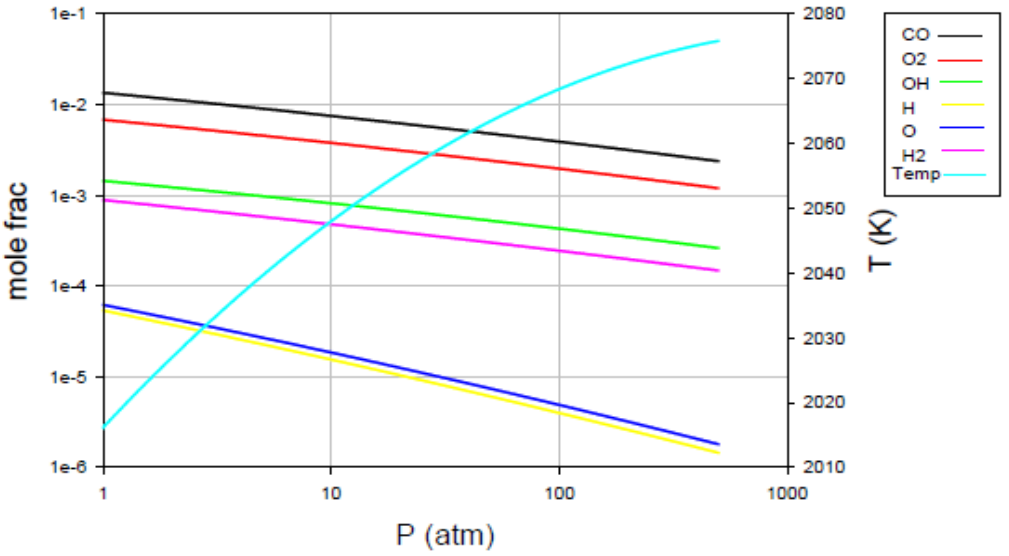


Figure adapted from Delimont, 2016, sCO2 symposium

Knowledge gaps

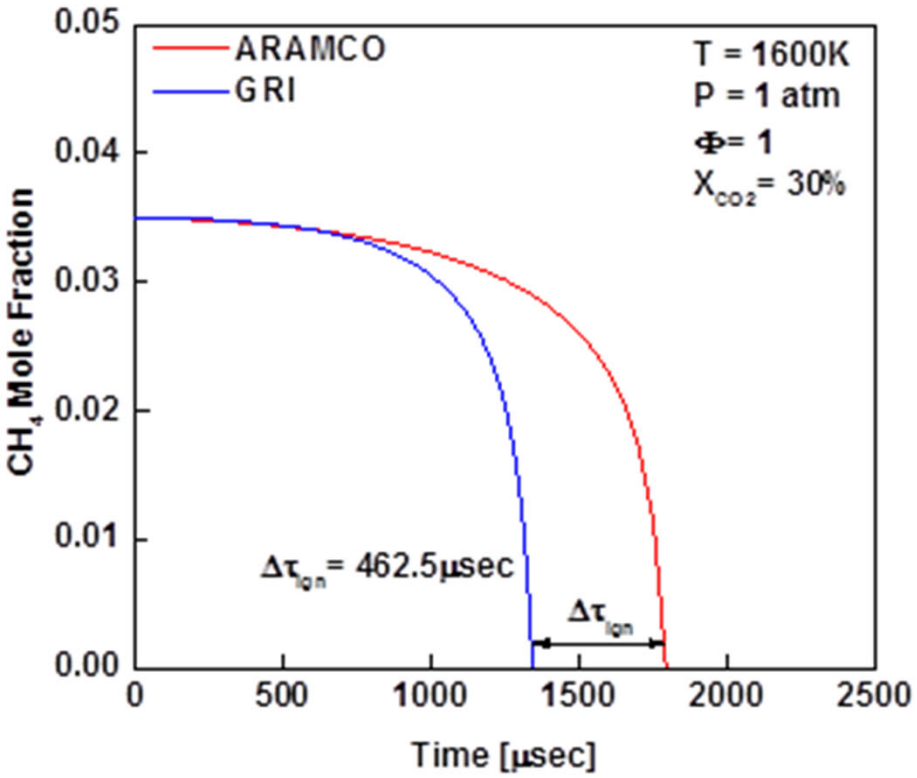
- Existing state-of-the-art, such as GRI-3.0 Mechanism, has only been validated for pressures up to 10 atm
- Mechanisms have not been developed for CO_2 diluted mixtures
- Updated/new mechanism will allow for accurate combustor modeling with multi-step combustion using a validated mechanism
- Current CFD combustion models do not consider non-ideal effects
- Thermodynamics and kinetics are currently unknown!!
- Fundamental work can shed light into this challenge

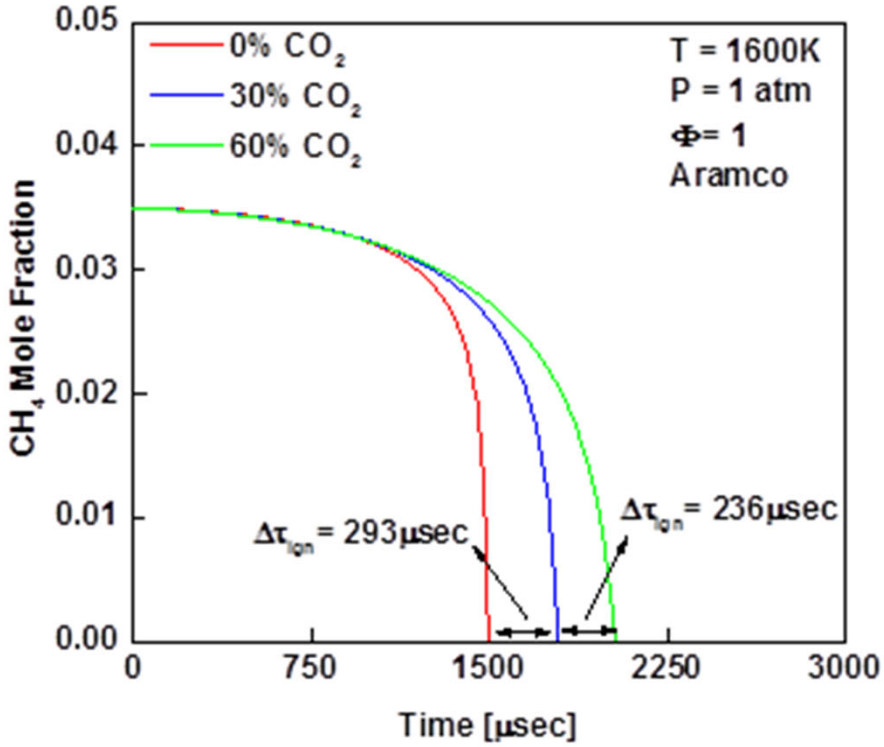


Effects of Increasing Pressure. Equilibrium calculation for $CH_4/O_2/CO_2$ at $\phi = 1$. Figure adapted from Strakey, 2014, sCO2 symposium

State-of-the-knowledge

State-of-the-art models differ in their predictions even at atmospheric pressure with high CO_2





- GRI 3.0 is still a widely used mechanism created 15 years ago
- Aramco Mech 2.0 is a recent well-validated mechanism

Combustion chemistry snapshot

MODEL

Reaction Mechanism Development

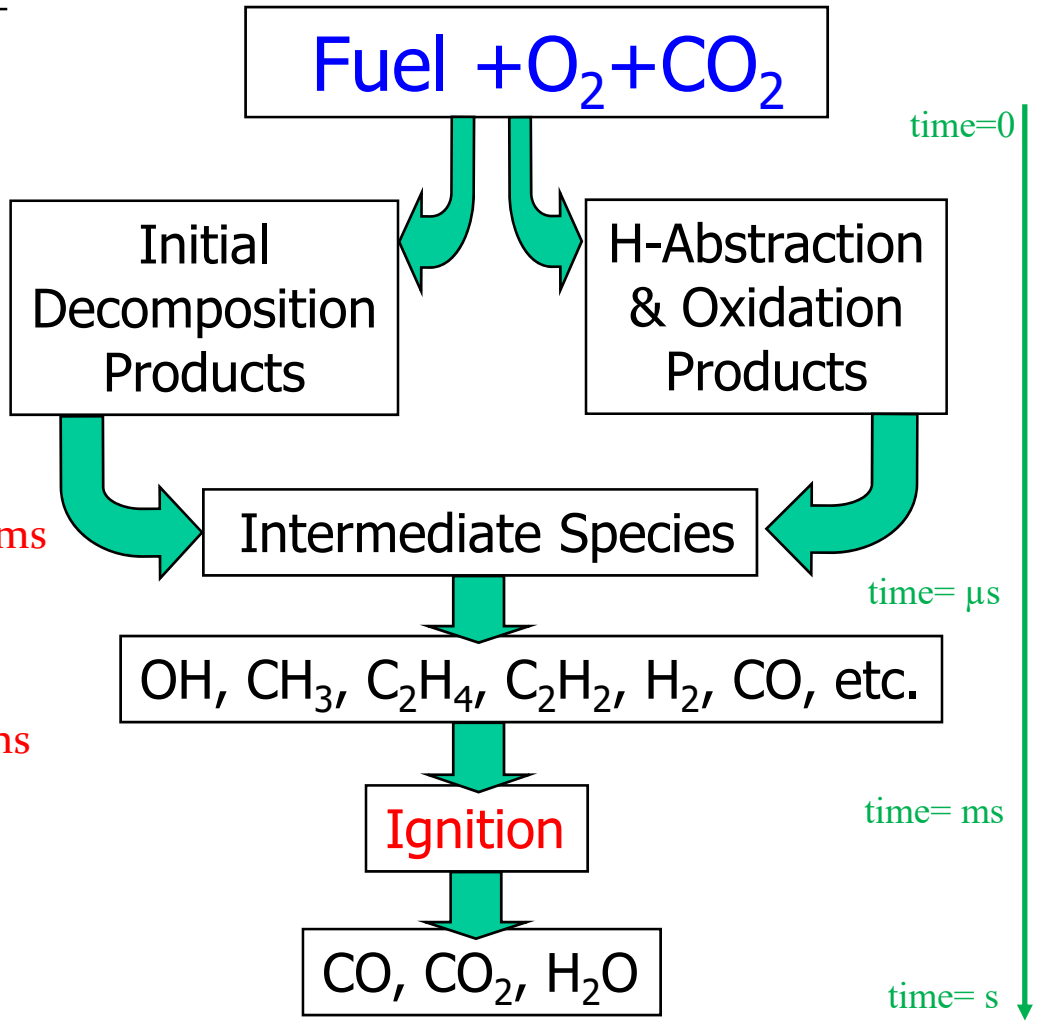
1. Decomposition Pathways

2. Intermediate Species Sub-Mechanisms

3. Full Mechanisms

4. Reduced Mechanisms

5. Validation



EXPERIMENTS

Kinetic Targets
(Shock Tubes, Flames Reactors)

1. Ignition Time Measurements

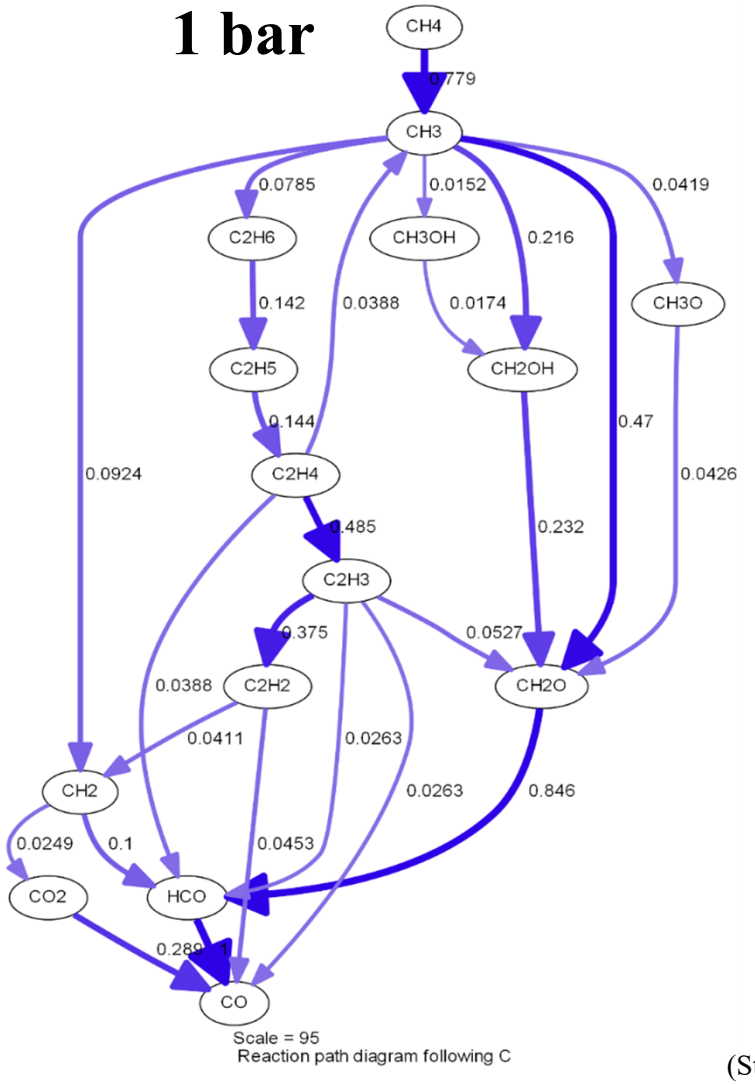
2. Species Time-Histories

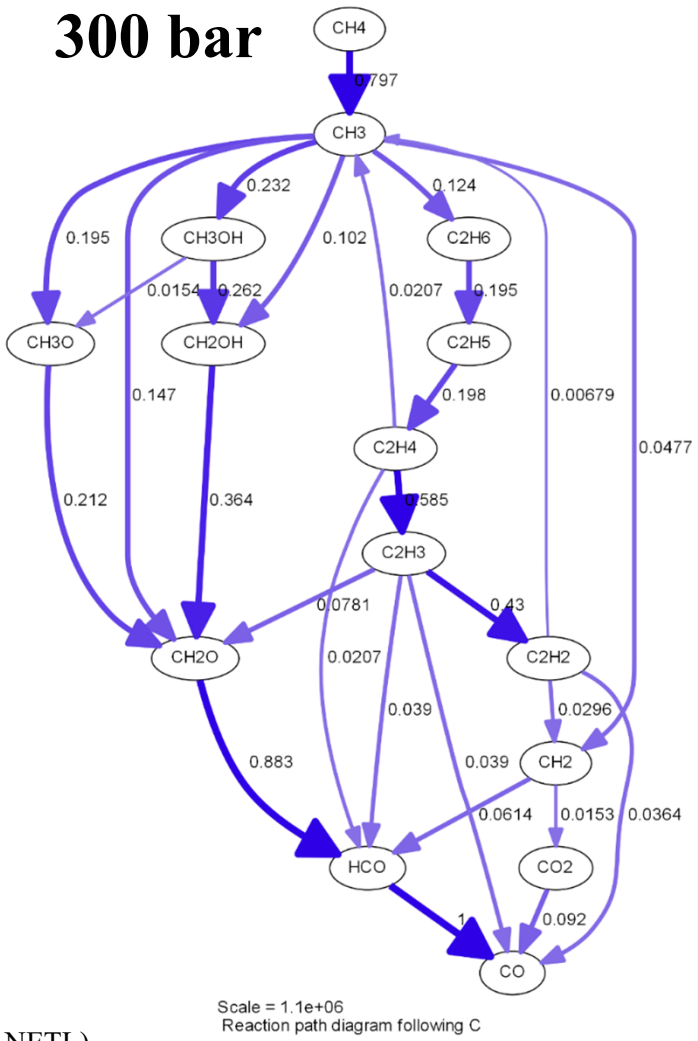
3. Direct Rate Measurements

4. Flame speed

5. Ignition energy, pressure rise

Combustion chemistry/kinetics are different at high pressure





(Strakey, SCO2 symposium 2018, NETL)

Project/Task Summary

Task 1: Project Management

Tasks 2&3: Acquire kinetics and ignition data in highly CO_2 diluted mixtures with shock tube experiments

Task 4: Refine and validate a chemical kinetic mechanism for Supercritical Carbon Dioxide (sCO_2) Mixtures

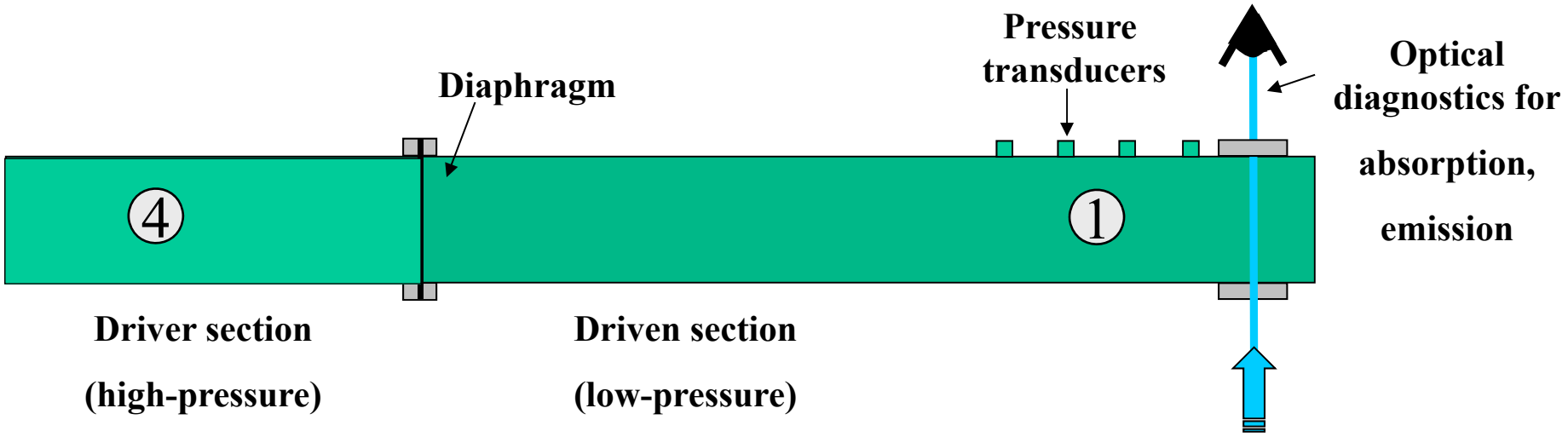
Task 5: Develop a CFD Code that utilizes mechanism for sCO_2 combustors

Overall Progress from this project in 3 years Oxy-Combustion/SCO_2

- 20 Journal Papers
  - 3 in J. Engineering for Gas Turbines and Power (ASME)
  - 4 in J. Energy Resources Technology (ASME)
  - 2 in Combustion and Flame
  - 7 in J. Physical Chemistry A
  - 2 in Energy & Fuels
  - 1 Int J Chemical Kinetics
  - 1 Proc. of Combust. Inst.
- > 30 conference papers at ASME Turbo Expo, sCO2 symposium, AIAA Meetings, Combustion Institute Meetings
- 4 additional journal papers currently in review

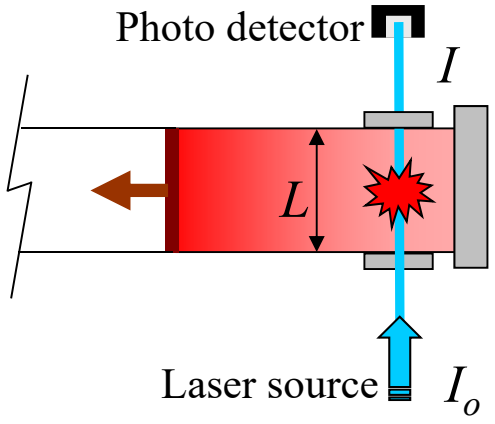
Sample Experiments Results

Shock tube operation: Pre-shock filling



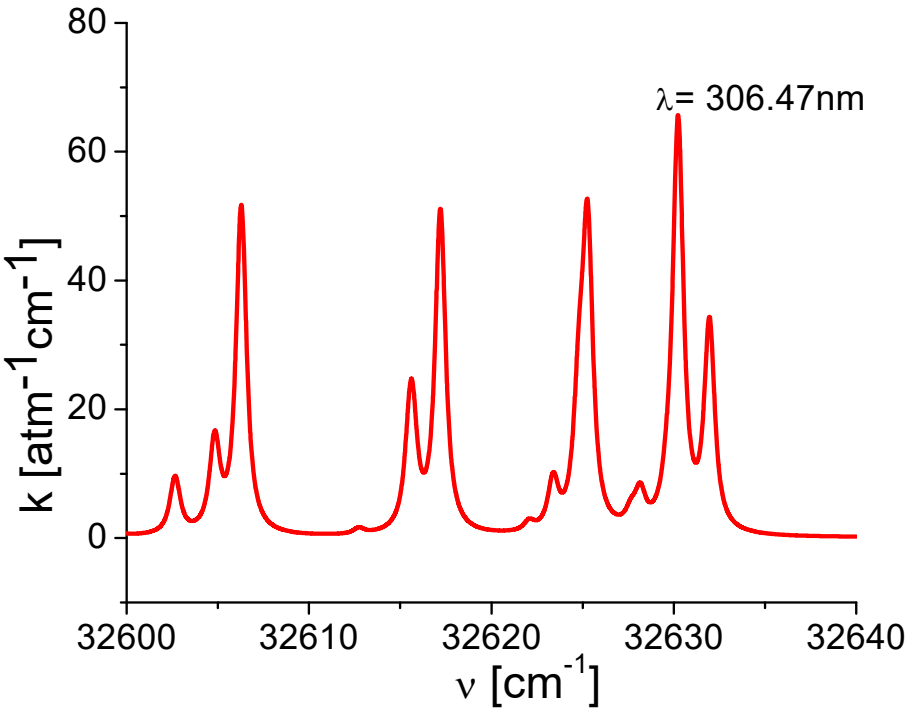
- Shock tubes are ideal for studying combustion chemistry
- Step change in T, P and well-defined time zero
- Simple fuel loading
- Accurate mixtures and pre-shock conditions

Laser absorption spectroscopy



Beer - Lambert law

$$I/I_o = \exp(-k_\lambda P_{total} X_{species} L)$$



Spectral absorption coefficient

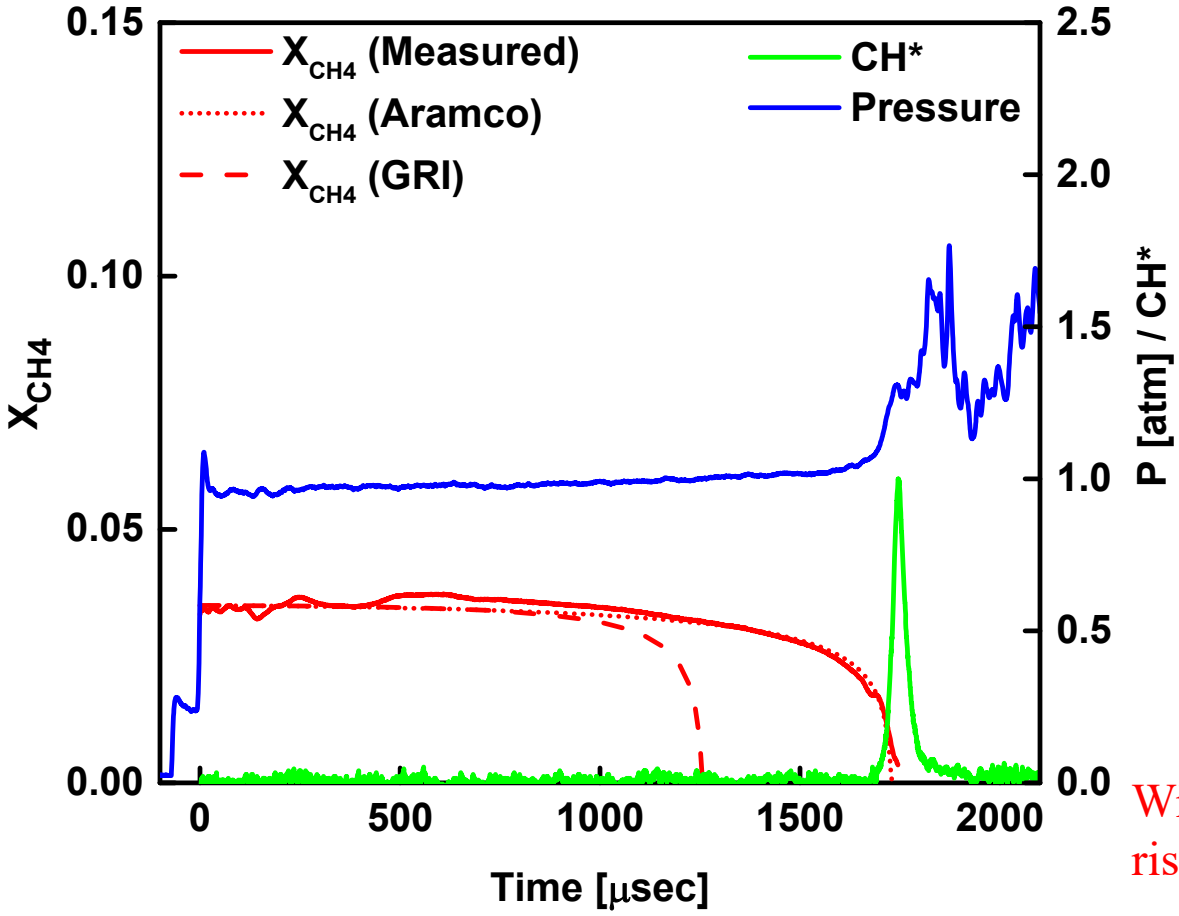
$k_\lambda = S(T) \cdot \Phi(T,P,X)$

S(T): line strength, Φ(T,P,X): line shape

Ignition Results: Without CO_2

- Comparison of measured and simulated methane concentration for

– Stoichiometric ignition of 3.5% CH_4 in Argon, 1600K



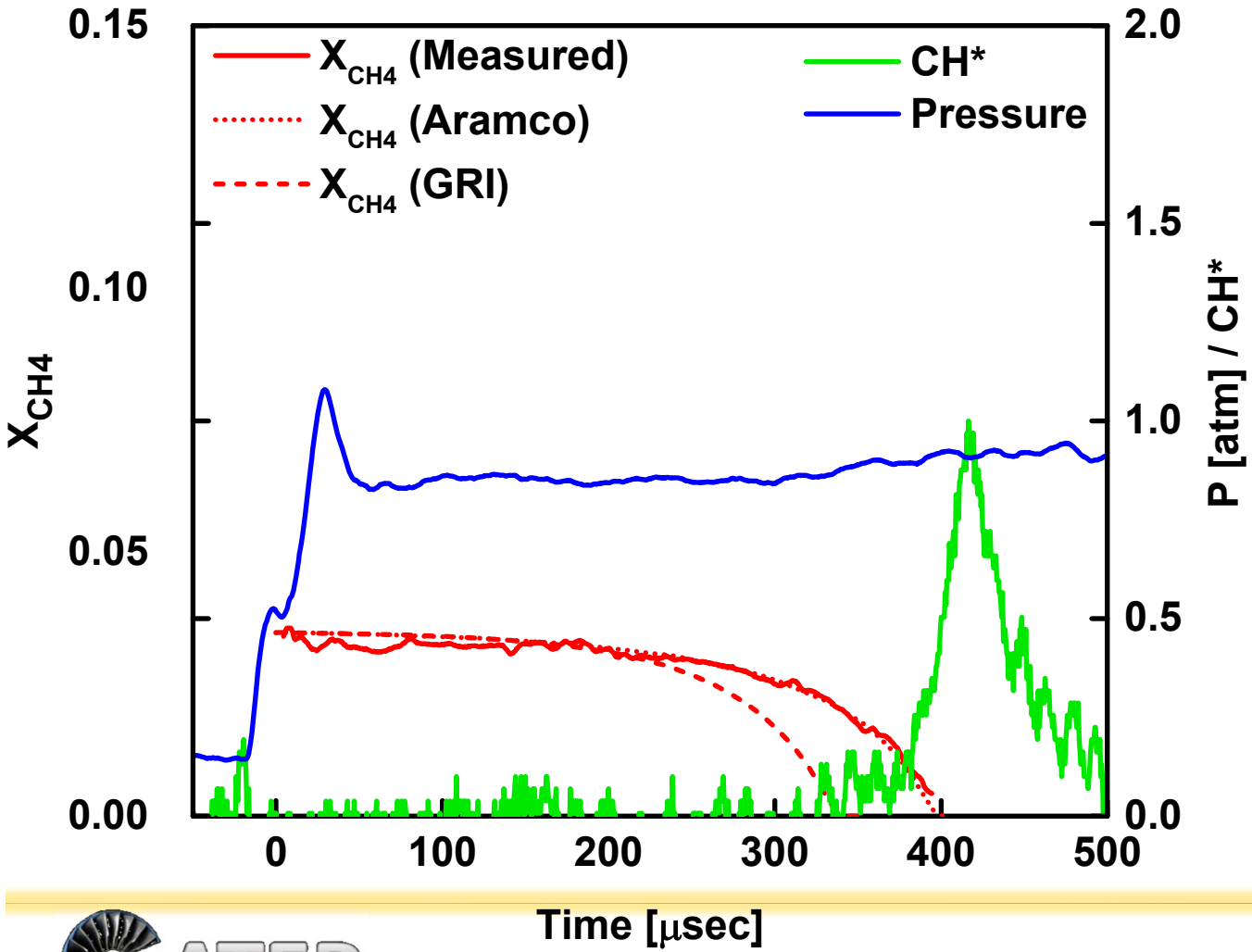
- Ignition delay times measured from the arrival of reflected shockwave to rise of the pressure trace
- Arrival of shockwave determined as midpoint of the second pressure rise (rise due to reflected shock)
- Rise of OH Emissions measured as the intersection between the baseline and the tangent line drawn from maximum rise of OH

With out CO_2 addition there is pressure rise after ignition

Ignition Results: 60% CO_2 addition

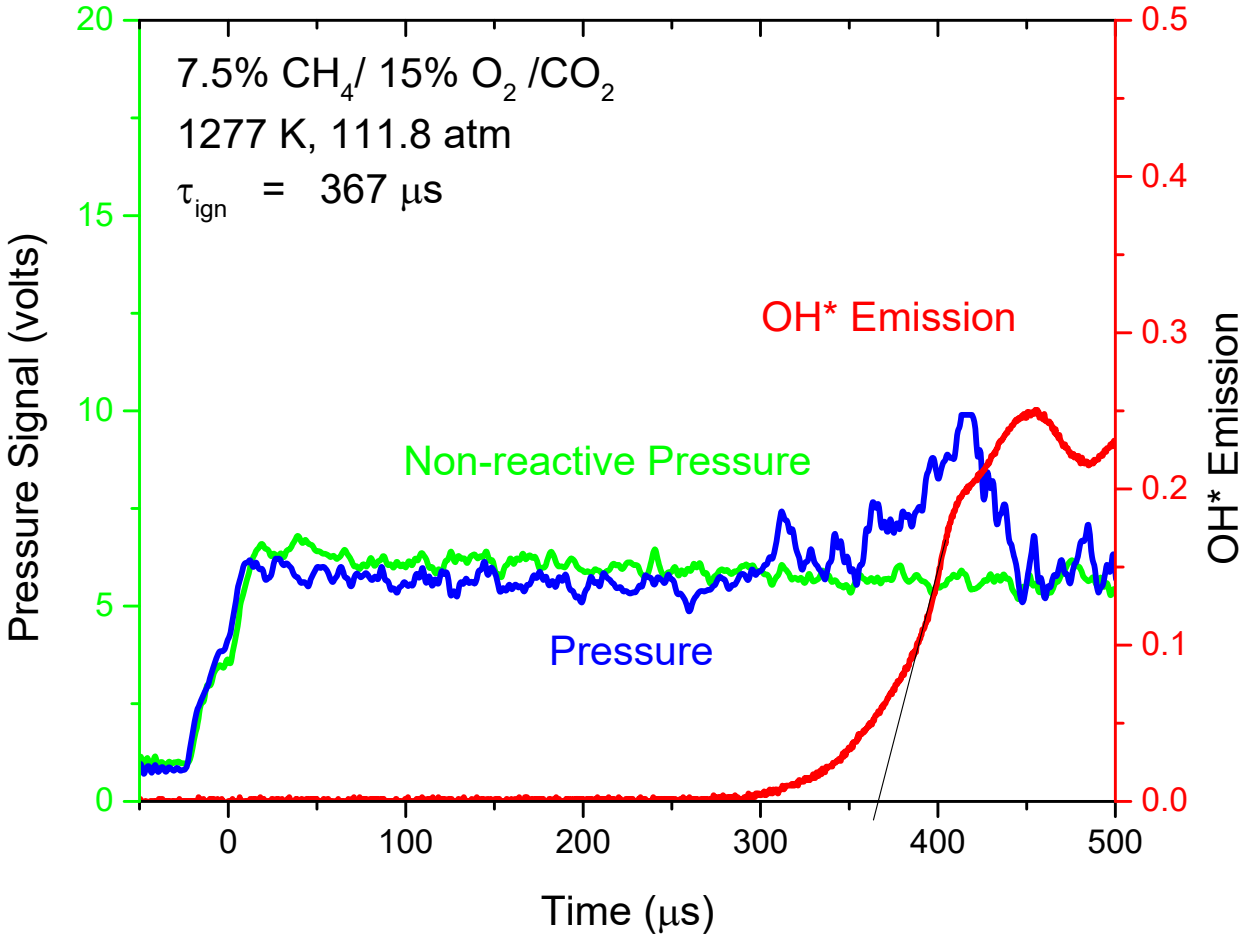
- Comparison of measured and simulated methane concentration for

– Stoichiometric ignition of 3.5% CH_4 in Argon diluted with 30% CO_2, 1600K



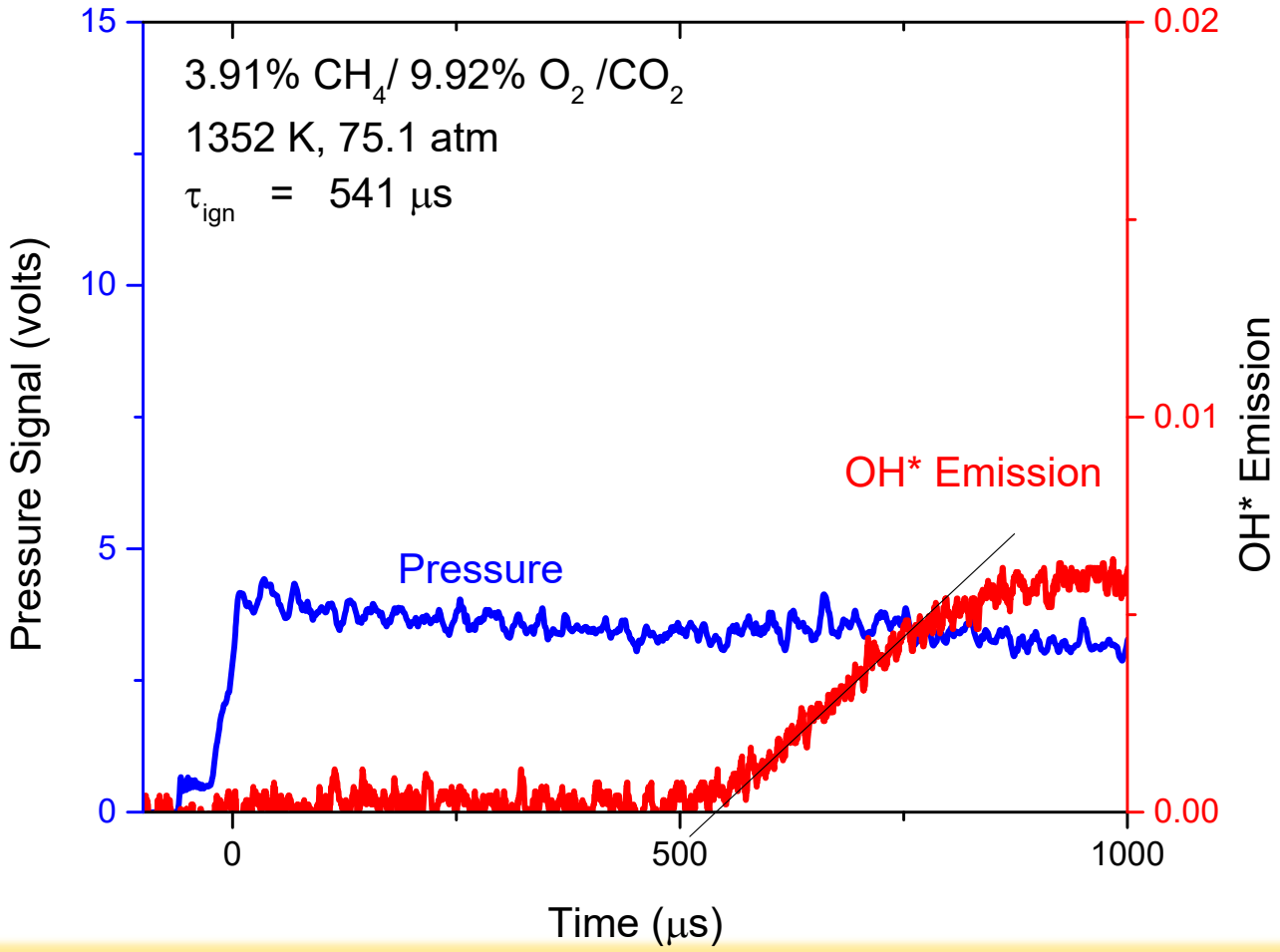
With CO_2 addition there is no pressure rise after ignition→ True observation for all mixtures?

Ignition Results in CH_4 Under SCO2 Conditions: 77.5% CO_2 addition



With CO_2 addition there is some pressure rise (7.5% fuel) after ignition→ but not as bad as the ones without CO_2

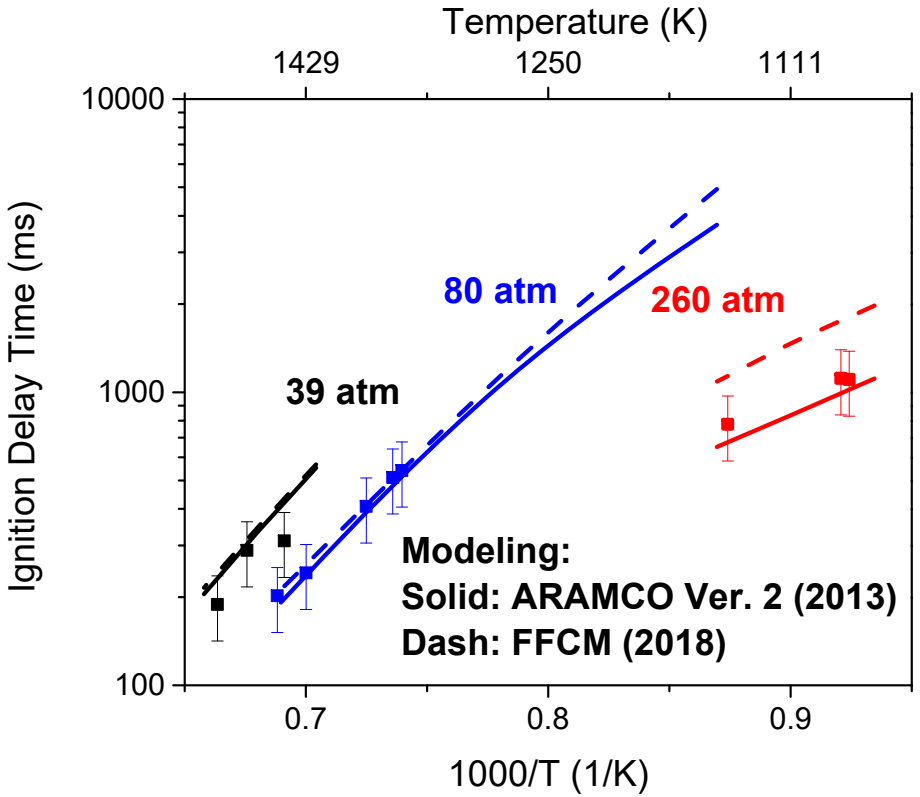
Ignition Results in CH_4/O_2 Under SCO_2 Conditions: 85% CO_2 addition



With CO_2 addition there is no pressure rise after ignition (4% fuel)

Low CH_4 Loading: 3.9% $CH_4/O_2/CO_2$ data: ϕ=0.78

85% CO_2 addition

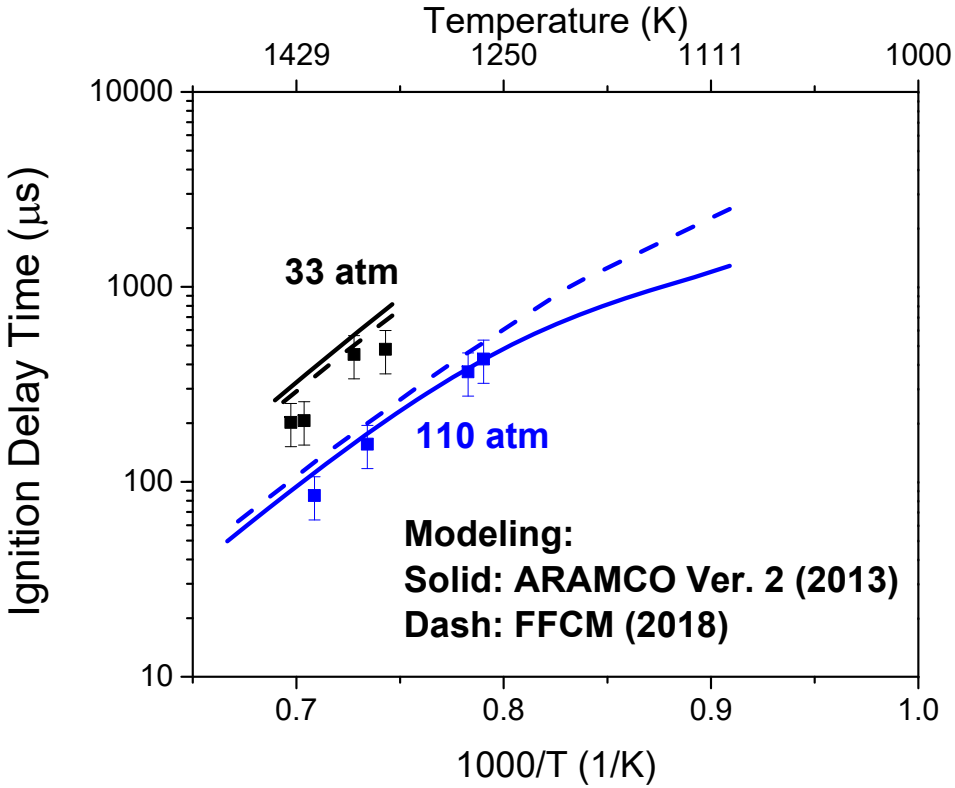


- **Small scatter in IDT data**
- **ARAMCO and FFCM in excellent agreement with IDT up to 80 atm**
- **But two models differ significantly at high pressure (260 atm)**

Next: How do the models compare with higher fuel loading?

High CH_4 Loading 7.5% $CH_4/O_2/CO_2$ data: ϕ=1.0

85% CO_2 addition



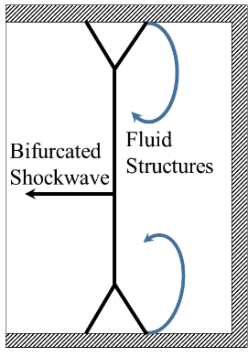
- **Good agreement of models with data at 33 atm**
- **Continue good agreement up to 110 atm**
- **But models diverge at low T**

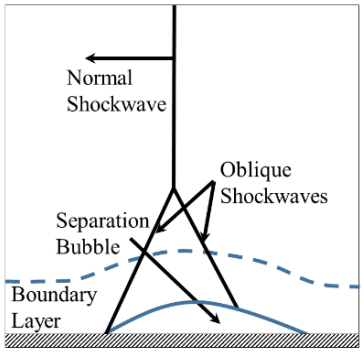
CO_2-diluted Ignition Experiments are challenging: High-Speed Imaging for Accurate Ignition Determination

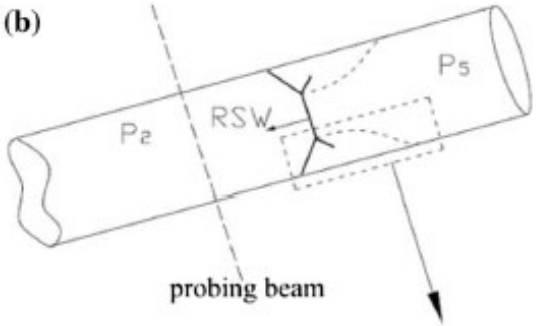
Reflected Shock Bifurcation

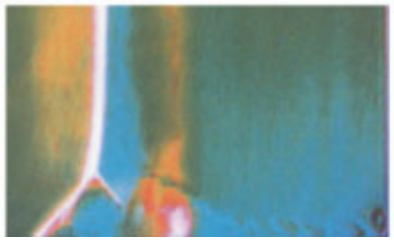
- Bifurcation is a result of differences in the energy level between the boundary layer and core flow. Occurs with diatomic and polyatomic molecules in the driven section

- Bifurcation induces inhomogeneities

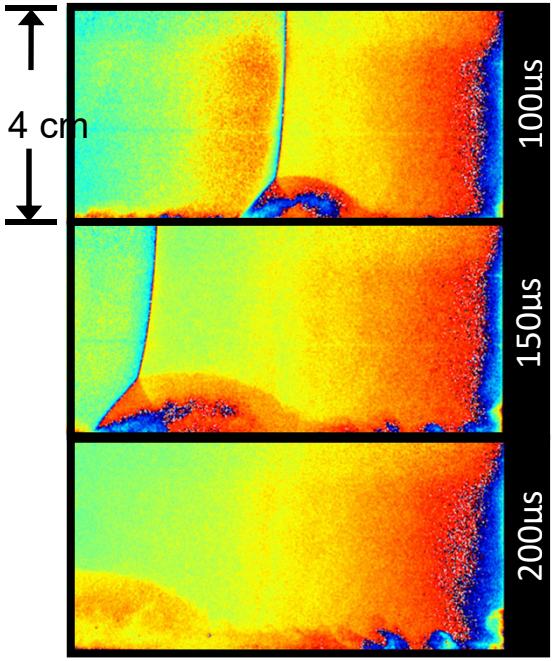






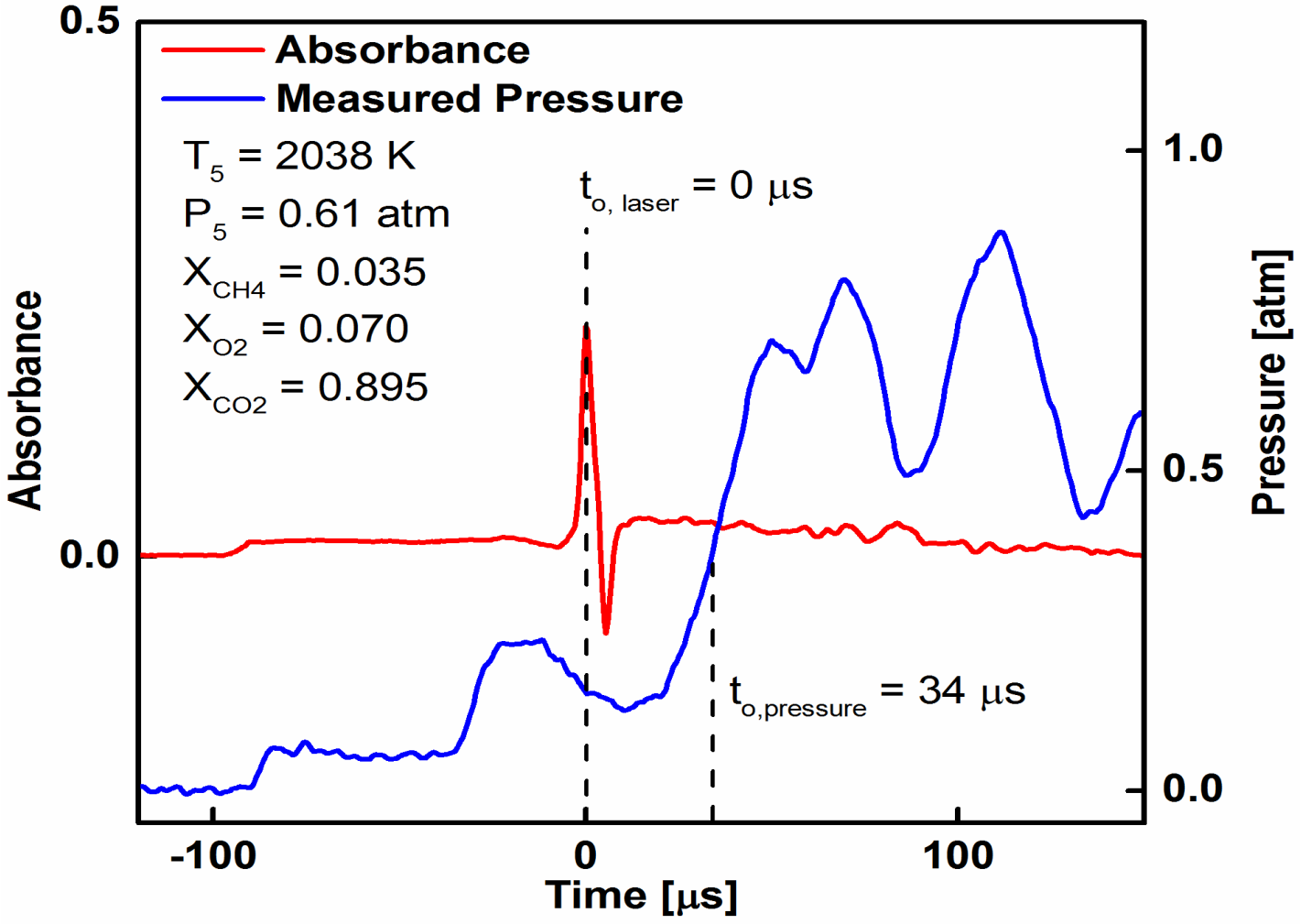


Adapted from
Kline et al. ISSW 1992
Penyazkov et al., 2016 SW



Adapted from
Yoo, Hanson, et al. 2010

Methane/O_2/CO_2 Ignition Imaging Results CO2=89.5%

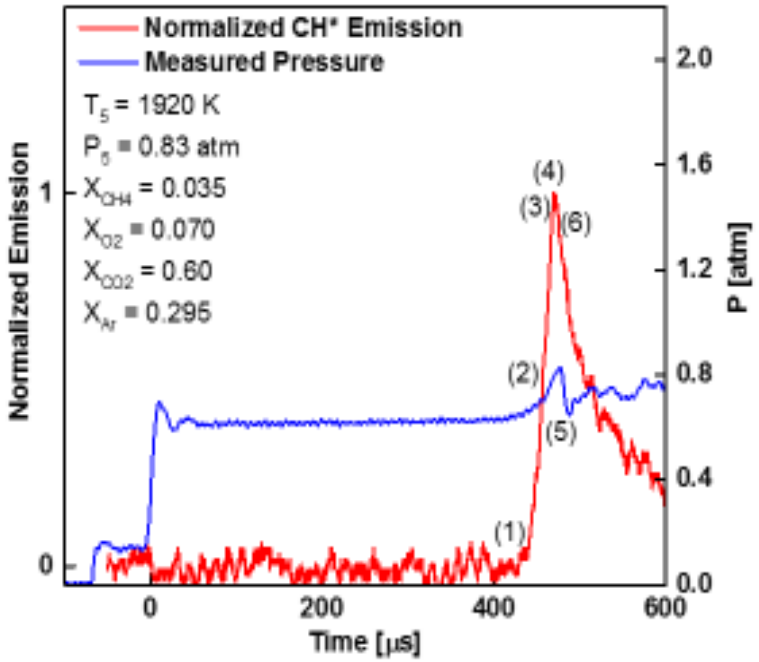


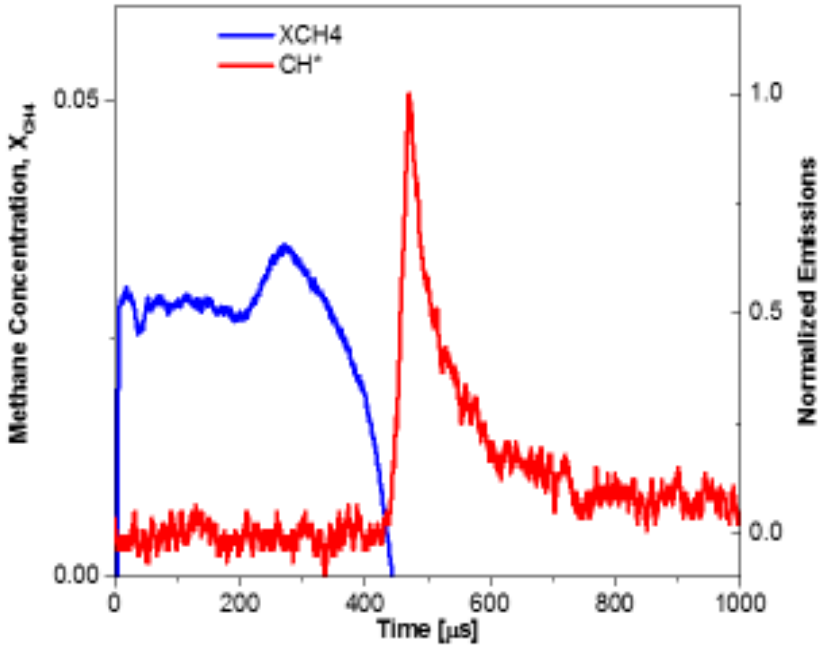
Experiments with CO2 addition is not trivial in shock tubes→ Boundary layer effects, shock bifurcation

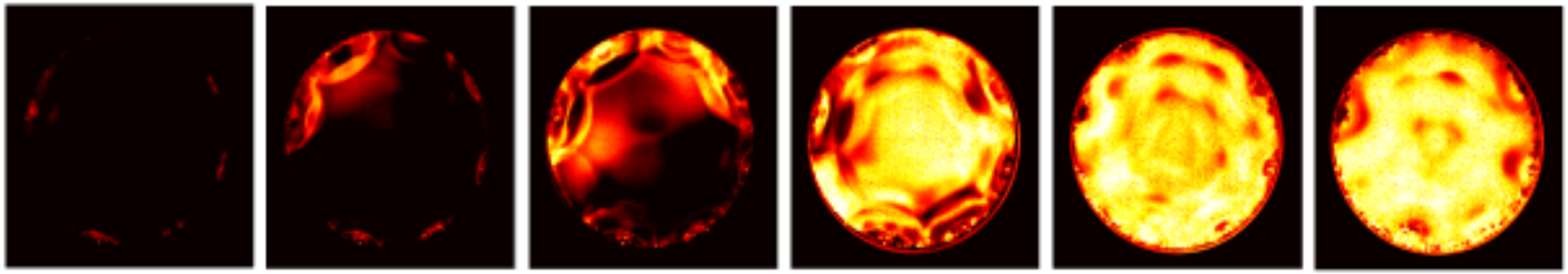
Solution →Use multiple diagnostics to study ignition process

Methane/O_2/CO_2 Ignition: High-Speed Imaging Results

CO_2=0 %





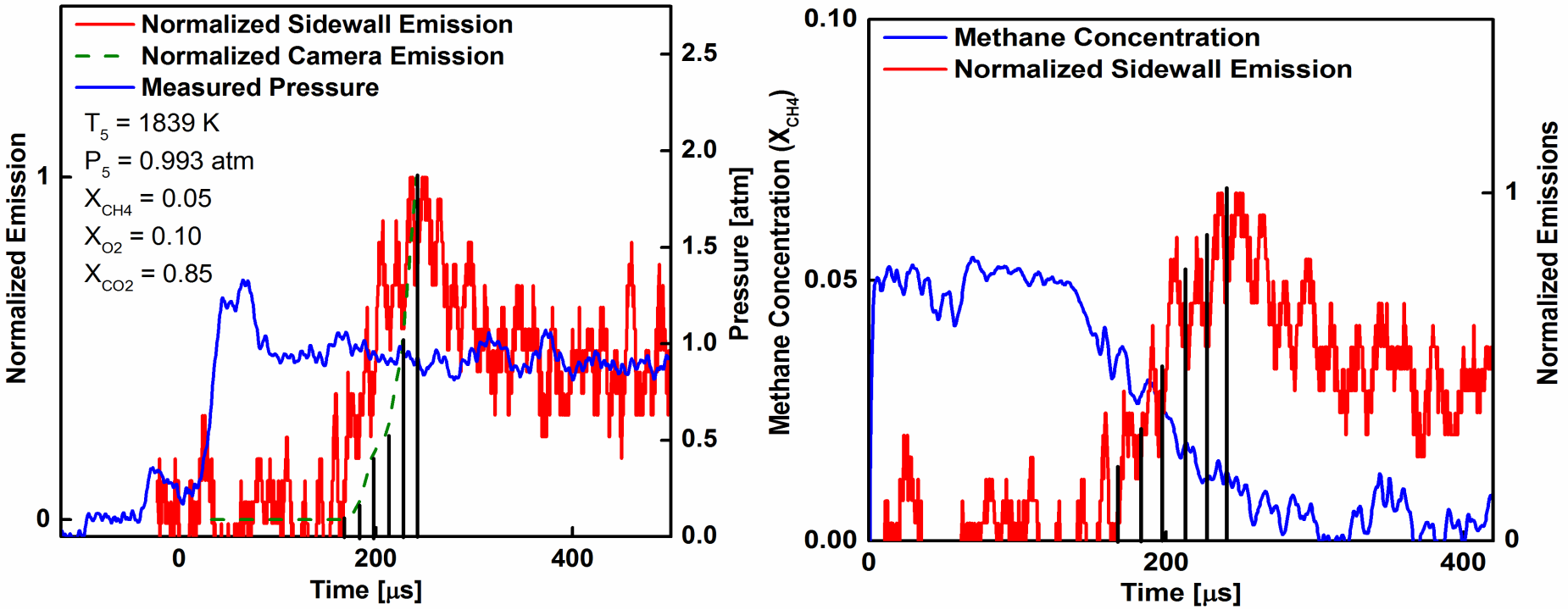


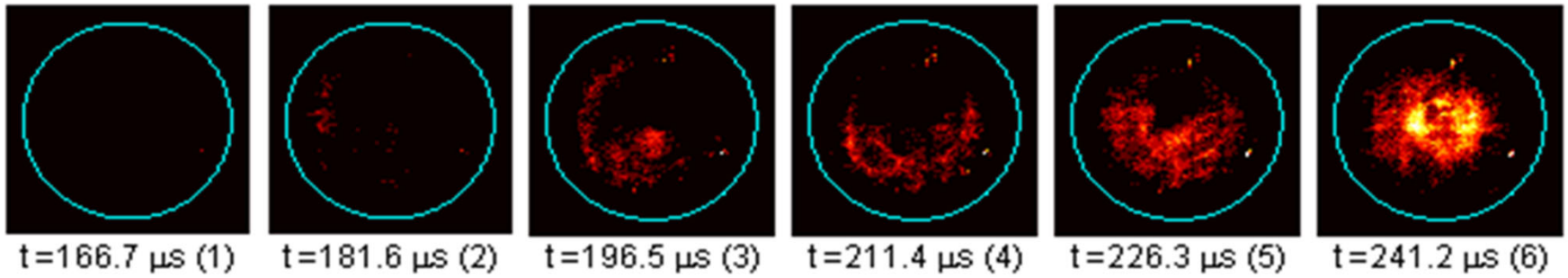
t = 420 μs (1) | t = 435 μs (2) | t = 449 μs (3) | t = 464 μs (4) | t = 479.3 μs (5) | t = 494 μs (6)

----------Ignition sequence imaged via high-speed (63, 000 fps)----------→

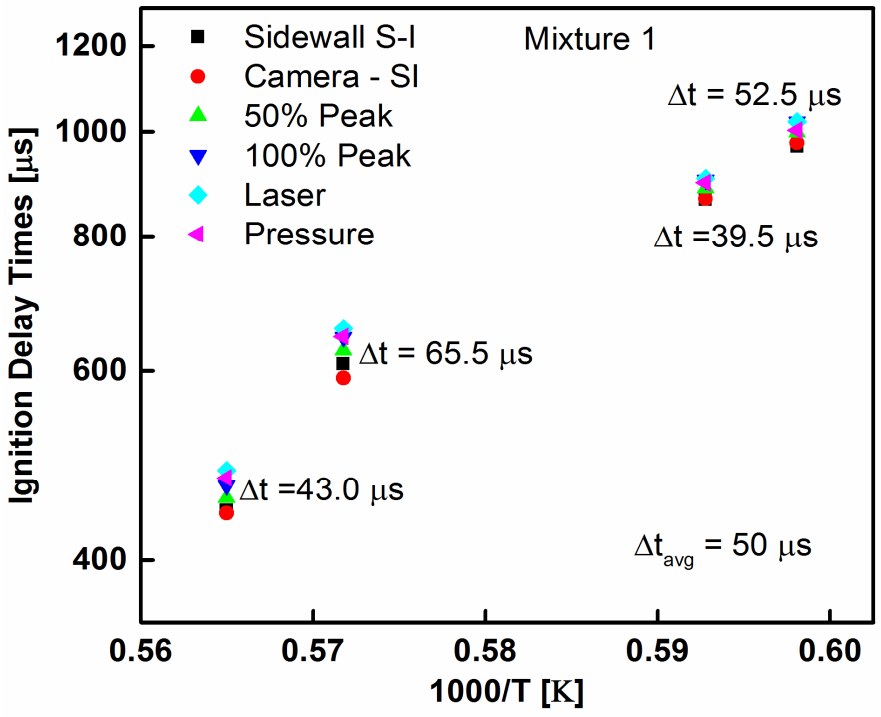
Methane/O_2/CO_2 Ignition Imaging Results

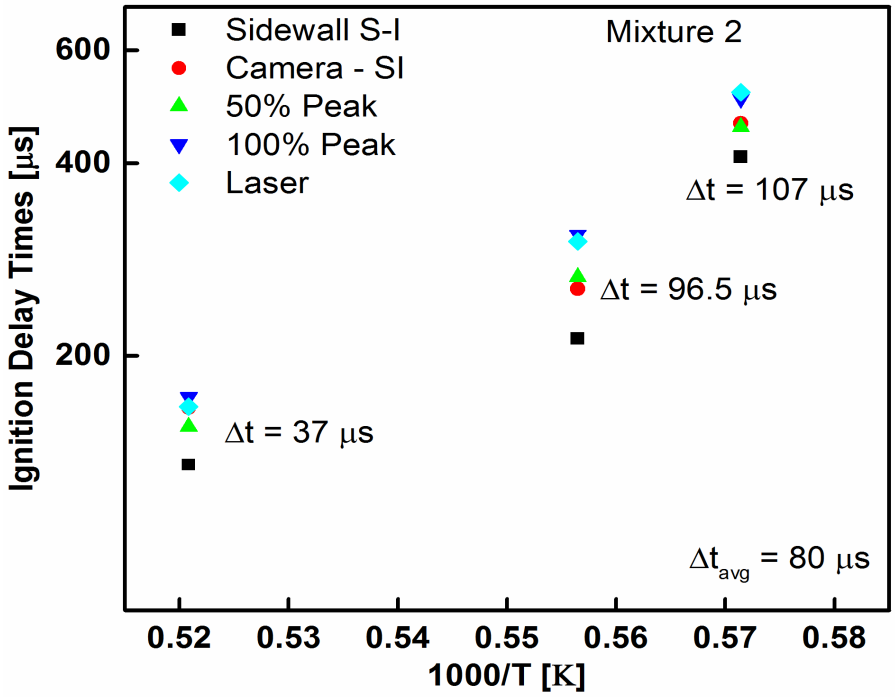
CO2=85%





Methane/O_2/CO_2 Ignition Results With Imaging





(a) Mixture 1: $XCH_4 = 0.035$, $XO_2 = 0.07$, $XCO_2 = 0.00$, $XAr = 0.895$. No CO_2

(b) Mixture 2: $XCH_4 = 0.035$, $XO_2 = 0.07$, $XCO_2 = 0.60$, $XAr = 0.295$. 60% CO_2

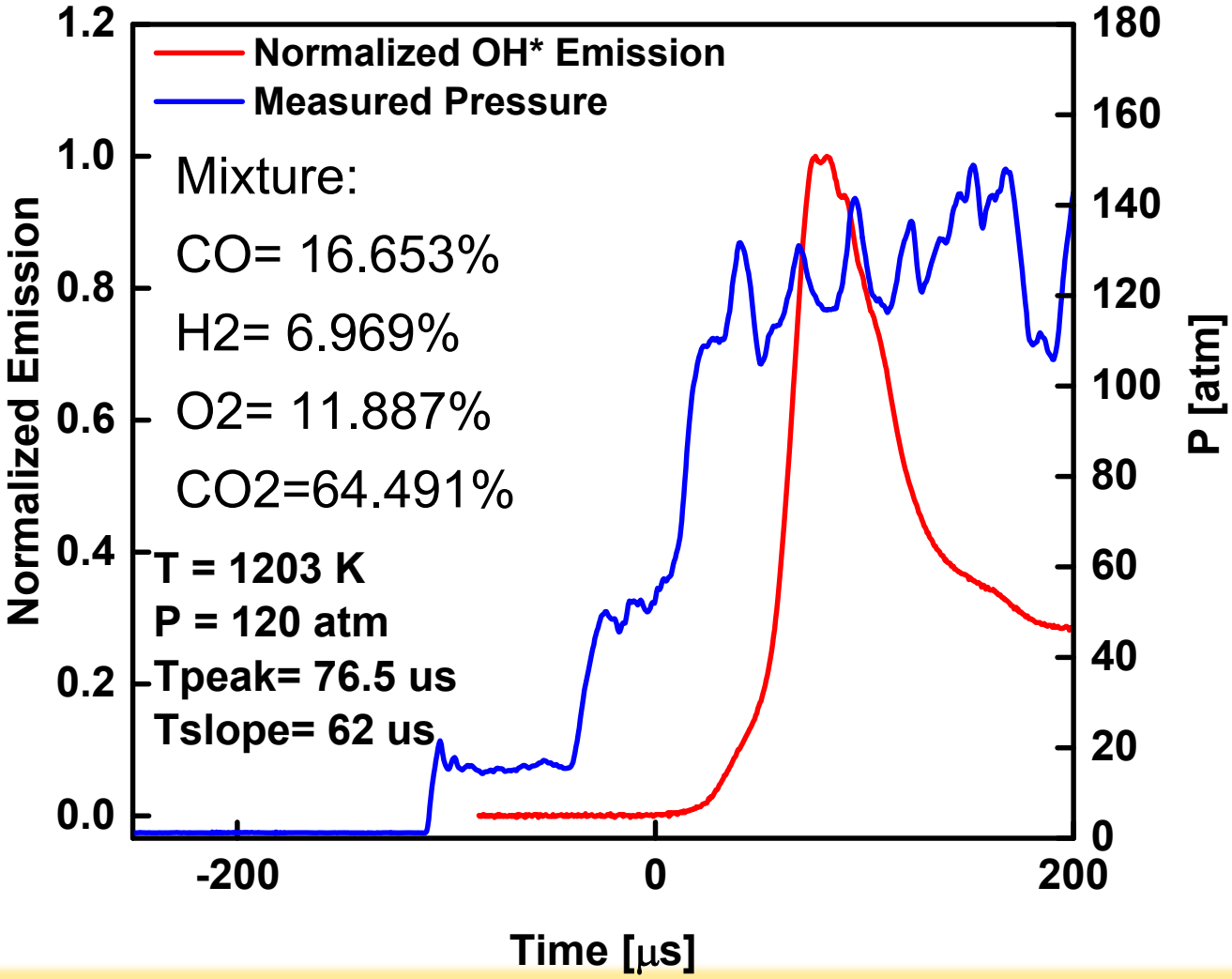
Difference in various definitions increase with addition of CO_2

However, the data can be compared to modeling predictions for various definitions

Select Syngas/O_2/CO_2 Ignition Delay Times

Note: Syngas fuel is a mixture of CO and H_2

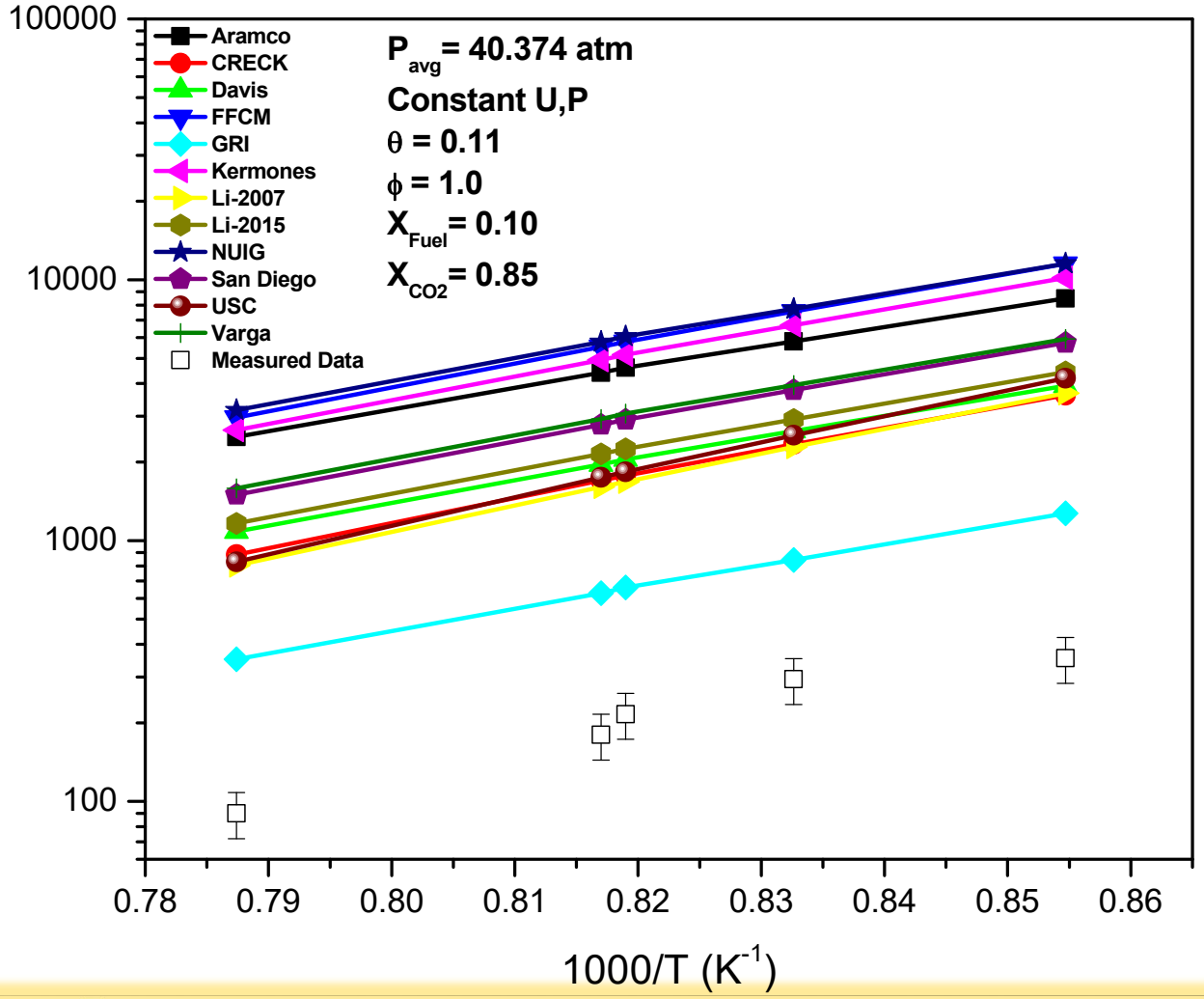
Ignition Results in syngas Under SCO2 Conditions: 65% CO_2 addition



With CO_2 addition there is no significant pressure rise after ignition

Syngas /O2/CO2 Ignition Delay Time Measurements: Comparisons with Modeling

CO_2=85%



12 Literature kinetic mechanisms tested

All mechanisms overpredict data at high pressure !

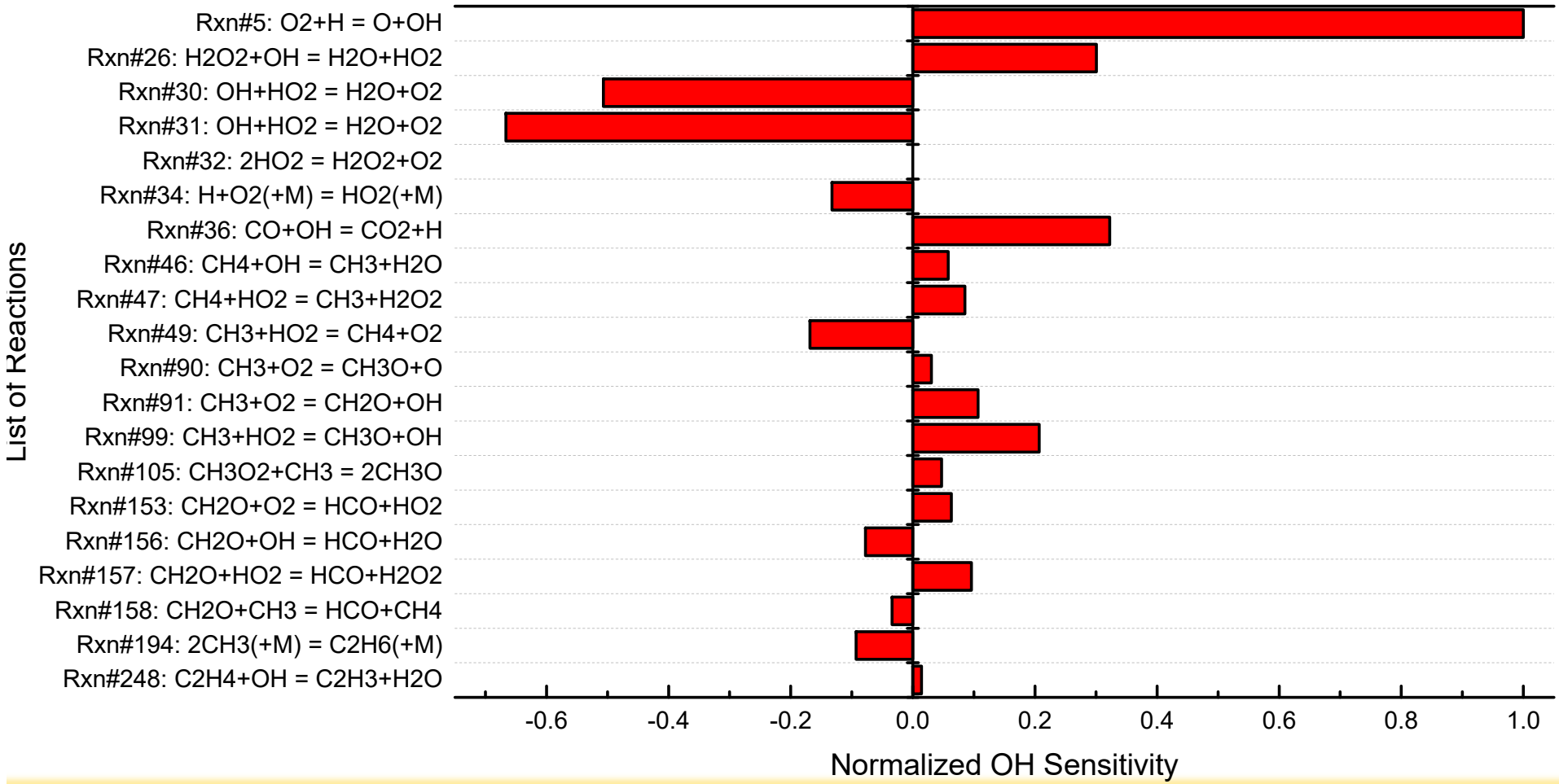
Reaction Mechanism for sCO2

Chemical Mechanism Development Summary

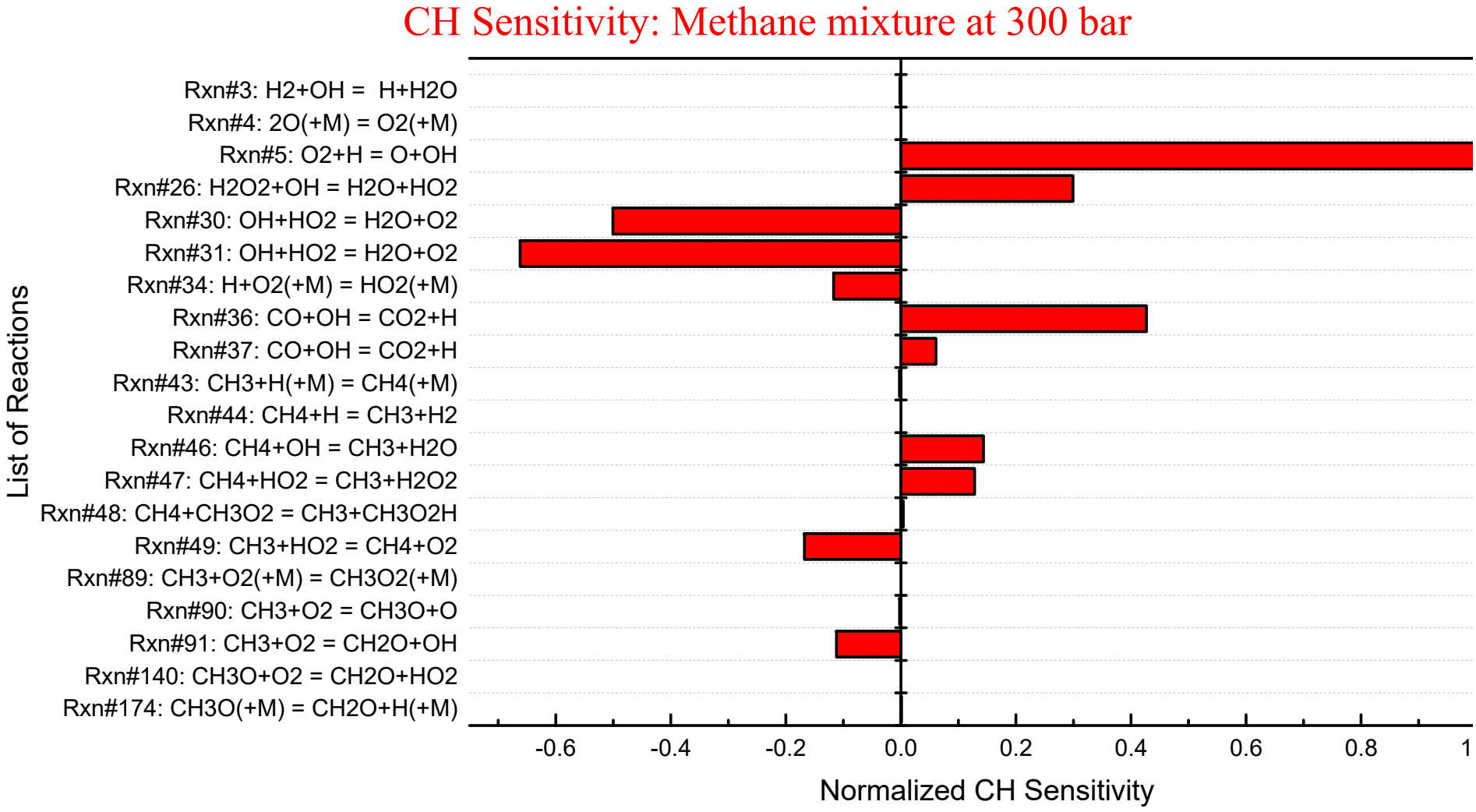
- Combustion kinetics model refinement/development
- Existing kinetic models are only valid at low pressures < 50 atm
- We used multi-scale simulations to extend their validity to mixtures up to 300 bar by:
  1. Quantum Mechanic simulations of the activation enthalpies in gas vs. CO_2 environment
  2. Molecular Dynamic simulations of reaction processes

Sensitivity Analysis

OH Sensitivity: Methane mixture 300 bar



Sensitivity Analysis



The important elementary steps in high-pressure C0-C4 fuel combustion

Table 4 Important reactions and the source of their rate constants used in the mechanism. Rate coefficients are in units of cal, mol, cm^3, K. Rate constants are calculated as $k = A*T^n*Exp(-Ea/RT)$ where T represents temperature and R represents the gas constant.

No.	Reaction	A	n	Ea	Ref.
1	$H+O_2=O+OH$	3.55E+15	−0.406	1.66E+04	[7]
2[c]	$CO+OH=CO_2+H$	2.20E+05	1.89	−1.16E+03	[7], A*1.24
3	$HCO+M=H+CO+M$	4.75E+11	0.7	1.49E+04	[6][a]
4	$H+OH+M=H_2O+M$	4.50E+22	−2	0.00E+00	[19][a]
5	C_3H_5-a$+H(+M)=C_3H_6(+M)$	2.00E+14	0	0.00E+00	[8]
	Low pressure limit:	1.33E+60	−12	5.97E+03	
	Troe parameters: 0.02, 1.10E+03, 1.10E+03, 6.86E+03				
6	$CH_3+CH_3(+M)=C_2H_6(+M)$	9.21E+16	−1.17	6.36E+02	[7][a]
	Low pressure limit:	1.14E+36	−5.246	1.71E+03	
	Troe parameters: 0.405, 1.12E+03, 69.6, 1.00E+10				
7	$CH_3+HO_2=CH_3O+OH$	1.00E+12	0.269	−6.88E+02	[7]
8	$CH_4+H=CH_3+H_2$	6.14E+05	2.5	9.59E+03	[7]
9	$HO_2+HO_2=H_2O_2+O_2$	4.20E+14	0	1.20E+04	[18][b]
		1.30E+11	0	−1.63E+03	
10	$CH_4+HO_2=CH_3+H_2O_2$	1.13E+01	3.74	2.10E+04	[7]
11	$CH_3O_2+CH_3=CH_3O+CH_3O$	5.08E+12	0	−1.41E+03	[7]
12	$CH_3+OH=CH_2(S)+H_2O$	4.51E+17	−1.34	1.42E+03	[7]
13	$CH_3+O_2=CH_2O+OH$	2.64E+00	3.283	8.11E+03	[7]
14	$CH_3+H(+M)=CH_4(+M)$	2.14E+15	−0.4	0.00E+00	[1][a]
	Low pressure limit:	3.31E+30	−4	2.11E+03	
	Troe parameters: 0.0, 1.00E-15, 1.00E-15, 40.0				
15[c]	$C_2H_4+H(+M)=C_2H_5(+M)$	1.95E+12	0.454	1.82E+03	[7][a], A*1.8
	Low pressure limit:	2.16E+42	−7.62	6.97E+03	
	Troe parameters: 0.975, 210, 984, 4.37E+03				

[a]Collision efficiencies: CH_4 2.0, CO 1.9, CO_2 3.8, C_2H_6 3.0, H_2O 6.0, H_2 2.0, Ar 0.7.
[b]Rate constant is the sum of two expressions.
[c]c.f. text.

Naik, C. V.; Puduppakkam, K. V.; Meeks, E. *J Eng Gas Turbines Power* 2012, 134, 021504.

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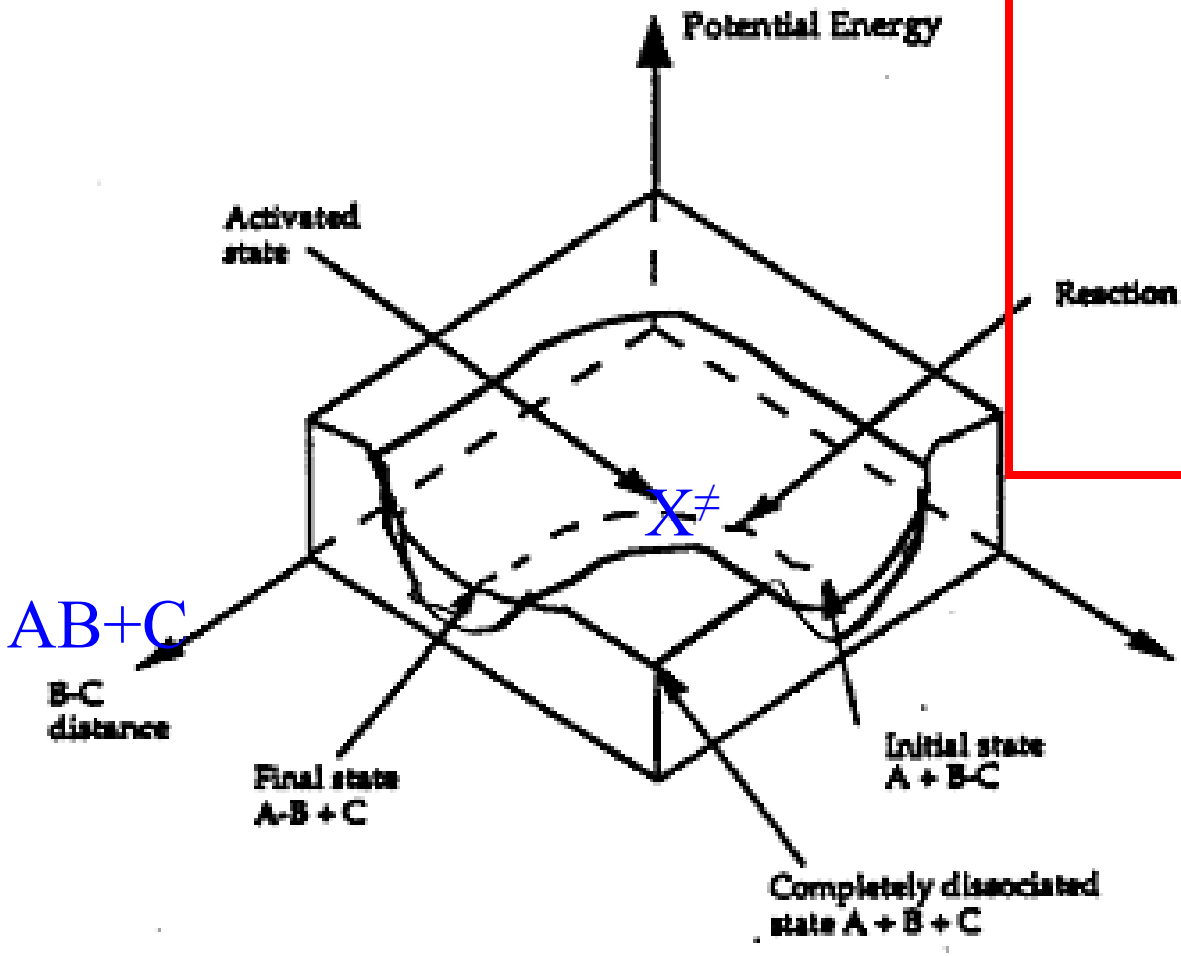
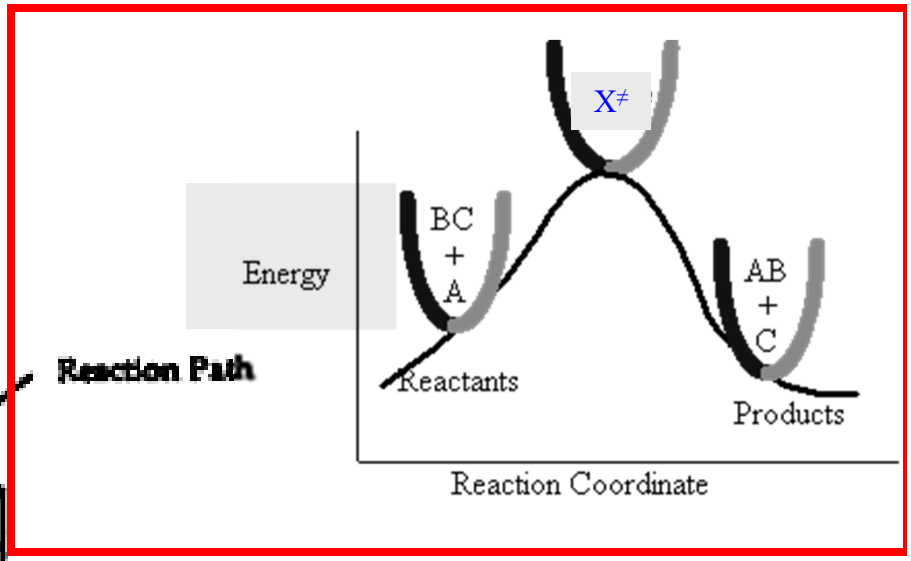
What is really happening during a reaction? Transition State Theory: 3-D potential energy surface

$A+BC \rightarrow X^{\neq} \rightarrow AB+C$

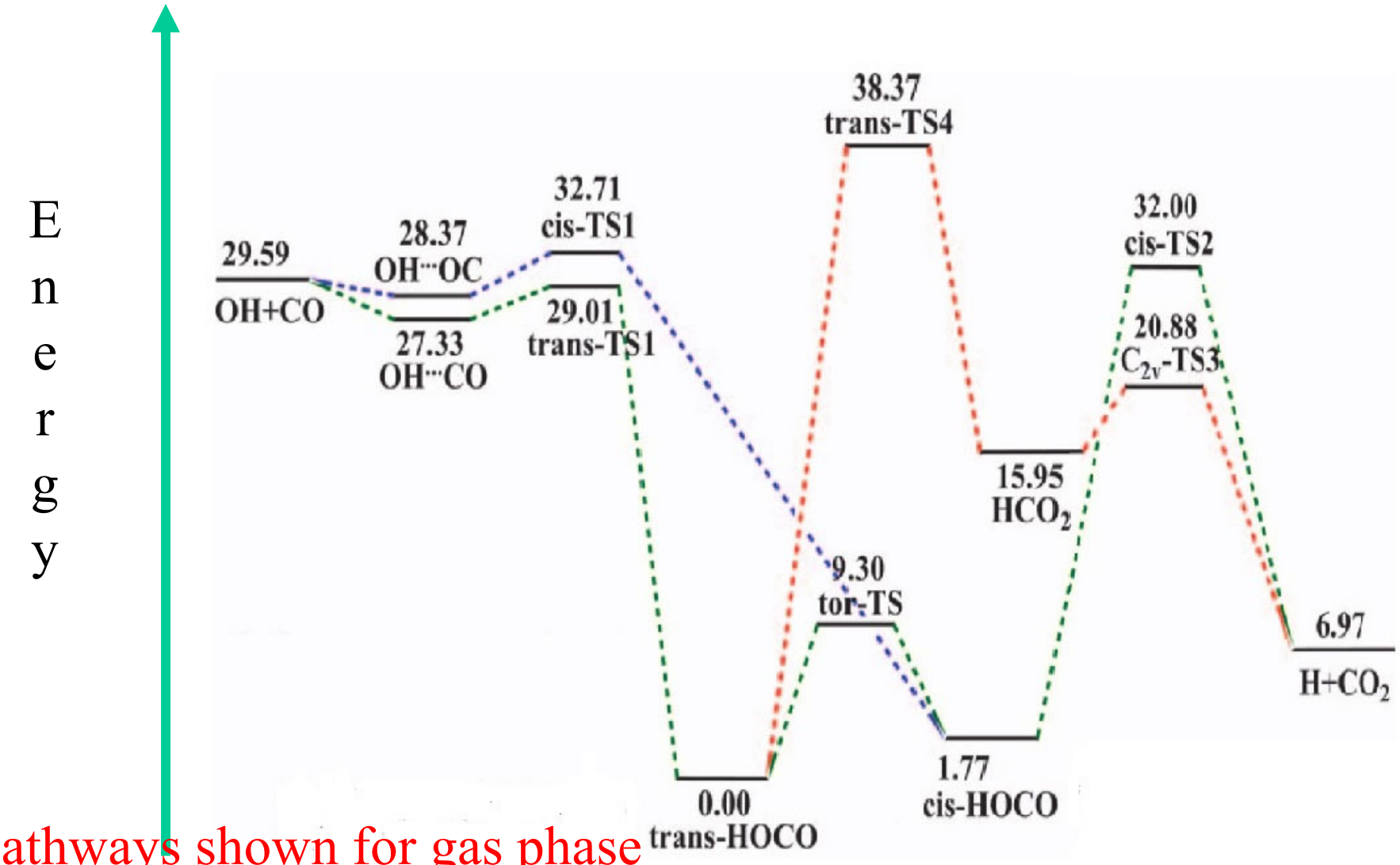




Need collisions

Figure adapted from Pilling and Seakins

Gas-Phase Heat release Reaction $CO+OH \rightarrow CO_2+H$



Pathways shown for gas phase

Effects of supercritical solvent within framework of Transition State Theory

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

Elementary Reaction $CO+OH \rightarrow CO_2+H$
(results with covalent CO_2 addition as a spectator: new mechanism discovered !!)

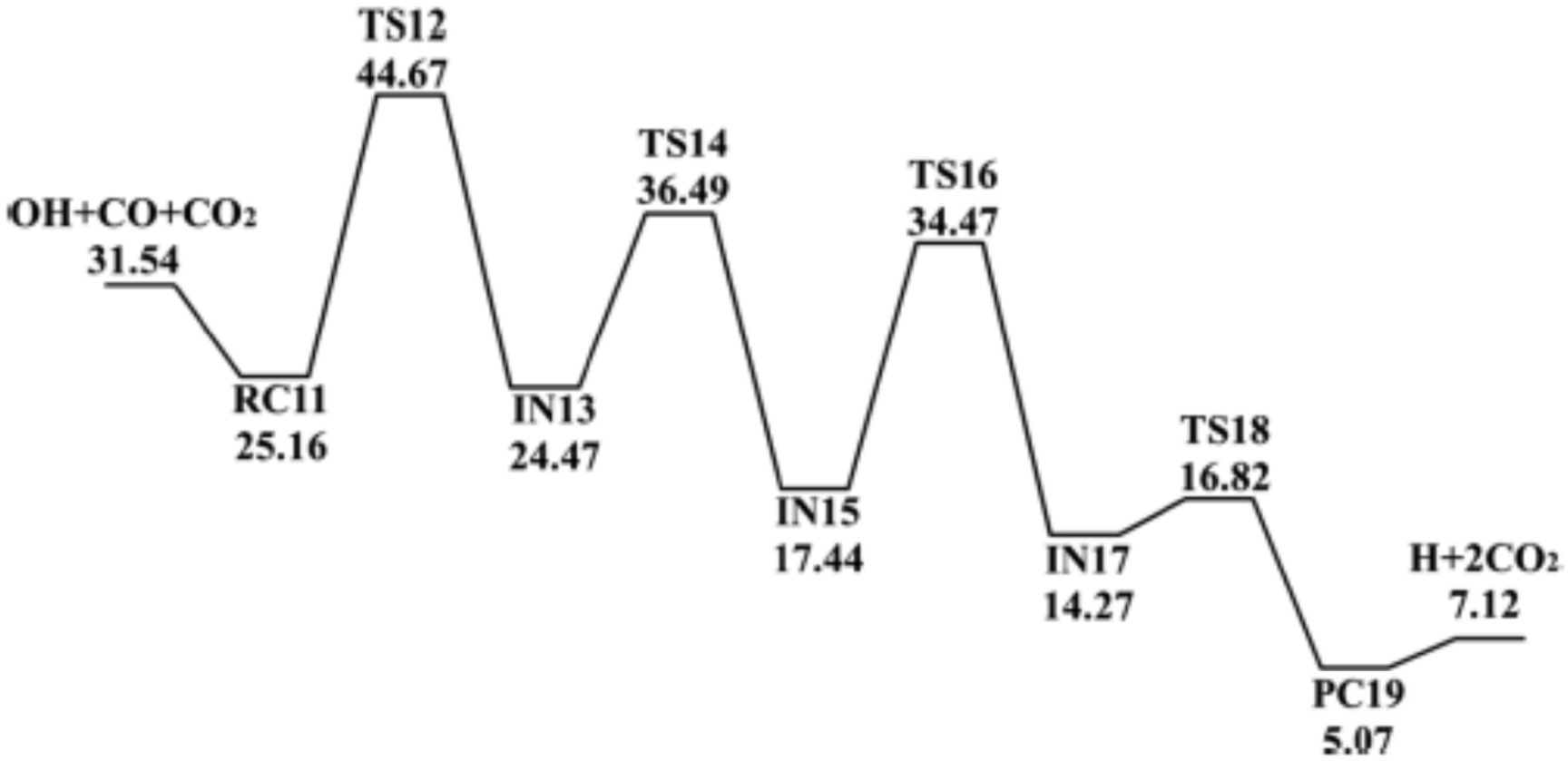


Figure 2. Relative energies (kcal/mol) of the reaction pathway shown on Scheme 1, with one covalently bound CO_2 molecule (*trans*-HOCO + CO_2 system is chosen as the reference point).

Elementary Reaction $CO+OH \rightarrow CO_2+H$ (results with spectator CO_2 molecule)

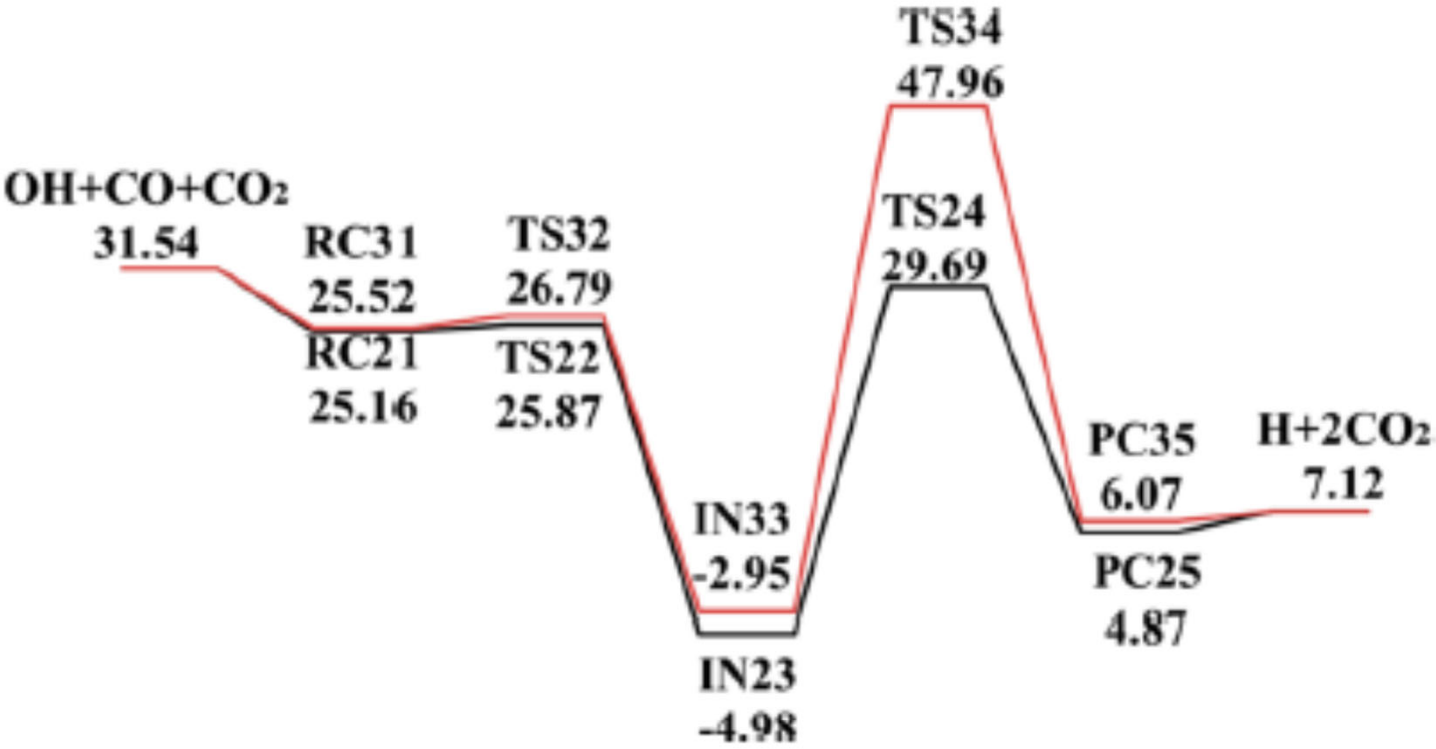
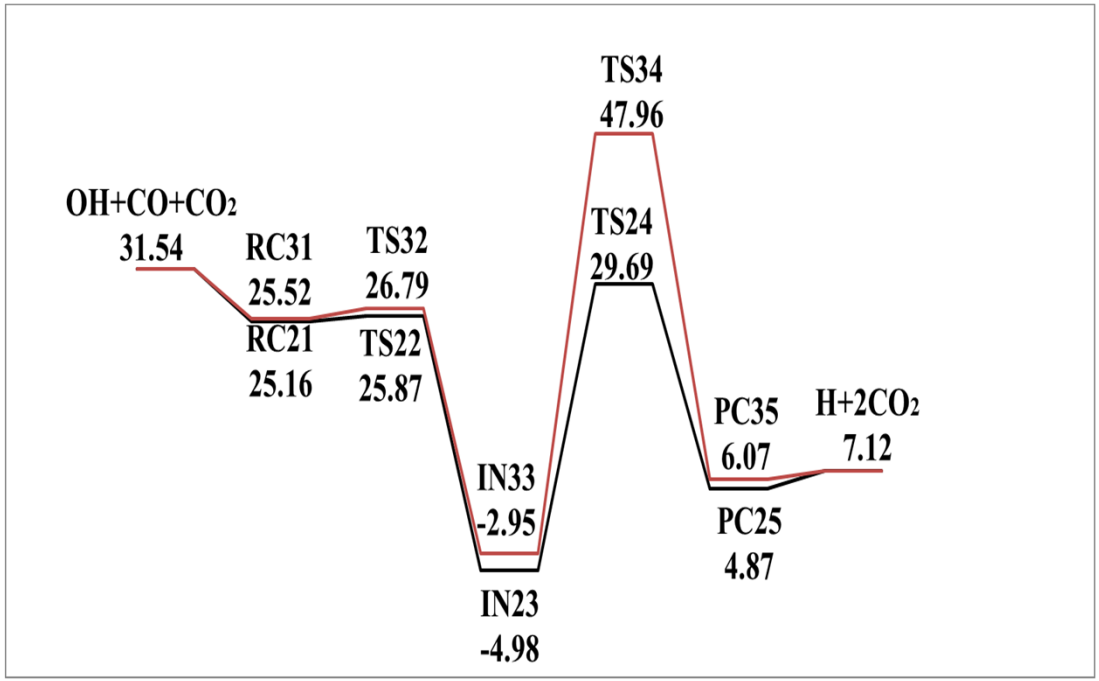


Figure 3. Relative energies (kcal/mol) of two of the reaction pathways shown shown on Scheme 2 (in black) and Scheme 3 (in red) with spectator CO_2 molecule (the *trans*-HOCO + CO_2 system is chosen as the reference point).

Elementary Reaction of $CO+OH \rightarrow CO_2+H$ (results with 1 additional spectator CO2)

Energy



- Pathways shown for CO2 autocatalytic effect published in J. Phys Chem A- Masunov & Vasu (2016)- above work
- CO_2 opens up new pathways and accelerates heat release
- Similar catalytic effects by CO2 seen in other reactions ($HO_2+HO_2 \rightarrow H_2O_2 + O_2$) but not in $H_2CO + HO_2 \rightarrow HCO + H_2O_2$

Molecular Dynamic Study: $CO+OH \rightarrow CO_2+H$ (results)

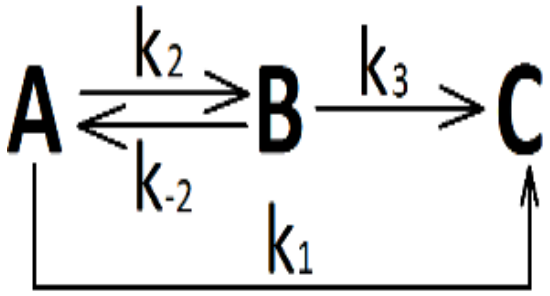
OVERALL REACTION: $\cdot OH + CO \rightarrow CO_2 + H\cdot$ (R1, k_1)

Actually goes through these 3 reactions including HOCO intermediate

$\cdot OH + CO \rightarrow HOCO\cdot$ (R2, k_2)

$HOCO\cdot \rightarrow \cdot OH + CO$ (R2r, k_{-2})

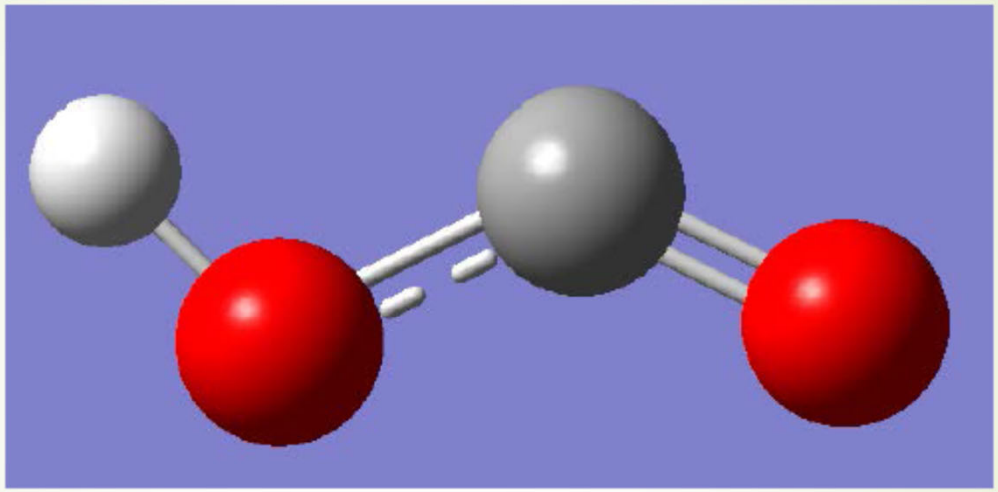
$HOCO\cdot \rightarrow CO_2 + H\cdot$ (R3, k_3)



$$k_1 = \frac{k_2 k_3}{k_{-2} + k_3}$$

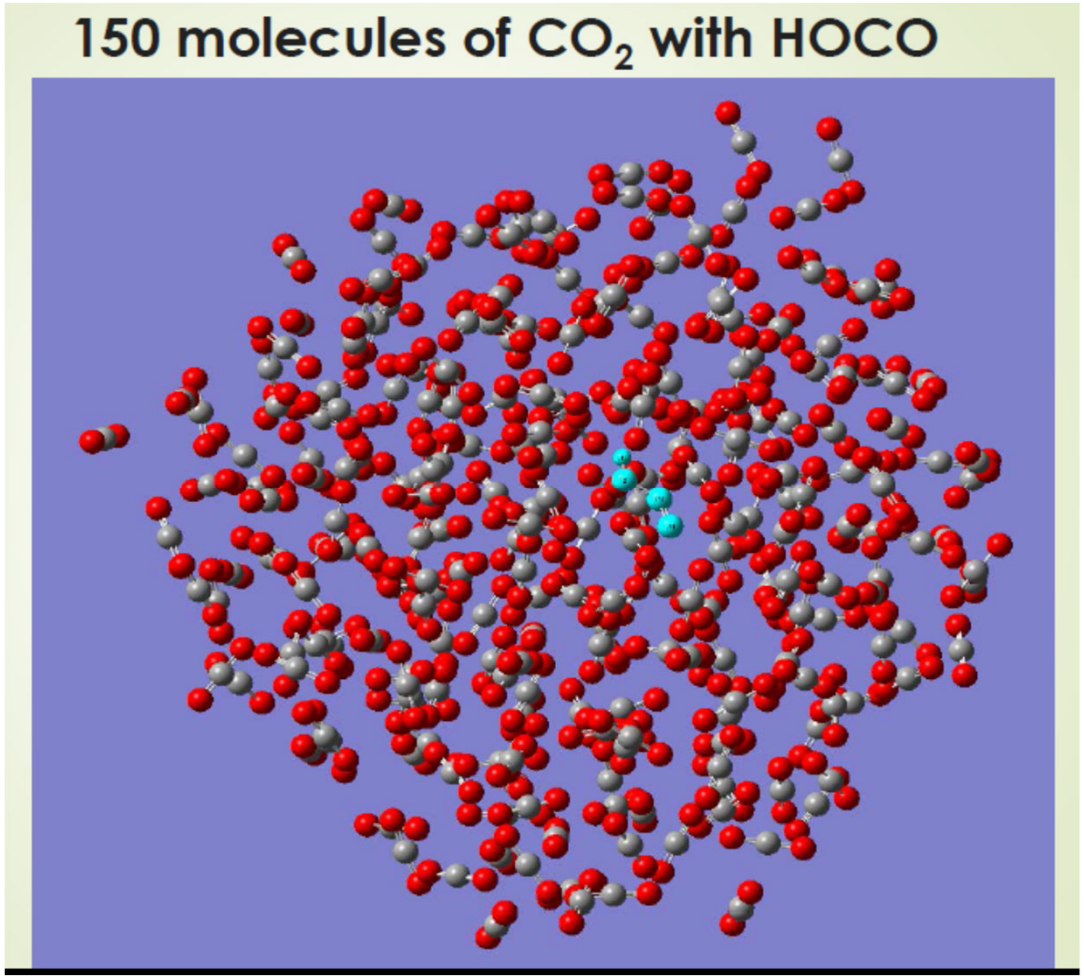
Molecular Dynamic Study: $CO+OH \rightarrow CO_2+H$ (results)

Molecule of intermediate in local minima



Optimized within DFT theory, and then this particle with optimized geometry was used for MD calculations

Molecular Dynamic Study: $CO+OH \rightarrow CO_2+H$ (results)

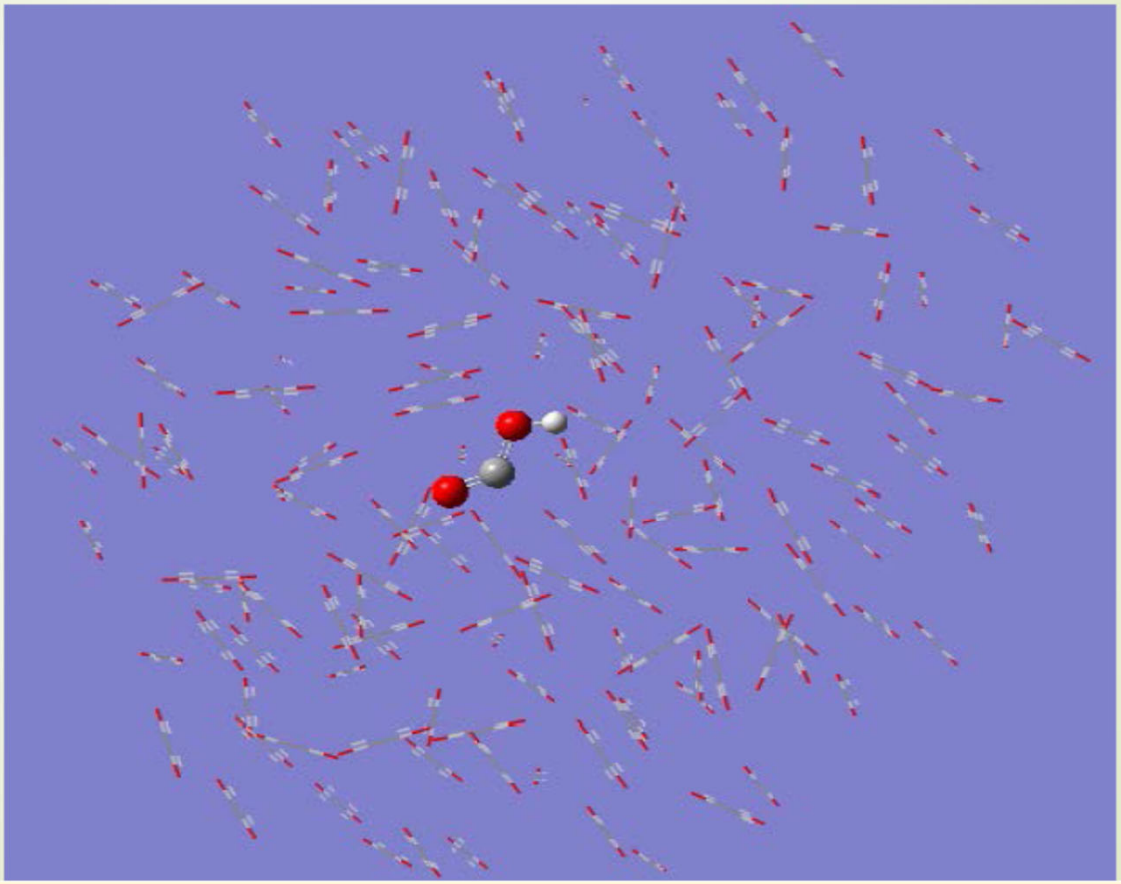


Molecular Dynamic Study: $CO+OH \rightarrow CO_2+H$ (results)

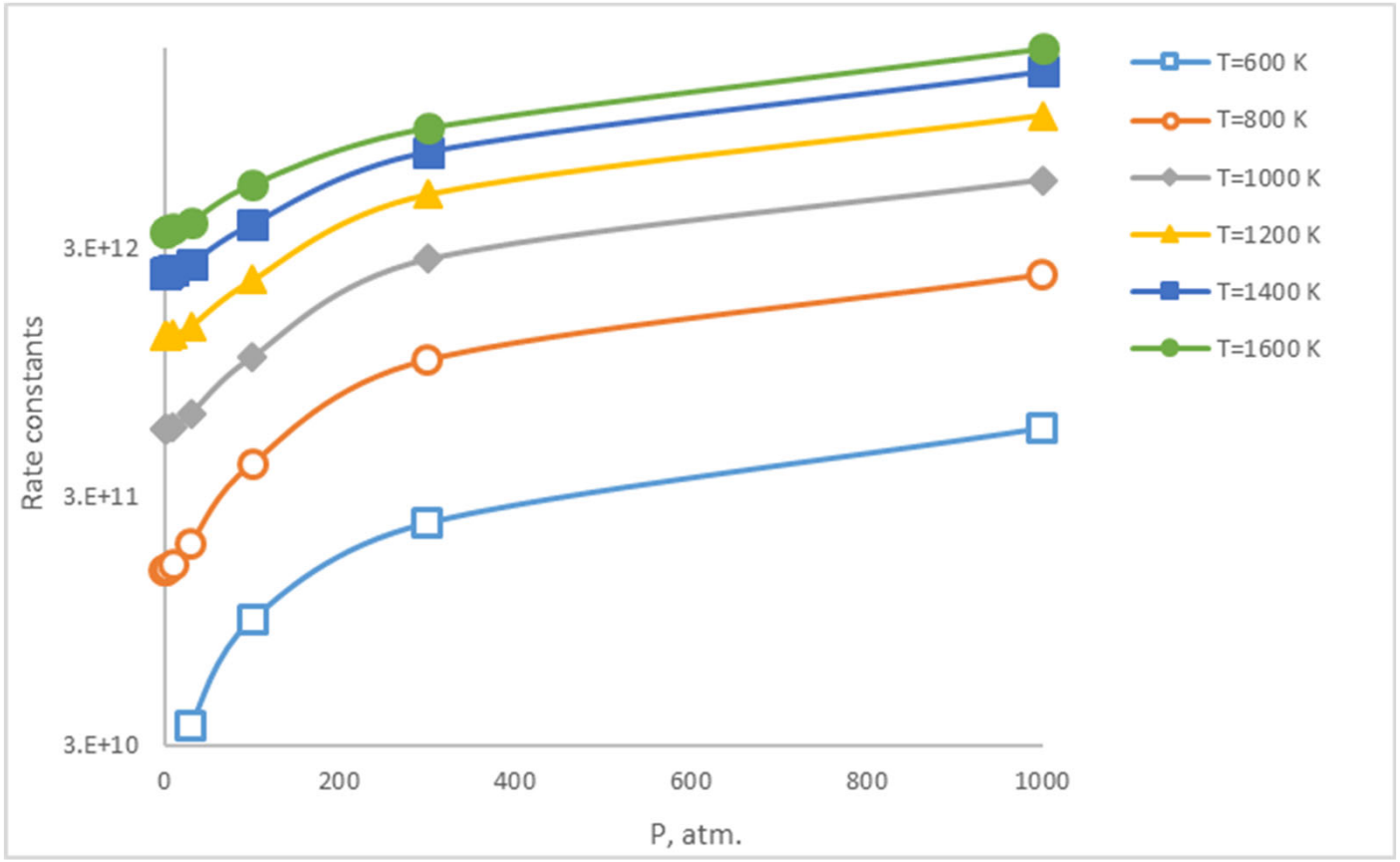
QM / MM model was used.

MM layer look like small tubes, QM layer – particle with balls

QM: MNDO; MM: force field CHARMM27



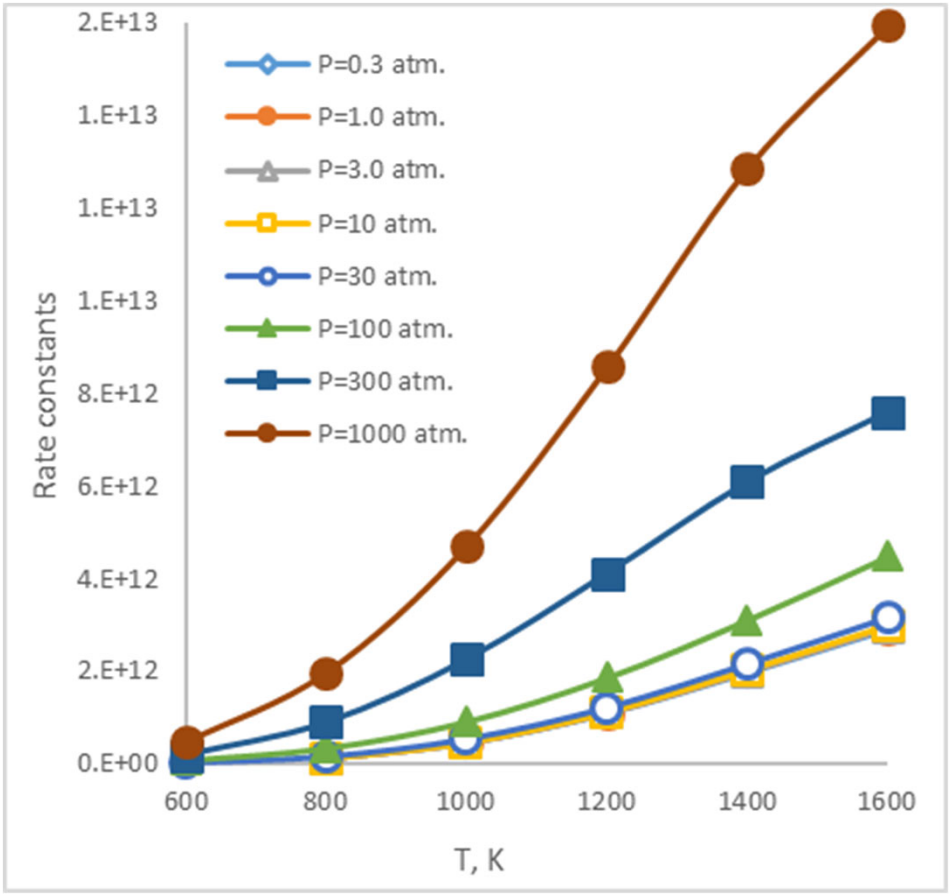
Molecular Dynamic Study: $CO+OH \rightarrow CO_2+H$ (results)



$$\cdot OH + CO \rightarrow CO_2 + H\cdot$$

$$(R1, k_1)$$

Molecular Dynamic Study: $CO+OH \rightarrow CO_2+H$ (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

Task 5: CFD development and implementation in OpenFOAM

- Real Gas Equations of State for sCO2
- Thermal properties for sCO_2 combustor
- CFD simulation status

sCO2 CFD Modeling

CFD Modeling Development

A CFD code is being developed using an existing open source CFD program called OpenFOAM, with the incorporation of a thermo-physical library and chemical kinetics mechanism that are applicable in the super critical regime. The resulting code will be able to simulate reacting and non-reacting CO2 flow through a large range of thermodynamic conditions, as experienced in a theoretical super critical engine cycle.

This will entail 4 steps;

1. Incorporate real gas equation of state.
2. Incorporate a super critical thermodynamic library.
3. Incorporate detailed sCO2 kinetic mechanism.
4. Incorporate the non-premixed CMC turbulent combustion model.

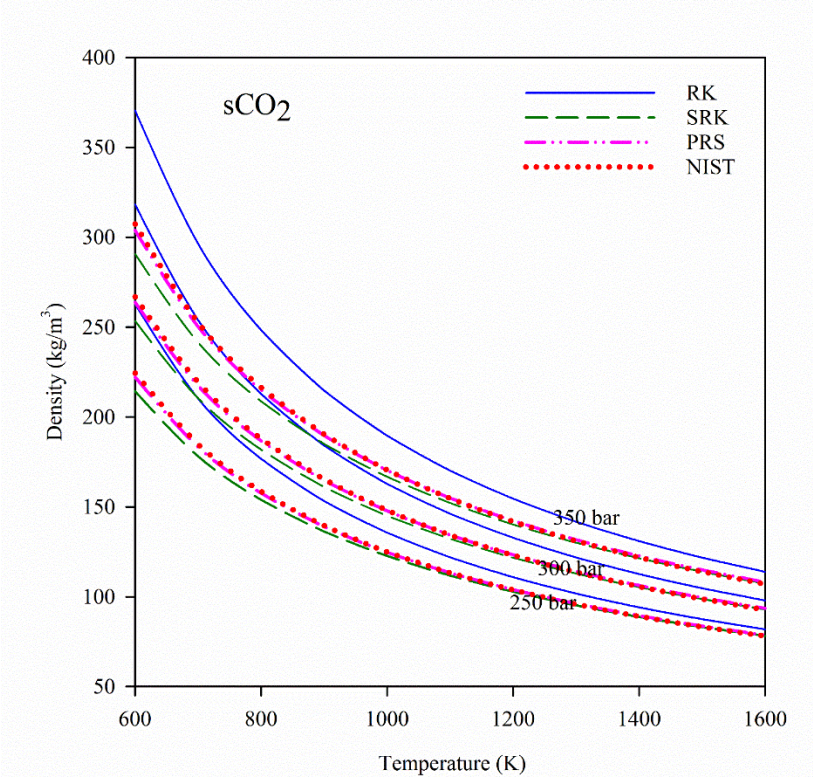
Once the CFD code is validated for supercritical CO2 flows, sensitivity and design studies will be performed on concept burners.

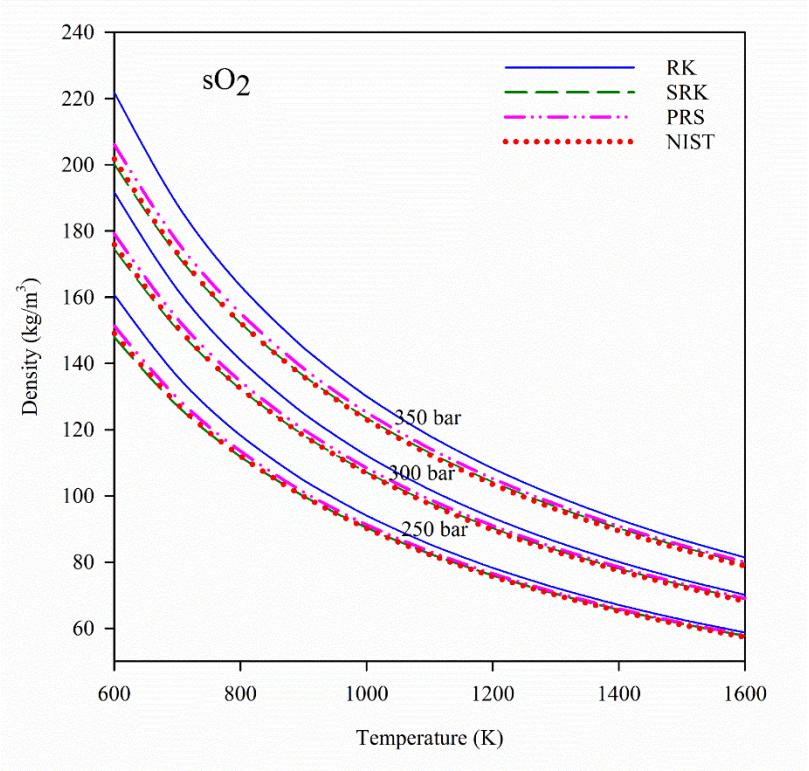
Objective

Objective: To identify necessary thermal and transport models for sCO_2 combustor simulations and to calculate elementary thermal properties for sCO_2 combustors.

- To find best equation of state for sCO_2 combustor modeling.
- To develop a model for 'compressibility factor'.
- To find best viscosity and thermal conductivity models.
- To quantify accurate elementary properties for sCO_2 combustors.

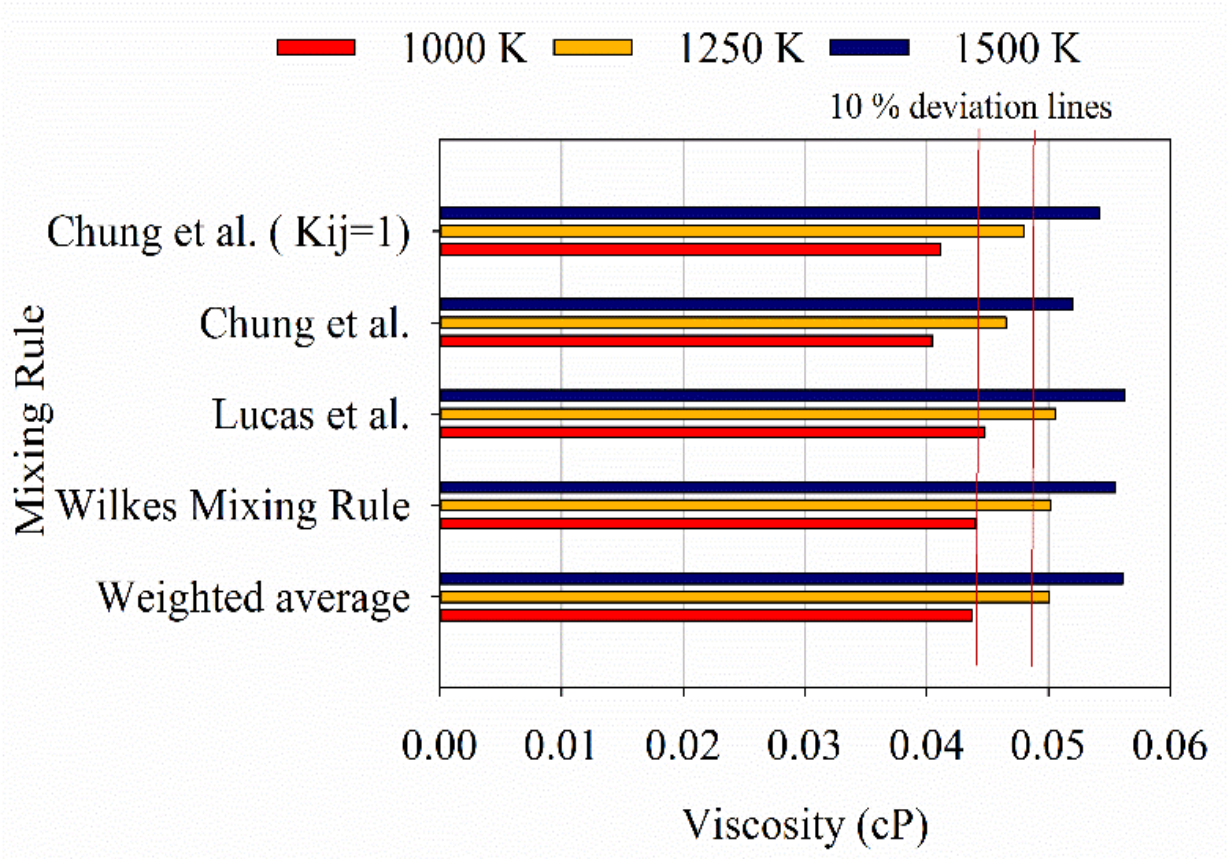
The comparison of EOS for sCO_2 and sO_2:





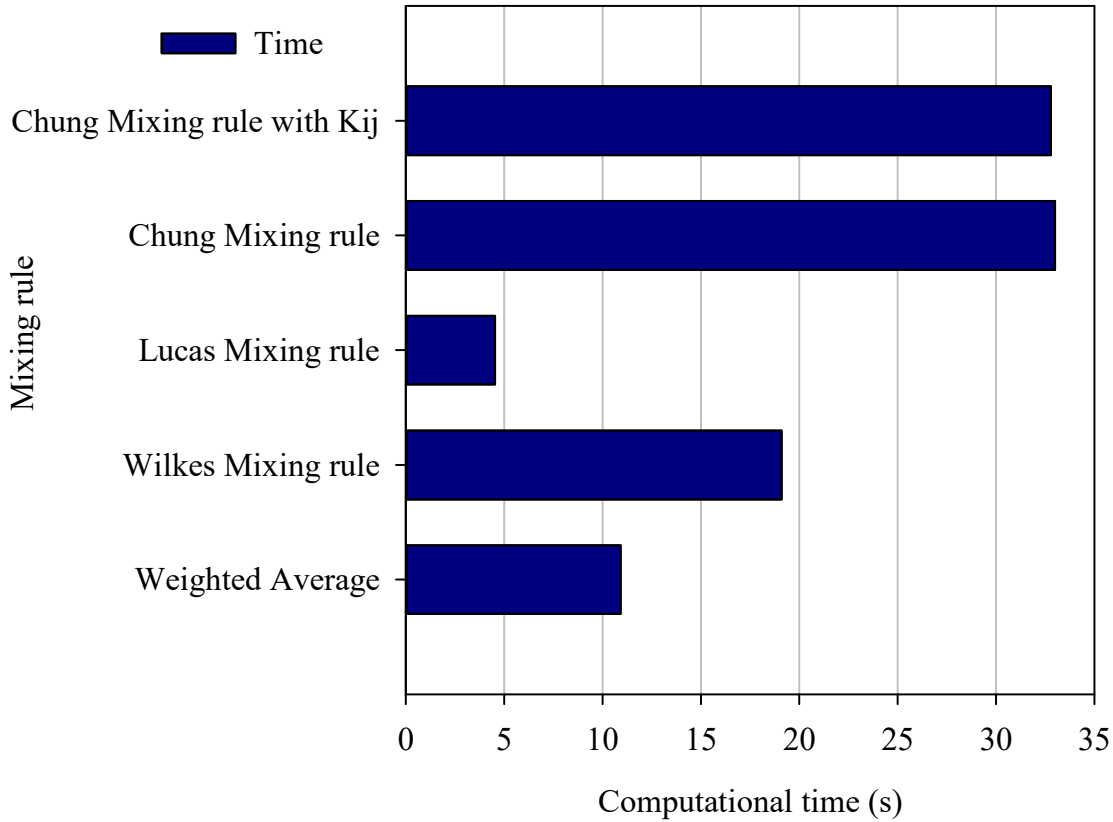
- PRS is accurate for sCO_2 and SRK is accurate for sO_2.
- The EOS has to be validate for mixtures of combustion.

Comparison of supercritical mixture viscosity mixture models:



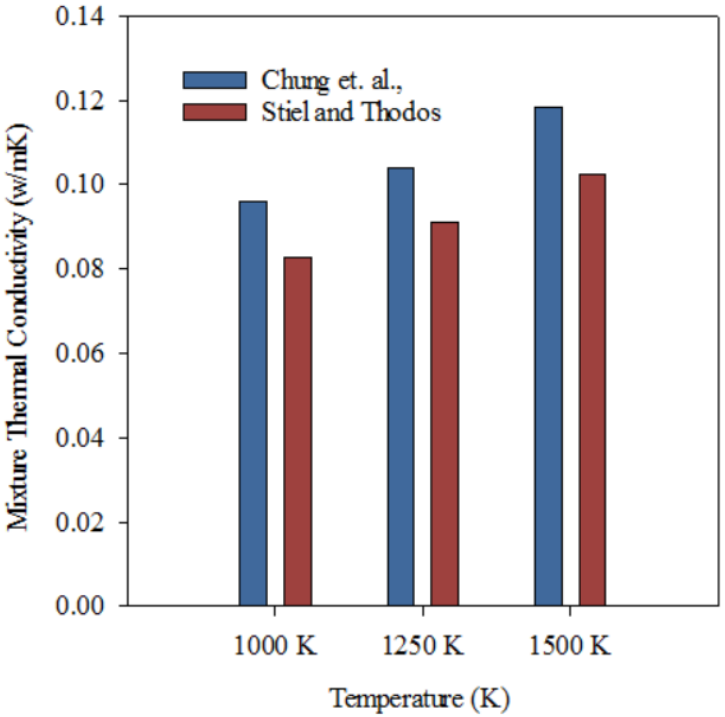
- No reference data to compare.
- Models predict within 10% of each other.
- Preferred model is identified based on the computational time.

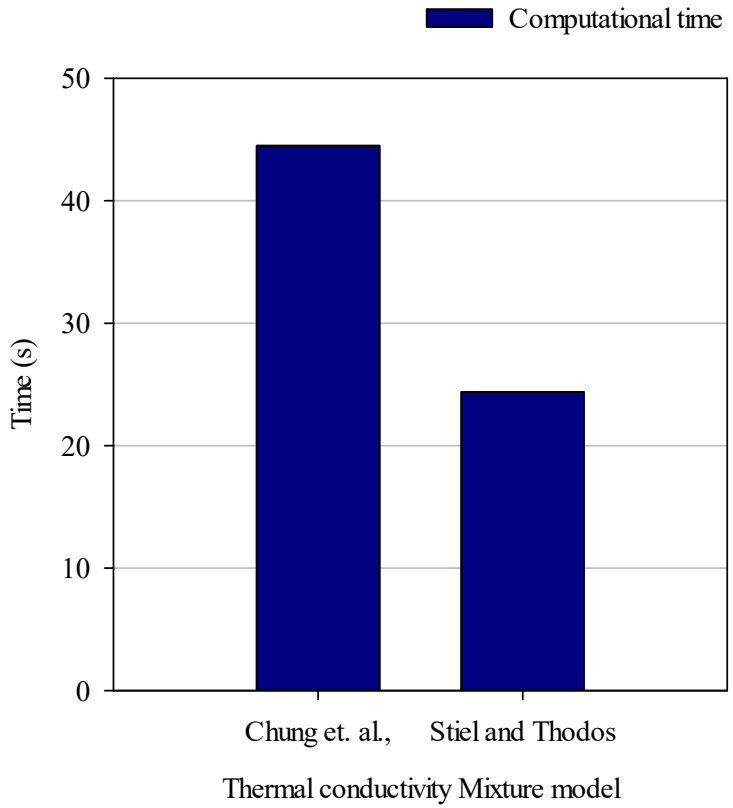
Comparison of supercritical mixture viscosity models:



- Times are calculated for 100,000 cells.
- Lucas et al., method is more suitable for detailed kinetic mechanisms and LES or DNS simulations.

Comparison of supercritical mixture thermal conductivity models:



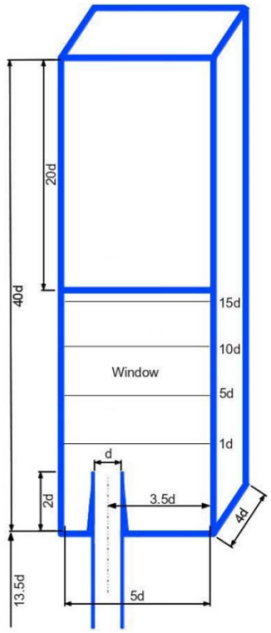


- Computational time calculated for 100,000 cells.
- Stiel and Thodos is the least expensive computationally and suitable for LES or DNS.

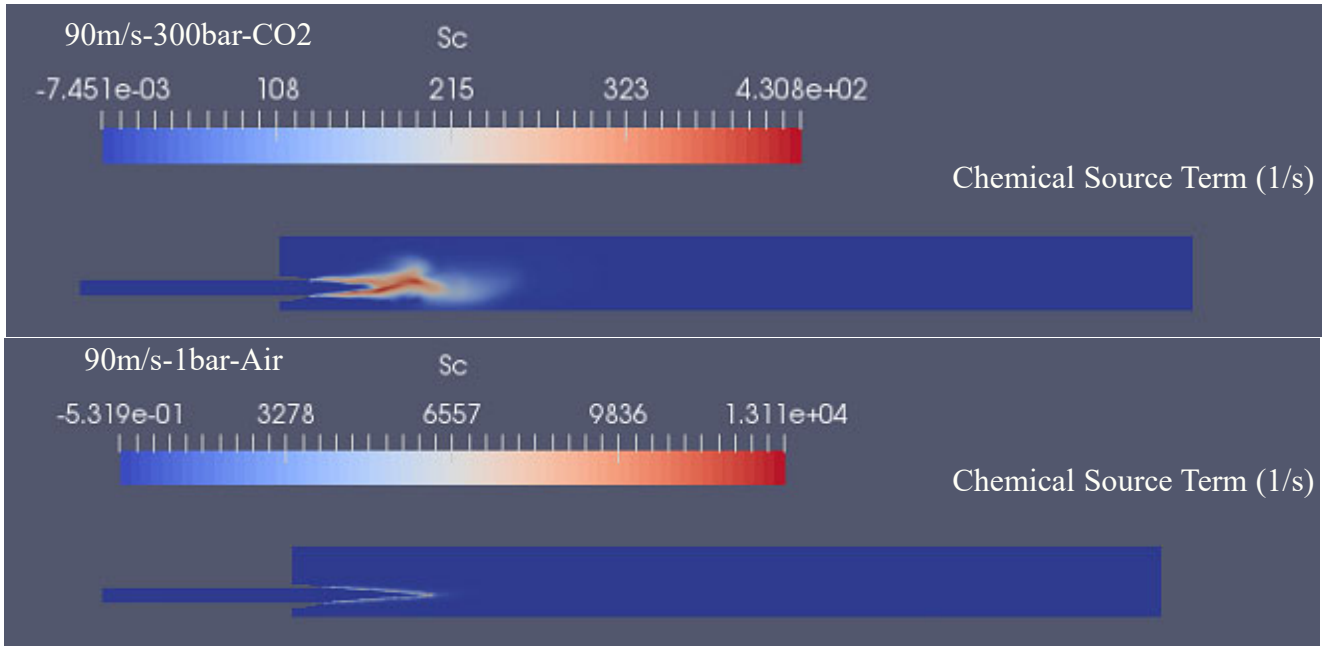
Property Conclusions

- Aramco 2.0 , CHEMKIN-RG and PCMC are coupled to investigate thermal properties of the sCO_2 mixture.
- Soave-Redlich-Kwong EOS is identified as the better accurate EOS for modelling sCO_2 combustion density.
- Several preliminary thermal properties of sCO_2 combustor are quantified. A model is suggested for 'Z' in sCO_2 combustor.
- Lucas et. al., method is identified as the accurate and computationally advantageous Viscosity correlation for sCO_2 combustion.
- An accurate and inexpensive method is proposed by using Stiel and Thodos thermal conductivity correlation.

Comparing conventional and supercritical combustion:



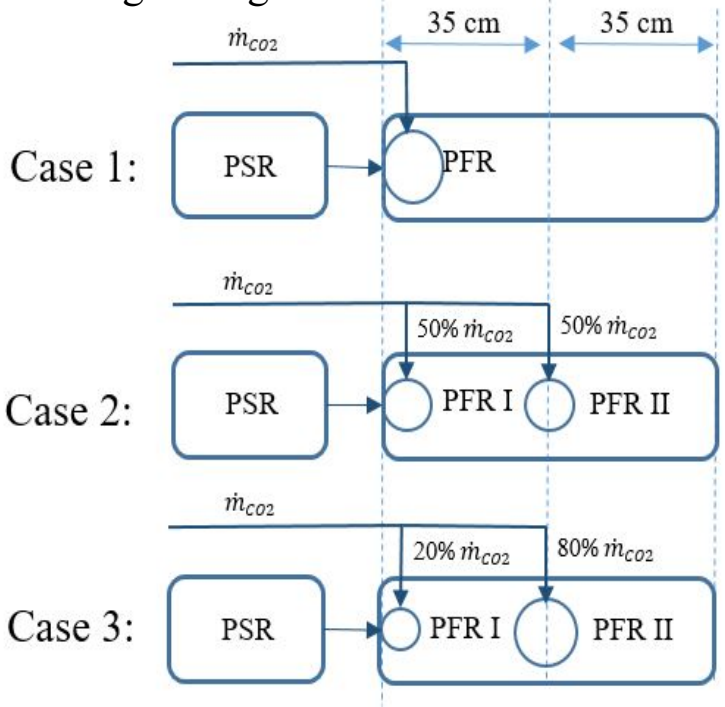
Simulated DLR-Jet



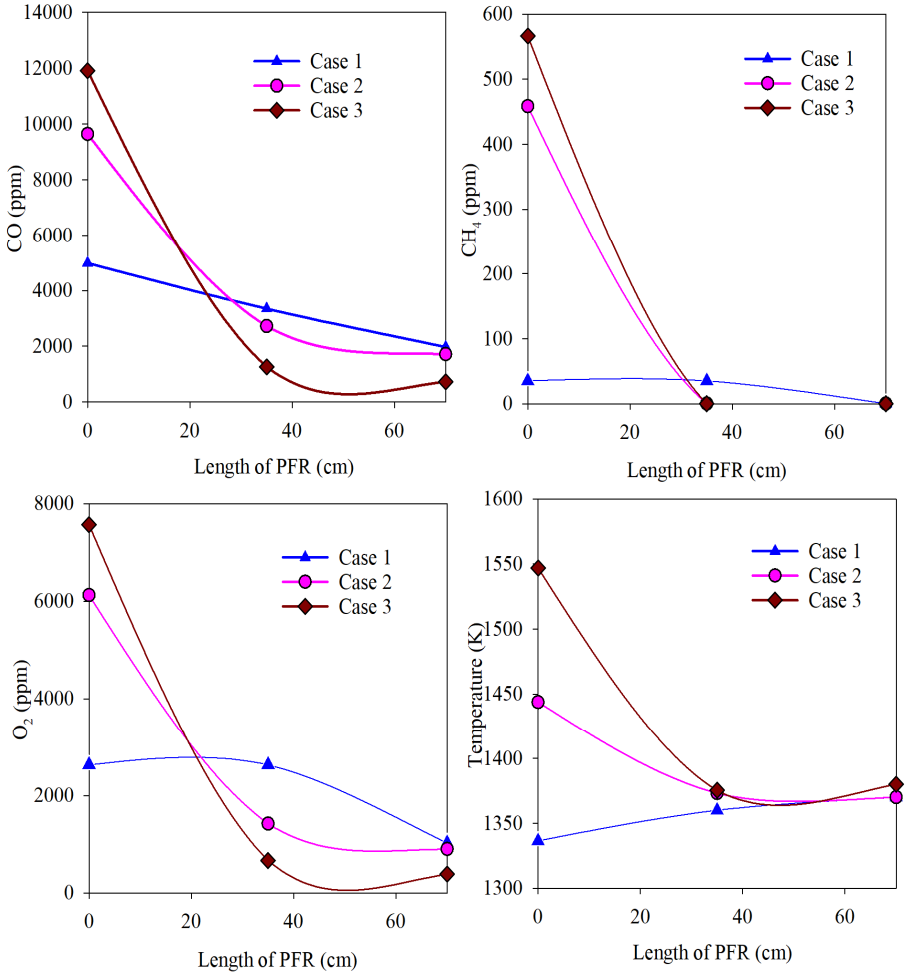
- Simulation is performed with the premixed CMC in the OpenFOAM RANS CFD code.
- The current PCMC-OpenFOAM model is capable of using large mechanisms. The current simulation uses 493 species and 2,714 reactions.
- Stoichiometric CH4/O2 with 95% by mass CO2.

Design strategy identified for future CFD simulation of dilution zone:

Mixing strategies in Dilution zone

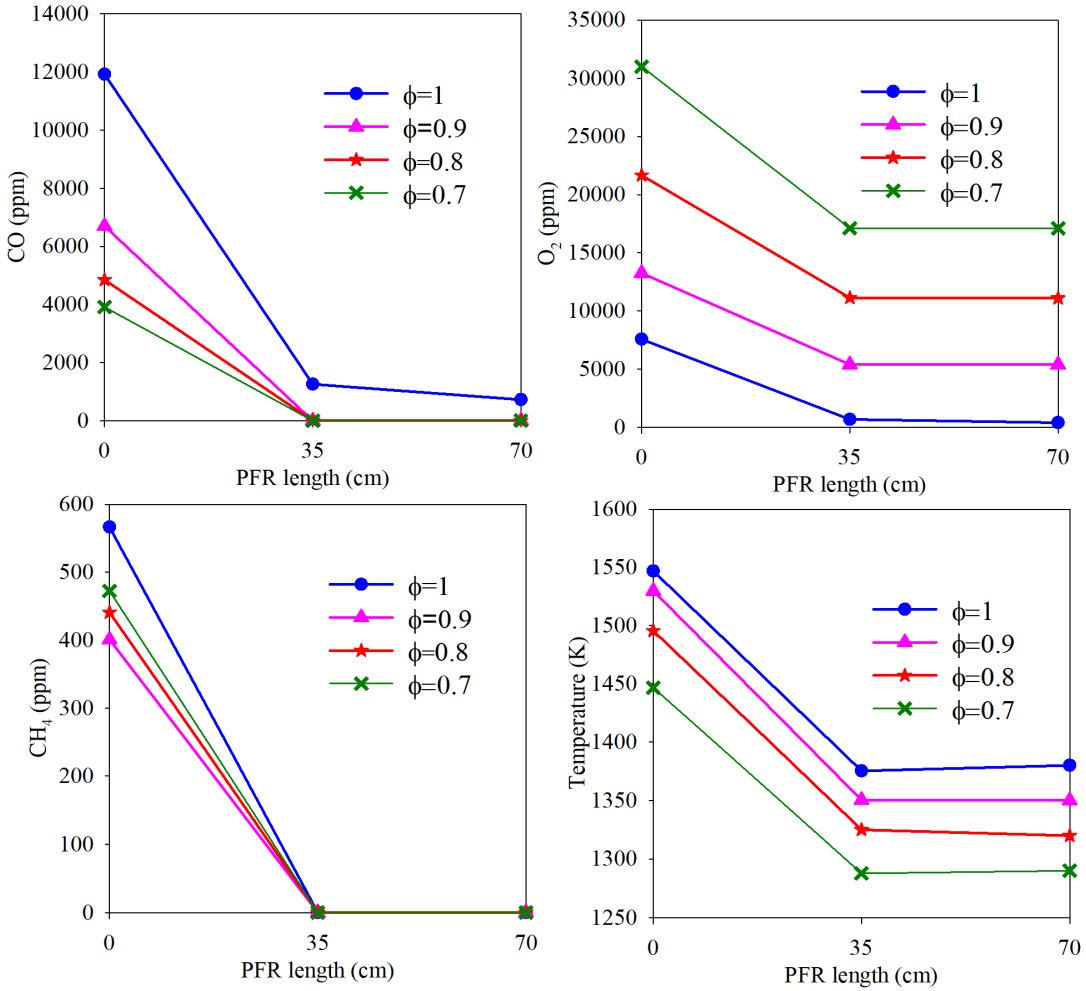


Effect of mixing strategy on PFR emissions



- Stoichiometric CH4/O2 with 95% CO2 by mass. Half of the CO2 injected in the PSR and the remainder added to the PFRs.
- Real gas code with detailed Aramco mechanism

Lean operating strategy identified



- Lean burn sCO2 reduces exit CO and shortens the reactor length.

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

Thank you,
Questions?

Vasu Lab 2016