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

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Project/Task Summary

Task 1: Project Management

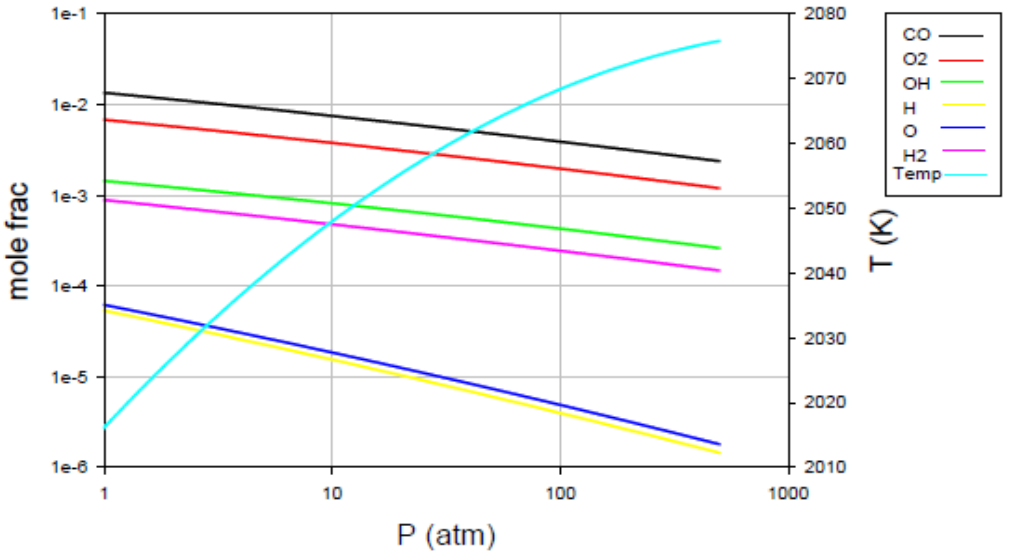
Tasks 2&3: Acquire kinetics and ignition data in highly CO_2 diluted mixtures with shock tube experiments

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

Motivation

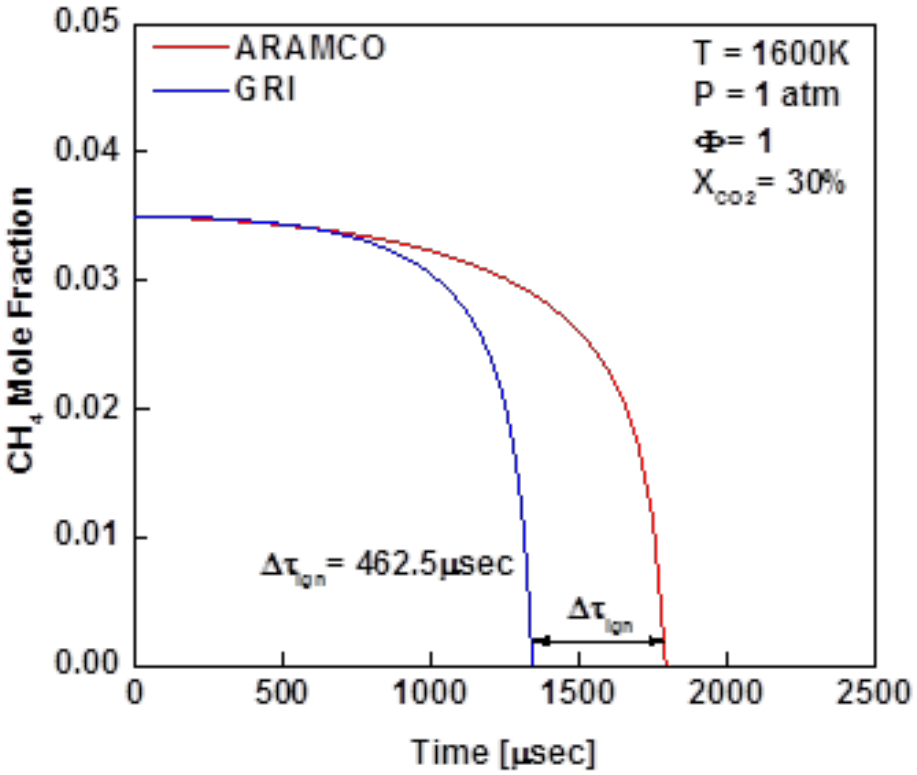
- Current state-of-the-art, such as GRI-3.0 Mechanism, has only been validated for pressures up to 10 atm
- Mechanisms have not been developed for CO_2 diluted mixtures
- Updated mechanism will allow for accurate combustor modeling with multi-step combustion using a validated mechanism
- Current CFD combustion models do not consider non-ideal effects

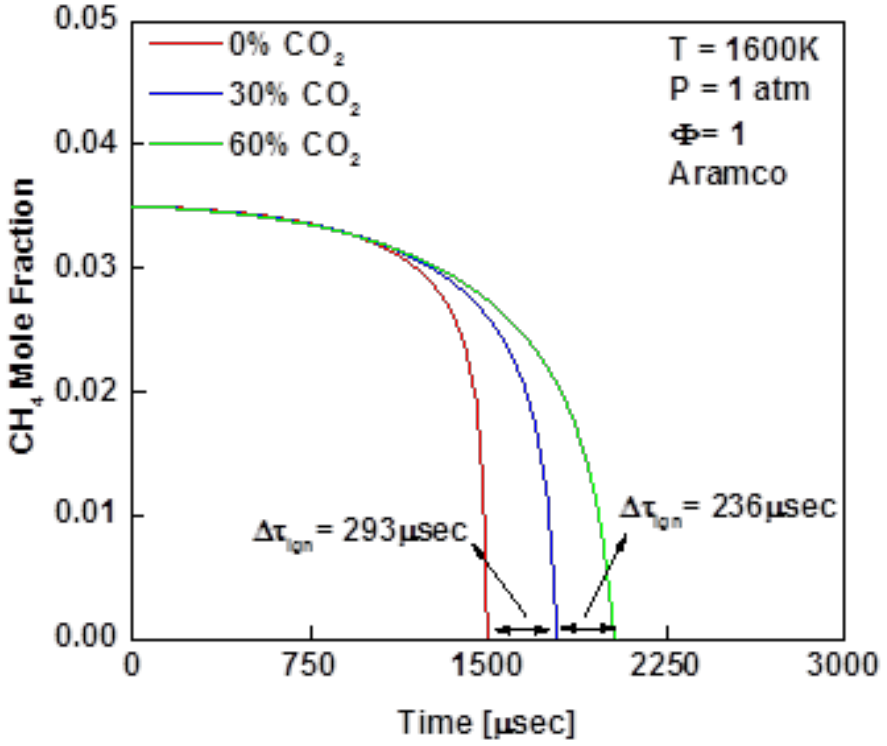


Effects of Increasing Pressure. Equilibrium calculation for $CH_4/O_2/CO_2$ at $\phi = 1$. Figure adapted from Strakey, 2014, sCO2 symposium

Motivation

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

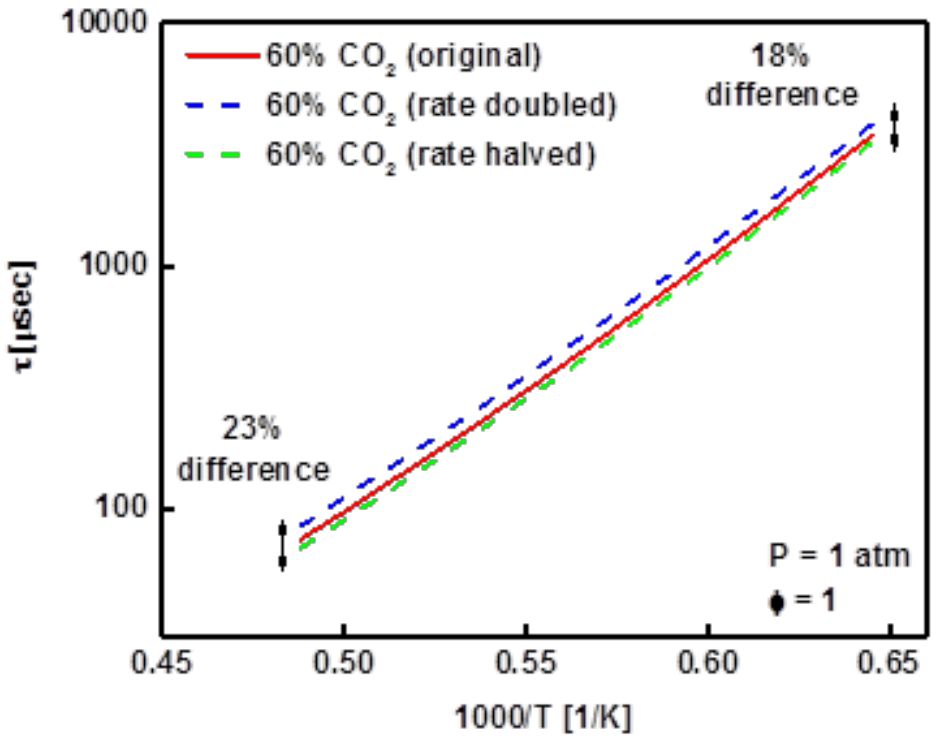


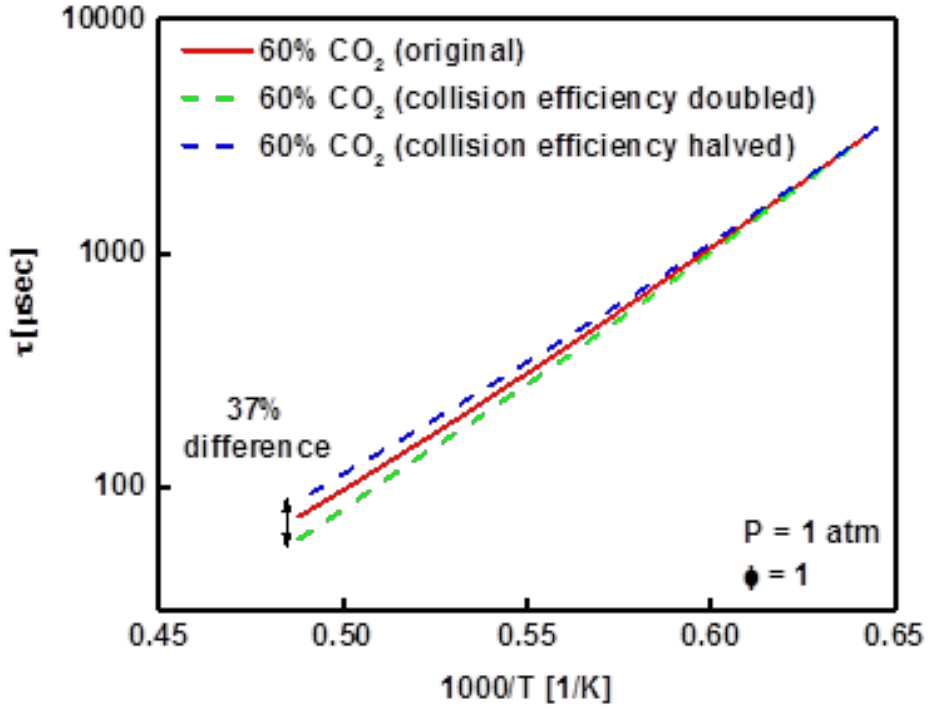


- GRI 3.0 is still a widely used mechanism created 15 years ago
- Aramco Mech 1.3 is a recent well-validated mechanism

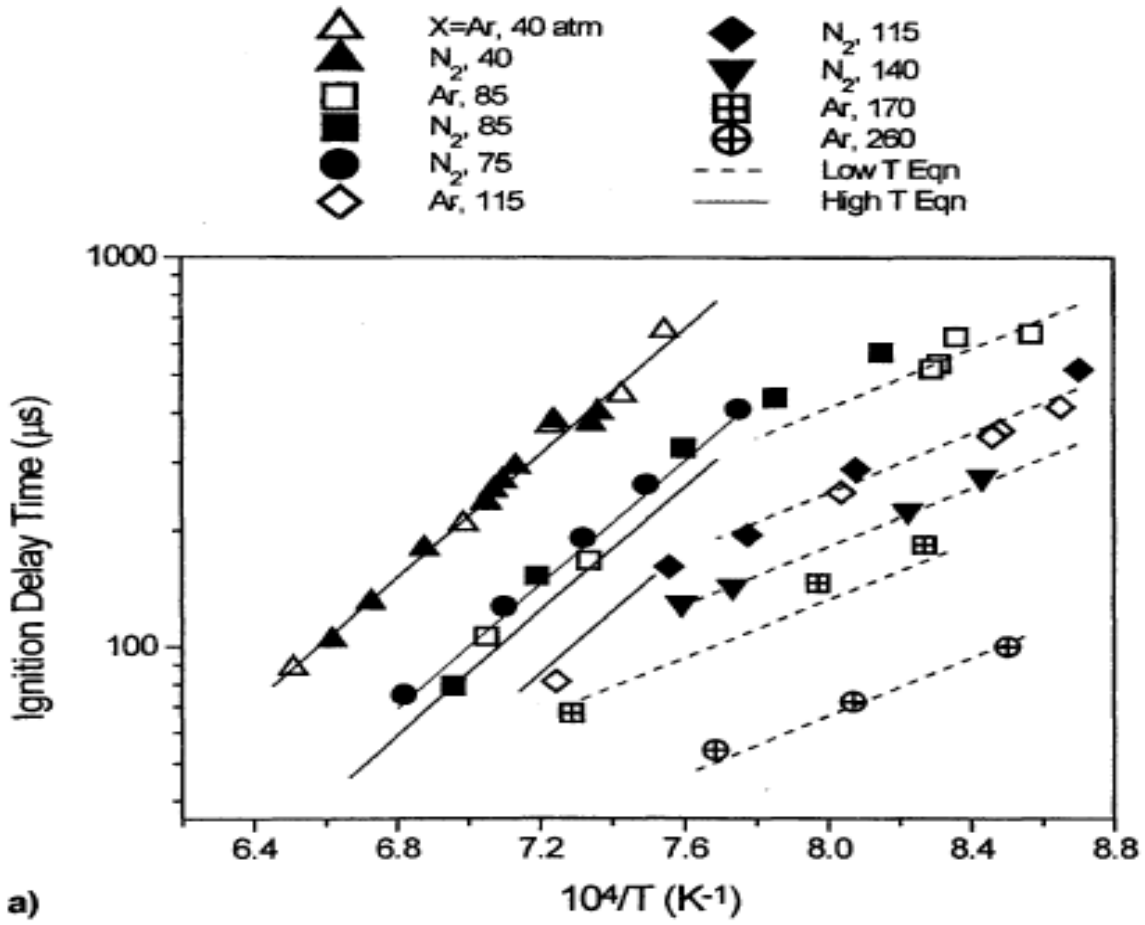
Motivation

Effect of CO+OH→CO2+H and third-body collision efficiency of CO2 on ignition times





Existing High-Pressure Methane Ignition Data



$CH_4/O_2/N_2/Ar$ 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 CO_2

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

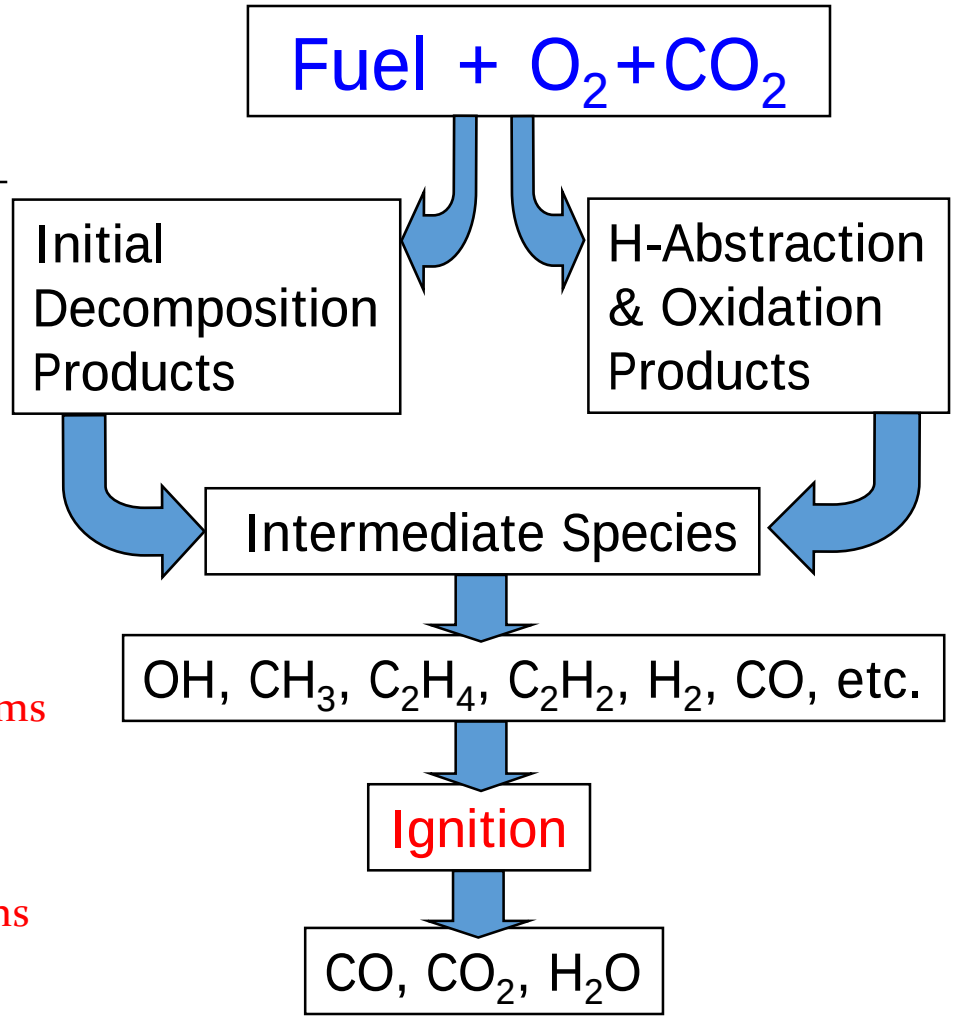
1. Decomposition Pathways

2. Intermediate Species Sub-Mechanisms

3. Full Mechanisms

4. Reduced Mechanisms

5. Validation



EXPERIMENT

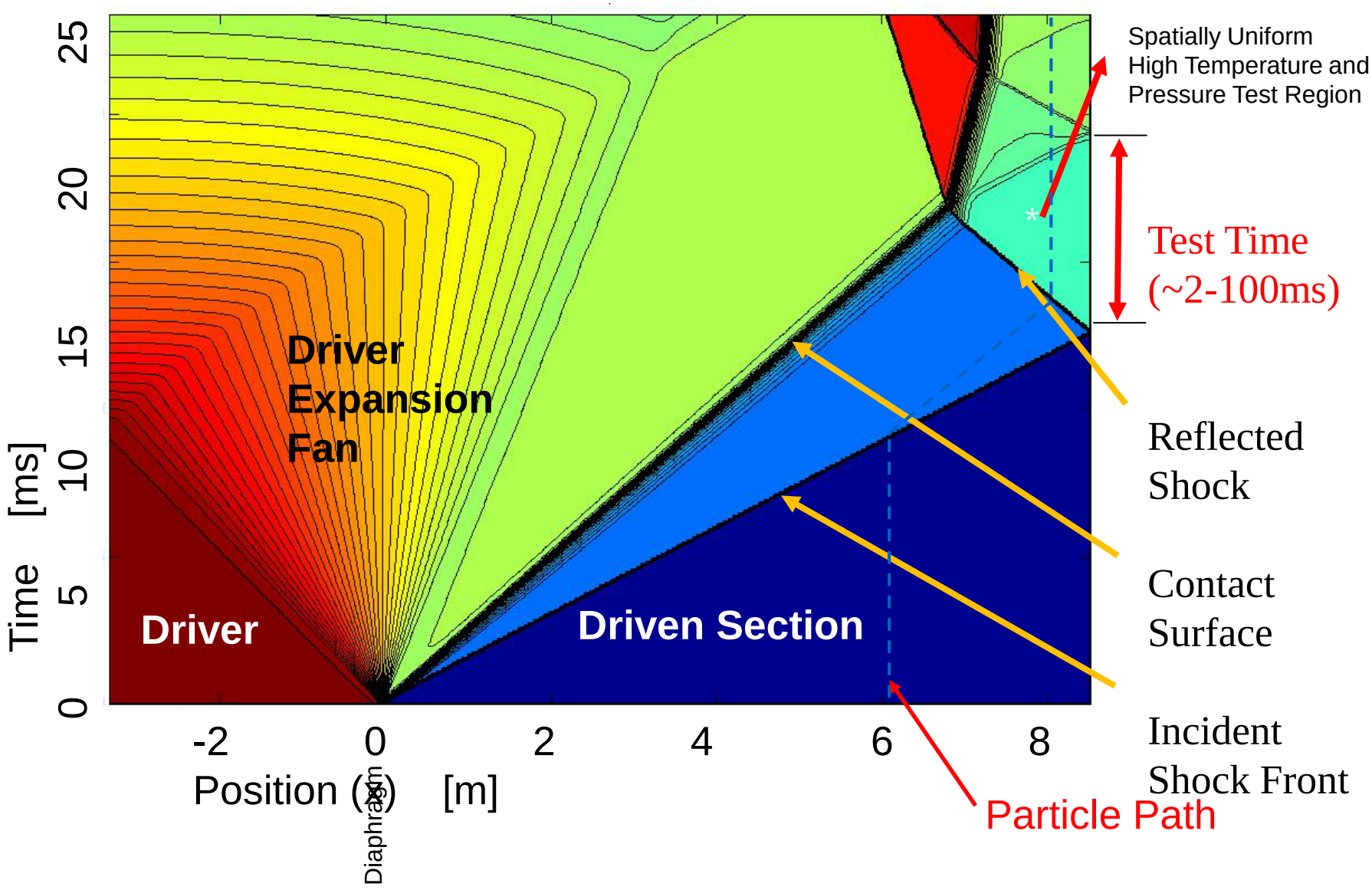
Kinetic Targets (Shock Tubes)

1. Ignition Time Measurements

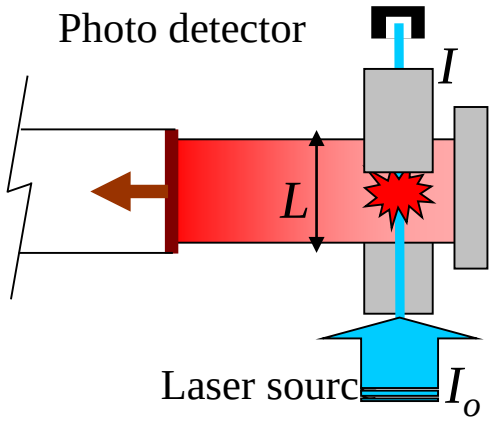
2. Species Time-Histories

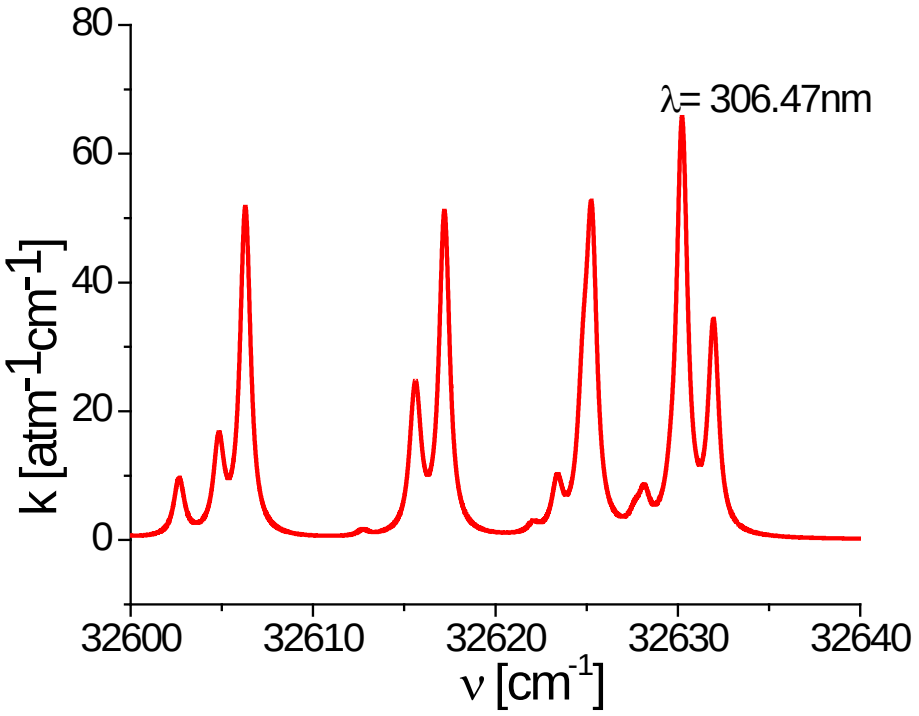
3. Direct Rate Measurements

Shock tube x-t diagram



Laser absorption spectroscopy





Beer - Lambert law

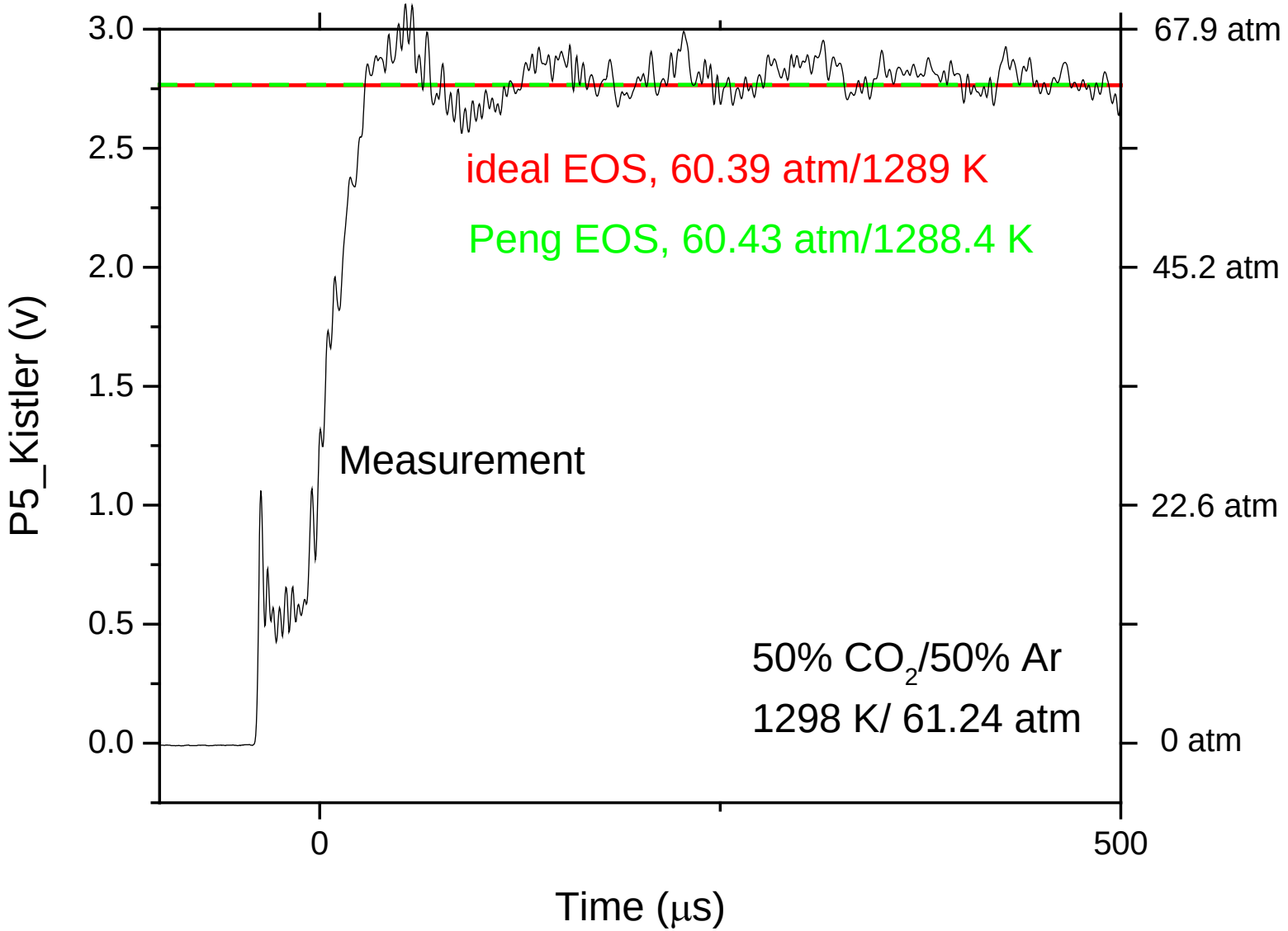
$$I/I_o = \exp(-k_\lambda P_{total} X_{species} L)$$

Spectral absorption coefficient

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

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

Tasks 2 & 3 Sample Results: Shock Tube



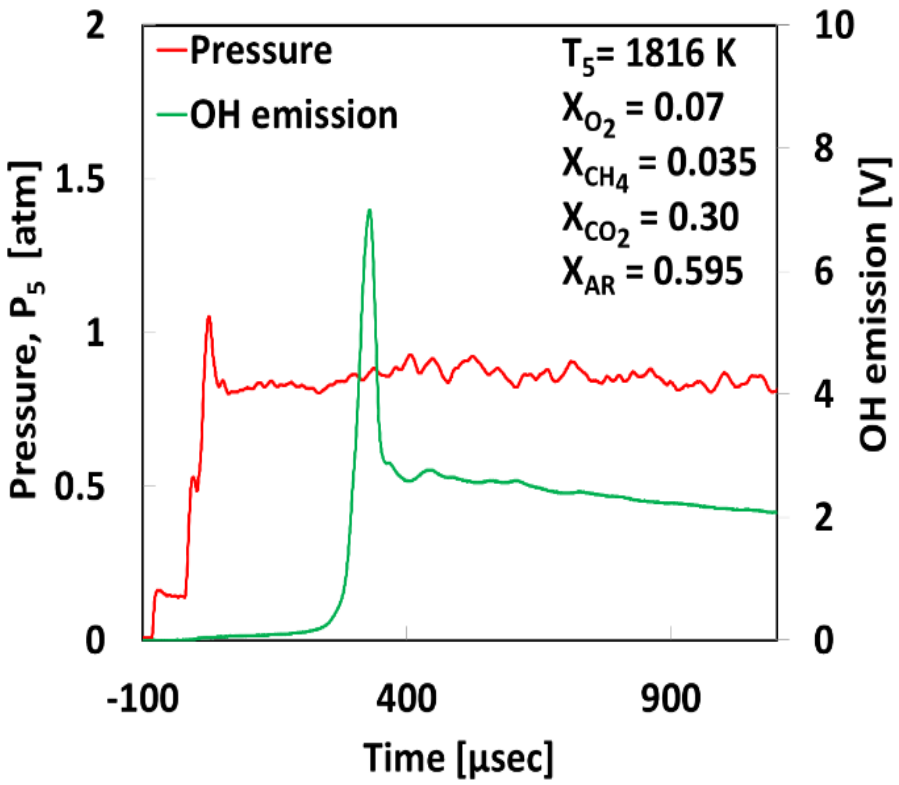
Reflected shock wave experiments: sidewall pressure profiles.
Reflected shock conditions: 1298K, 61.24atm, 50% CO2/50% argon mixture.

Ignition Delay Time Measurements

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

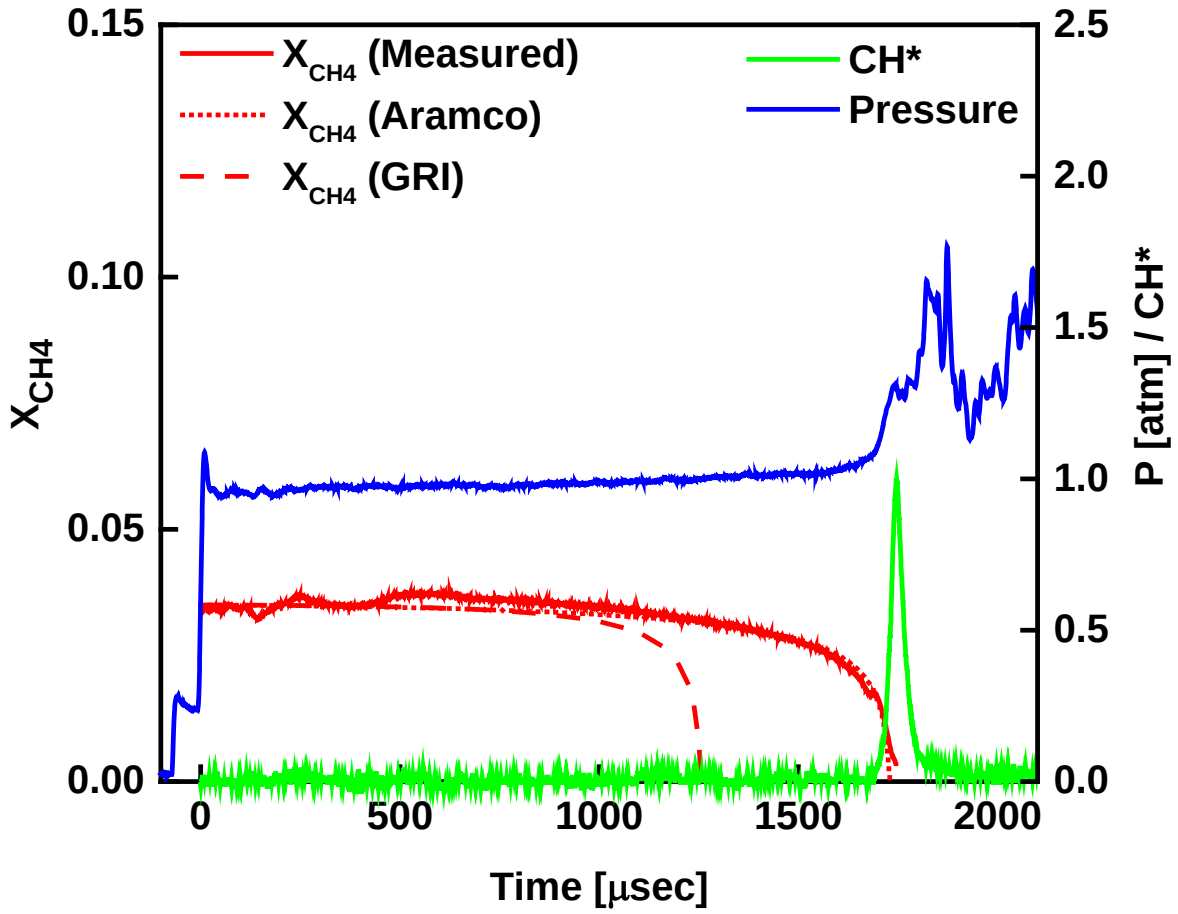
Arrival of shockwave determined as midpoint of the second pressure rise (rise due to reflected shock)

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

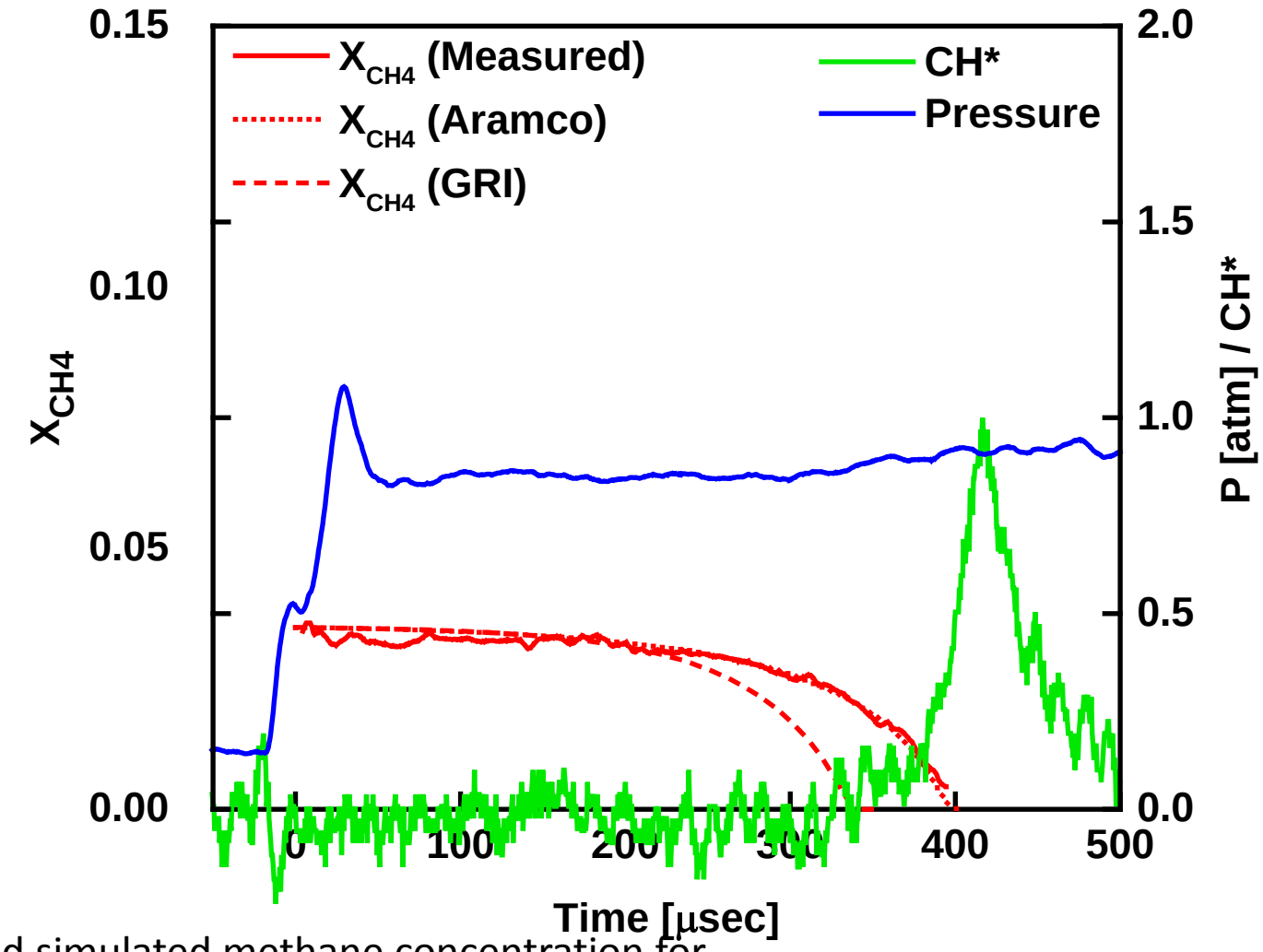


Methane Concentration Results

- Comparison of measured and simulated methane concentration for
  - Stoichiometric ignition of 3.5% CH_4 in Argon, 1600K



Methane Concentration Results

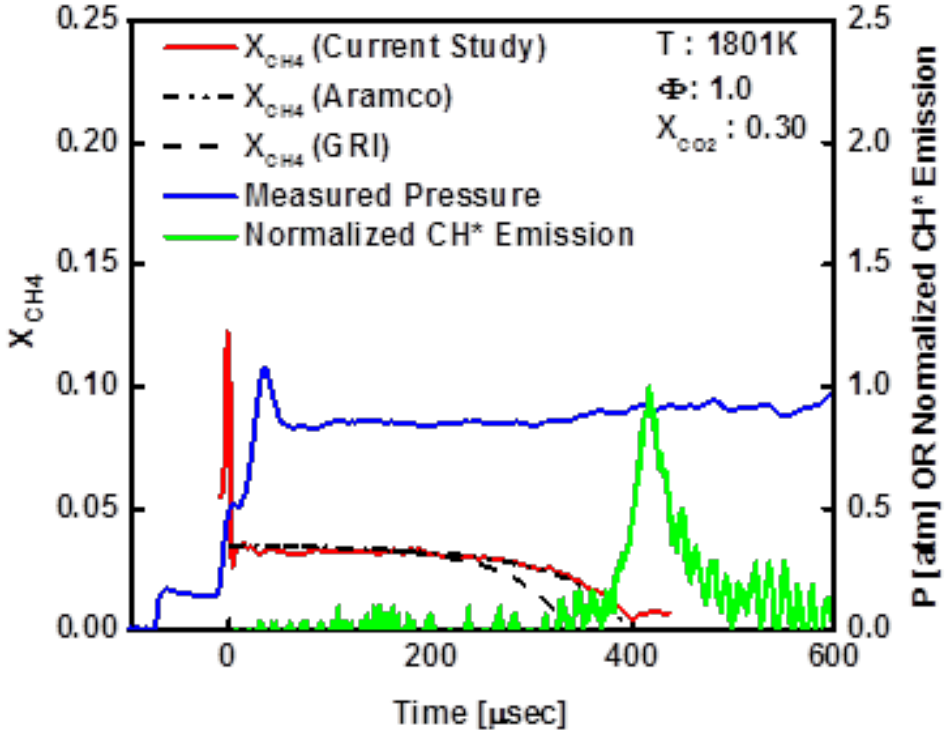


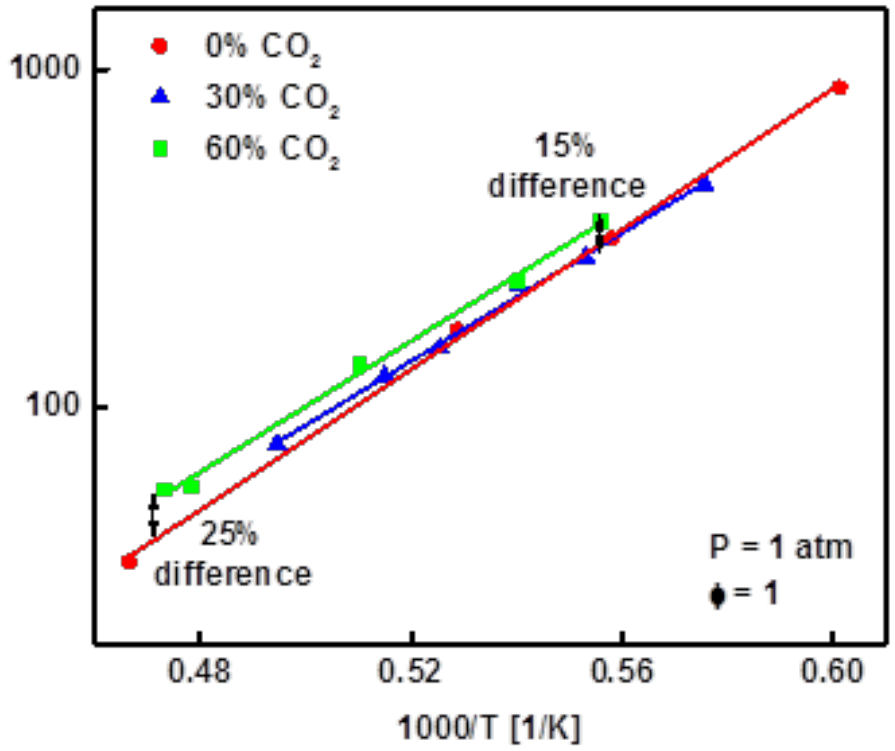
- Comparison of measured and simulated methane concentration for
  - Stoichiometric ignition of 3.5% CH_4 in Argon diluted with 30% CO_2, 1600K

Methane Ignition and Concentration Results

(Combustion and Flame, Koroglu, Vasu, et al. 2016)

- Comparison of measured and simulated methane concentration for
  - Stoichiometric ignition of 3.5% CH_4 in argon/CO_2
  - GRI predictions are wrong for both ignition time and concentrations even at low pressures !!

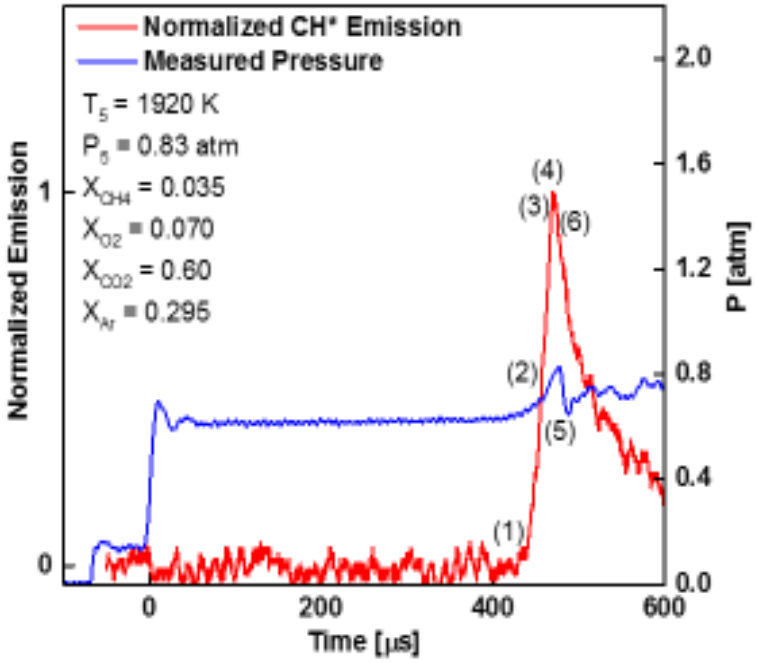


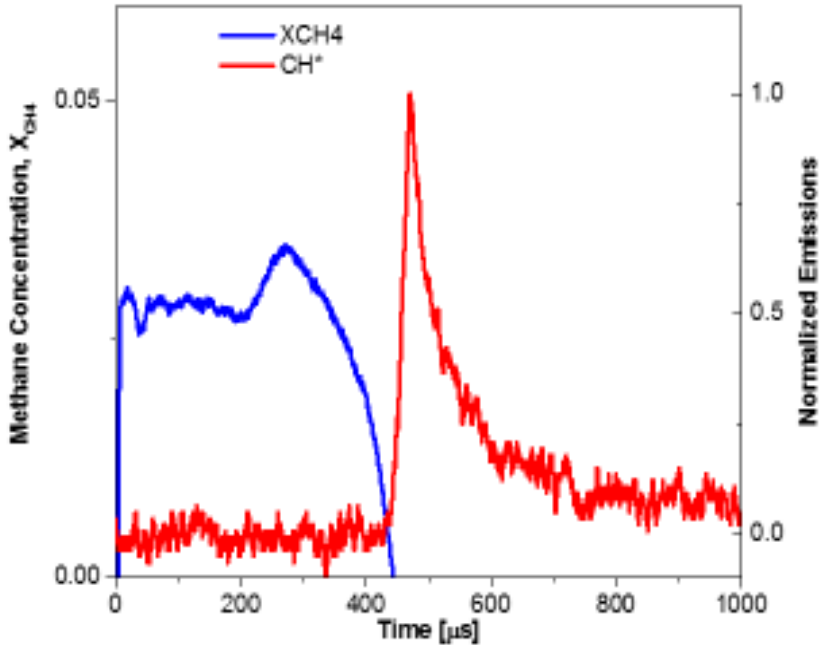


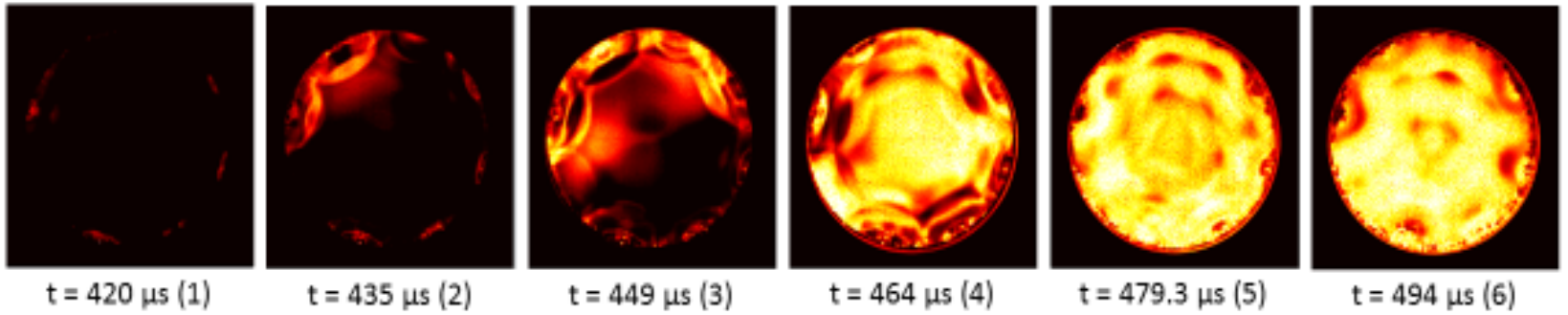
Methane/O_2/CO_2 Ignition:
High-Speed Imaging for Accurate Ignition Determination

Methane/O2/CO2 Ignition: High-Speed Imaging Results

XCO2=0



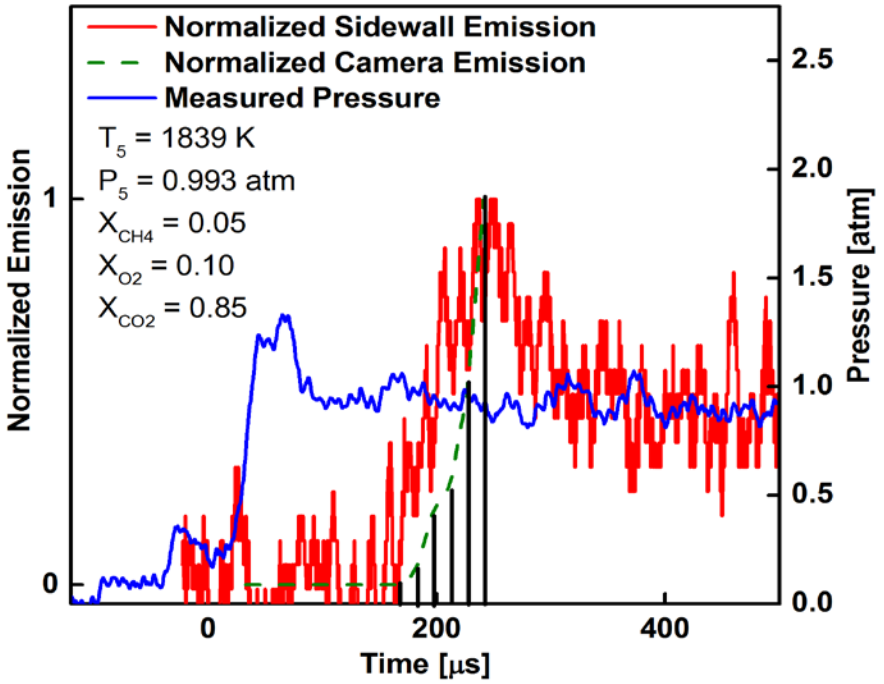


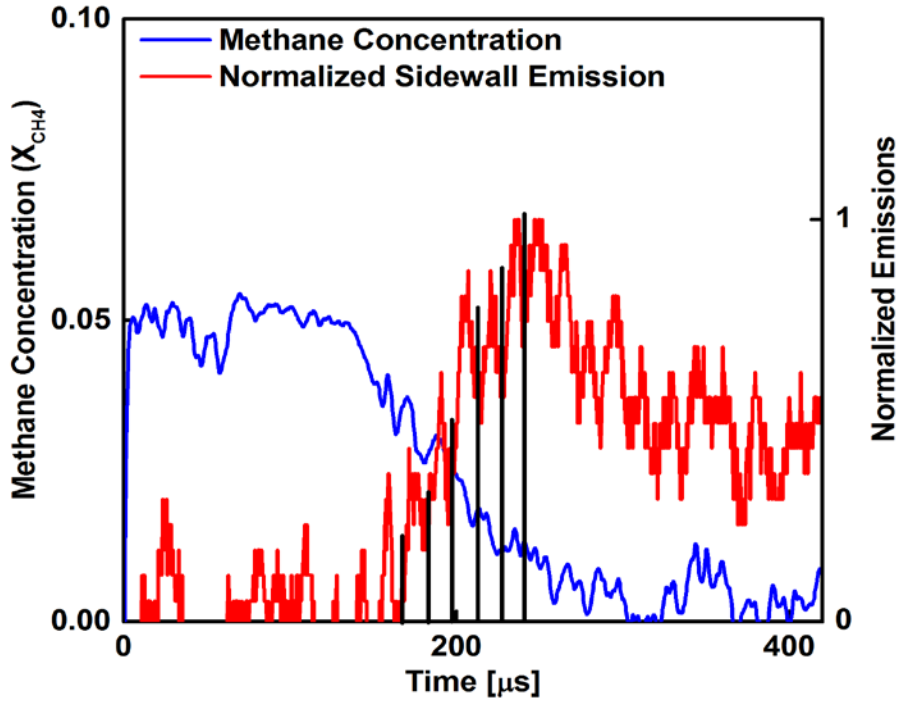


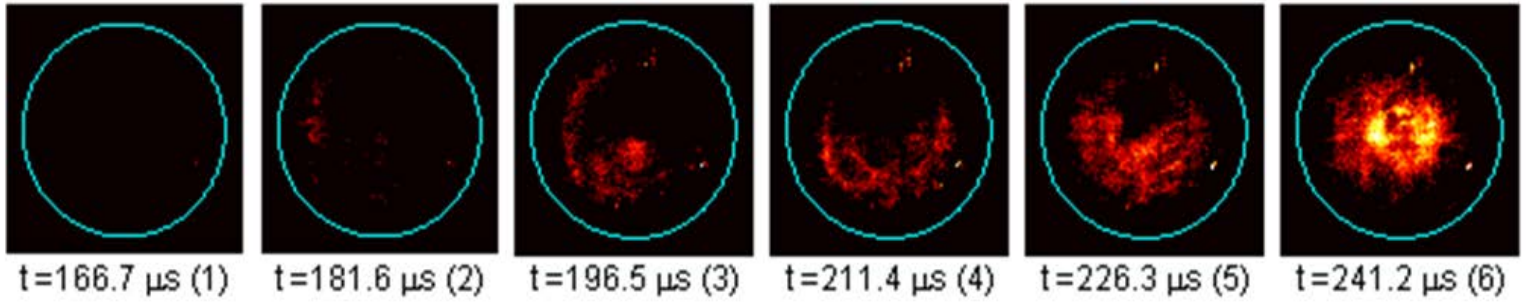
t = 420 μs (1) t = 435 μs (2) t = 449 μs (3) t = 464 μs (4) t = 479.3 μs (5) t = 494 μs (6)

Methane/O2/CO2 Ignition Imaging Results

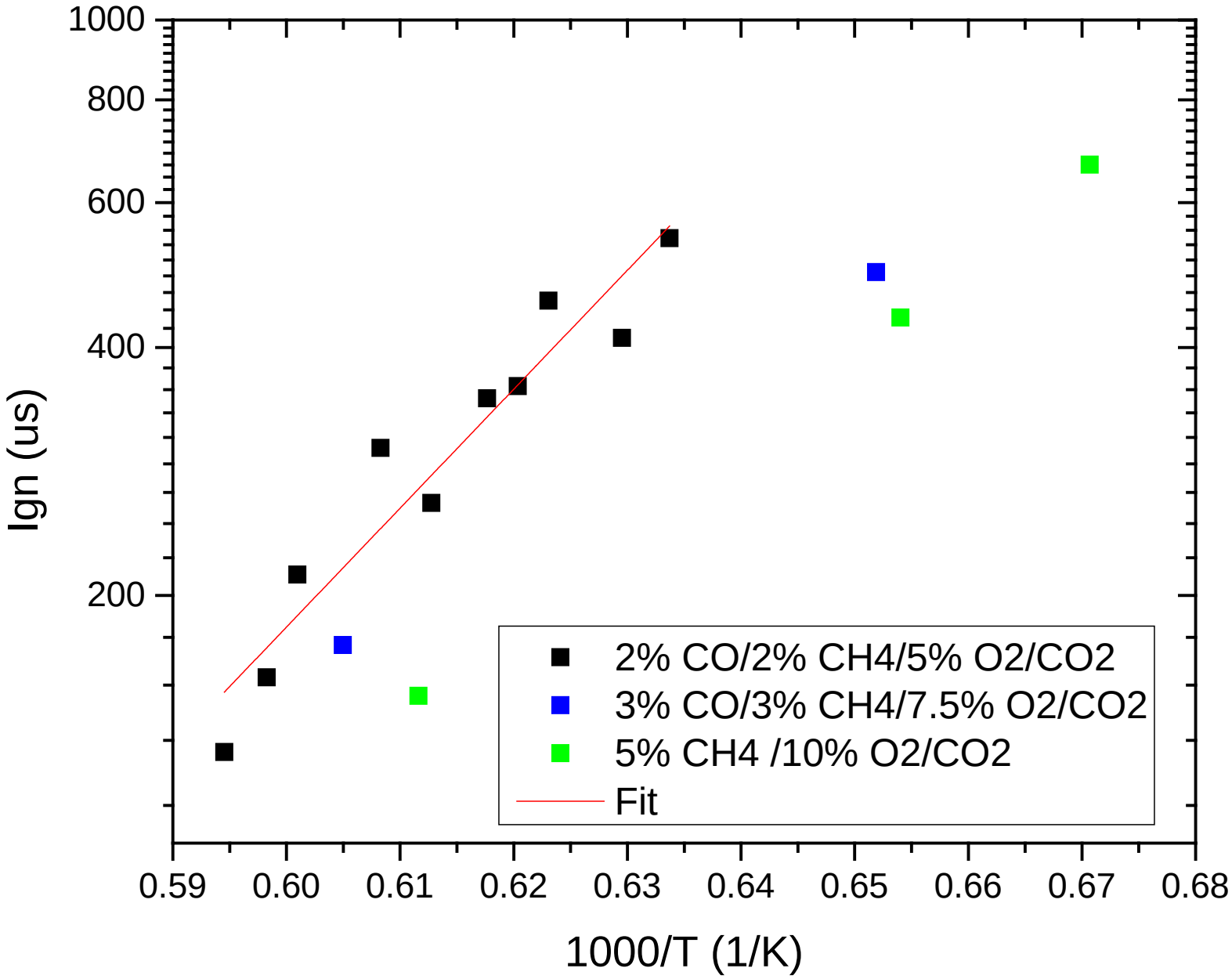
CO2=85%







2%CH_4/2%CO/5%O_2/85%CO_2 12 atm

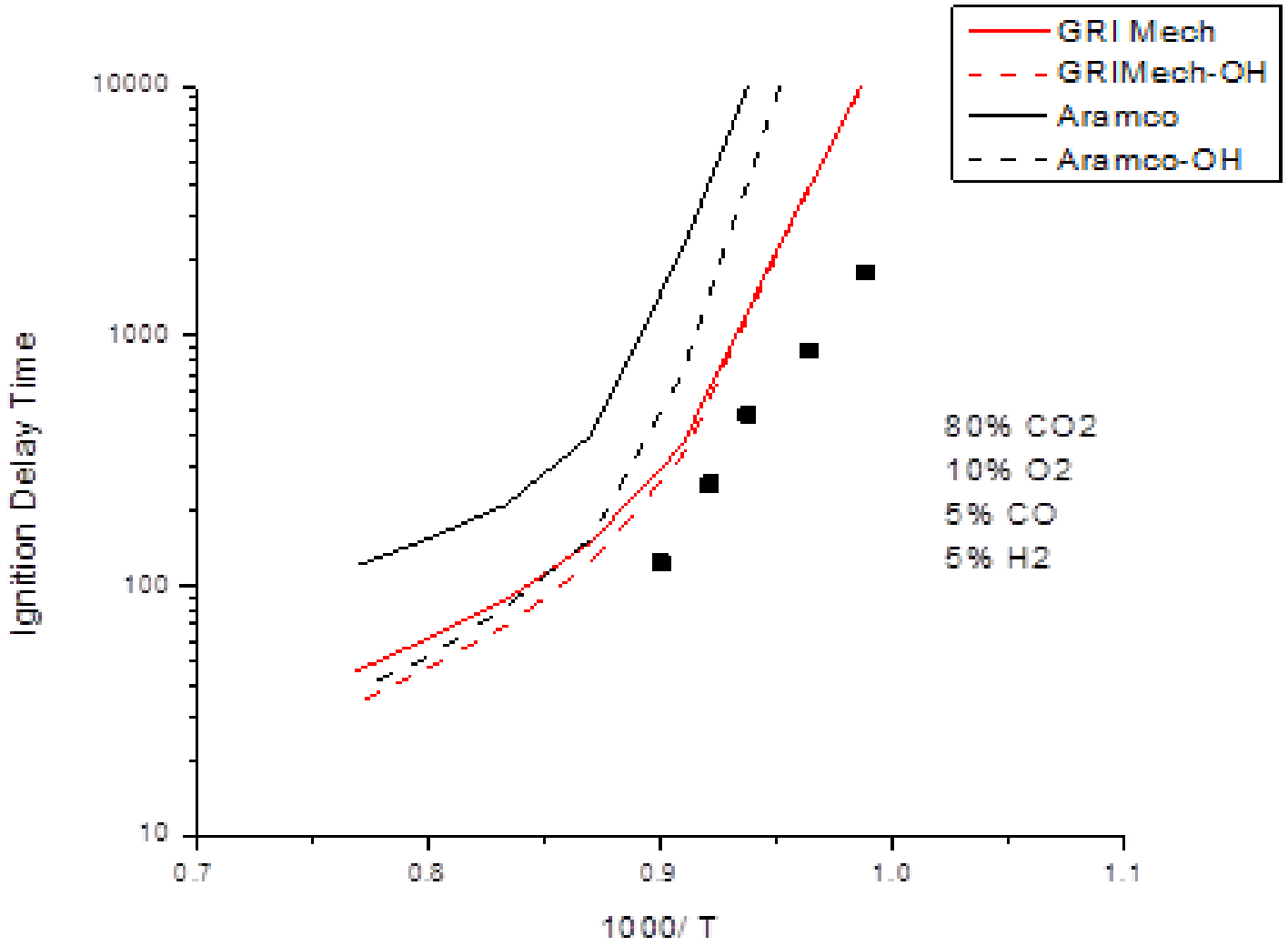


Syngas/O2/CO2 Ignition Delay Times

Syngas fuel is a mixture of CO and H_2

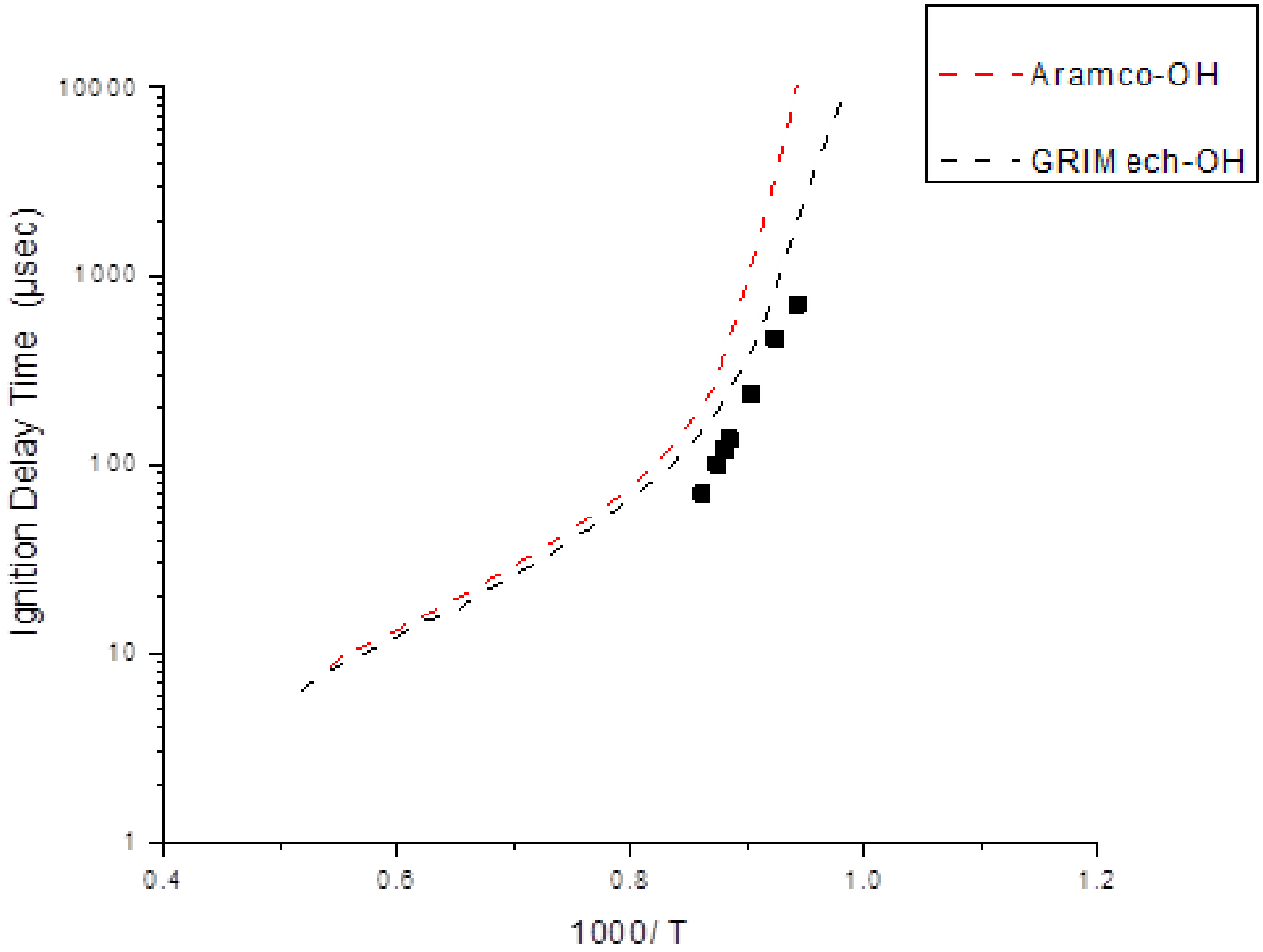
Syngas /O2/CO2 Ignition Delay Time Measurements

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

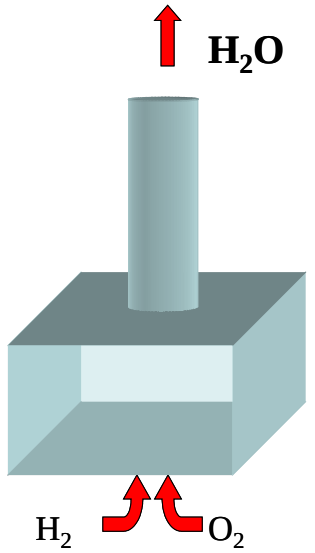
Simplest fuel system: Hydrogen/Oxygen $\mathbf{2H_2 + O_2 \rightarrow 2H_2O}$

- requires 19 reactions and 8 species to fully describe chemistry (not including NOx):

Kinetic mechanism

$H_2 + O_2 \rightarrow H + HO_2$
$H + O_2 \rightarrow OH + O$
$OH + H_2 \rightarrow H_2O + H$
$O + H_2 \rightarrow OH + H$
$OH + OH \rightarrow O + H_2O$
$O + HO_2 \rightarrow O_2 + OH$
$H + HO_2 \rightarrow OH + OH$
$OH + HO_2 \rightarrow H_2O + O_2$
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$
$H_2O_2 + OH \rightarrow H_2O + HO_2$

$H_2O_2 + H \rightarrow H_2O + OH$
$H_2O_2 + H \rightarrow HO_2 + H_2$
$H_2O_2 + O \rightarrow HO_2 + OH$
$H_2O_2 + M \rightarrow OH + OH + M$
$O + O + M \rightarrow O_2 + M$
$H + OH + M \rightarrow H_2O + M$
$H_2 + M \rightarrow H + H + M$
$H + O_2 + M \rightarrow HO_2 + M$
$H + O + M \rightarrow OH + M$



Larger fuels:

	# Reactions	# Species
Natural gas in air (includes NO_x)	325	53

- A rate coefficient must be prescribed for each chemical reaction
- k (T) = A x exp(-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 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.

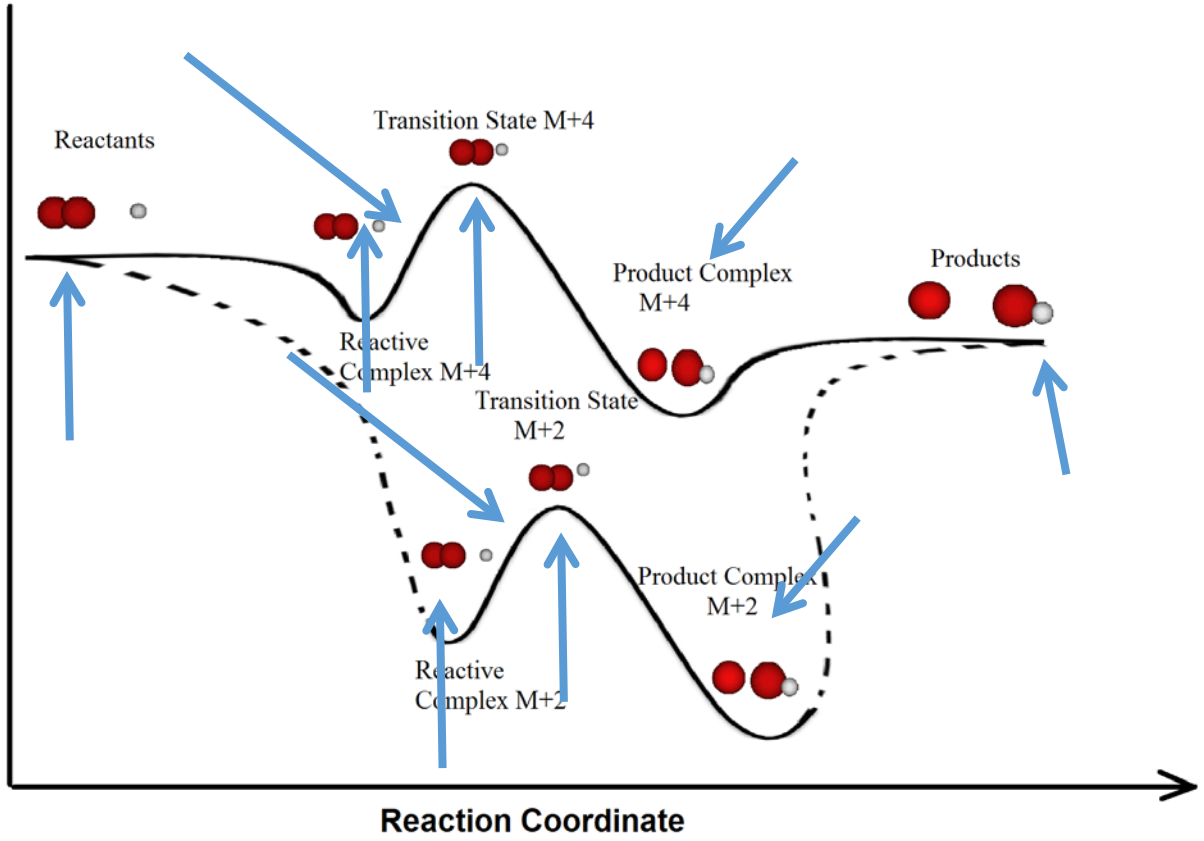
No.	Reaction	A	n	Ea	Ref.
1	$H+O_2=O+OH$	3.55E+15	−0.406	1.66E+04	[7]
2[c]	$CO+OH=CO_2+H$	2.20E+05	1.89	−1.16E+03	[7], A*1.24
3	$HCO+M=H+CO+M$	4.75E+11	0.7	1.49E+04	[6][a]
4	$H+OH+M=H_2O+M$	4.50E+22	−2	0.00E+00	[19][a]
5	C_3H_5-a$+H(+M)=C_3H_6(+M)$	2.00E+14	0	0.00E+00	[8]
	Low pressure limit:	1.33E+60	−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.

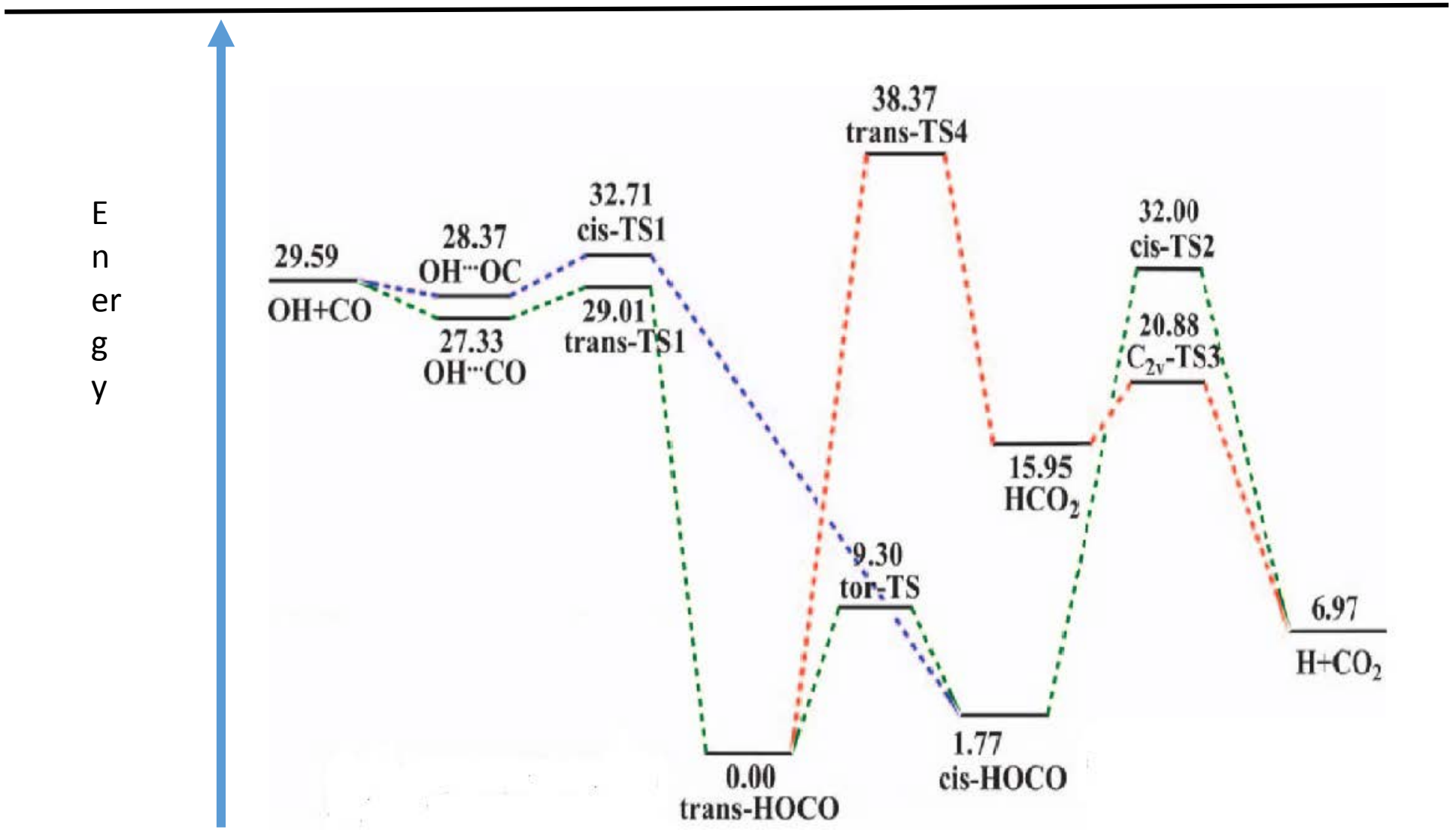
Naik, C. V.; Puduppakkam, K. V.; Meeks, E. *J Eng Gas Turbines Power* 2012, 134, 021504.

Gas-Phase Combustion Reaction $H+O_2 \rightarrow O+OH$

- Five distinct steps along Reaction (
  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 corresponding to two multiplicitie
- QST3 method will be used to locat
- IRC method will be used to connec



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

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 (CO_2 may be involved in TS structure)
- Products and TS may be stabilized by CO_2 to a different degree (thus, changing $\Delta H^{\neq}$)

Task 4 Sample Results: Quantum Mechanical Calculations

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

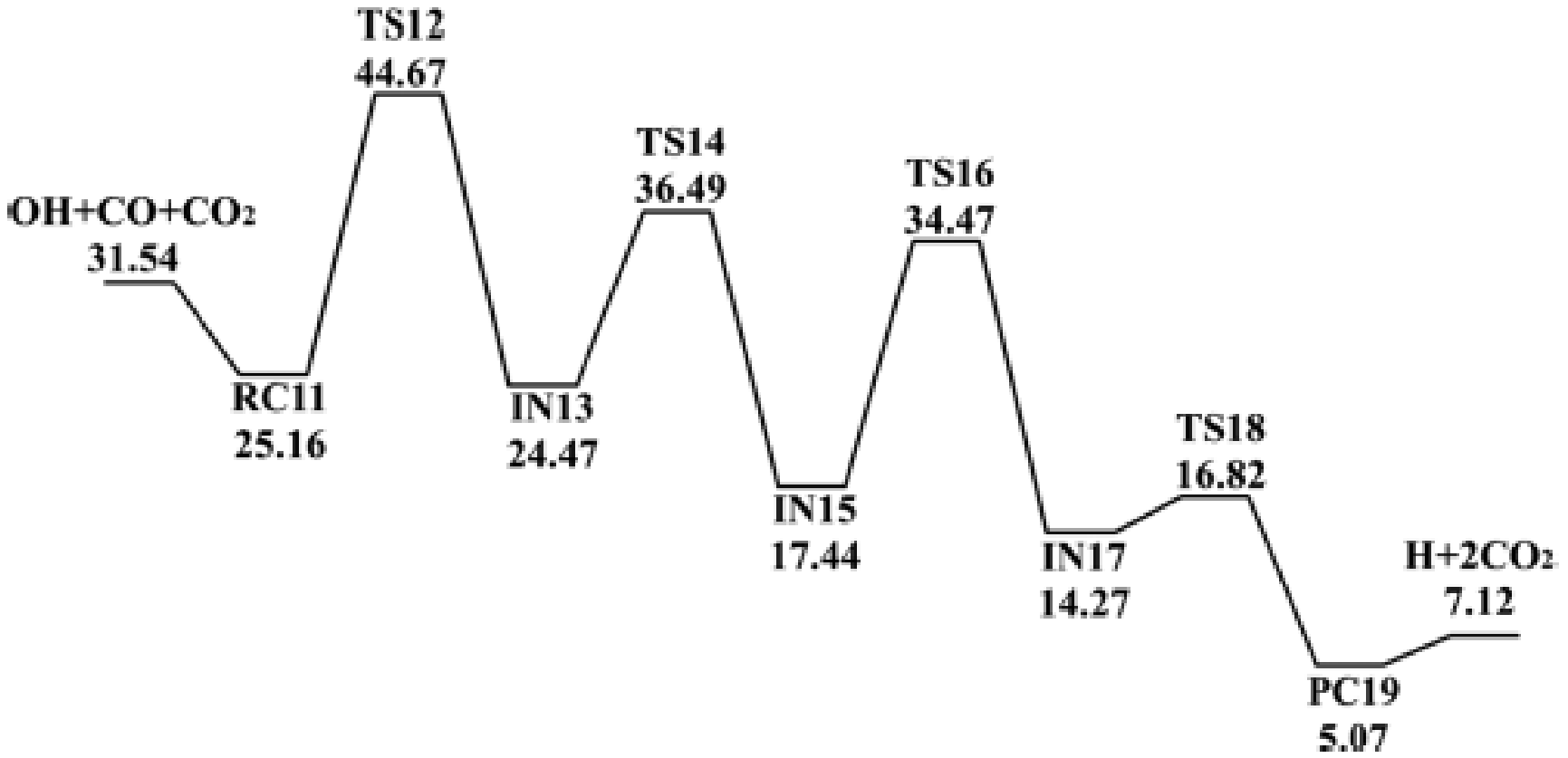
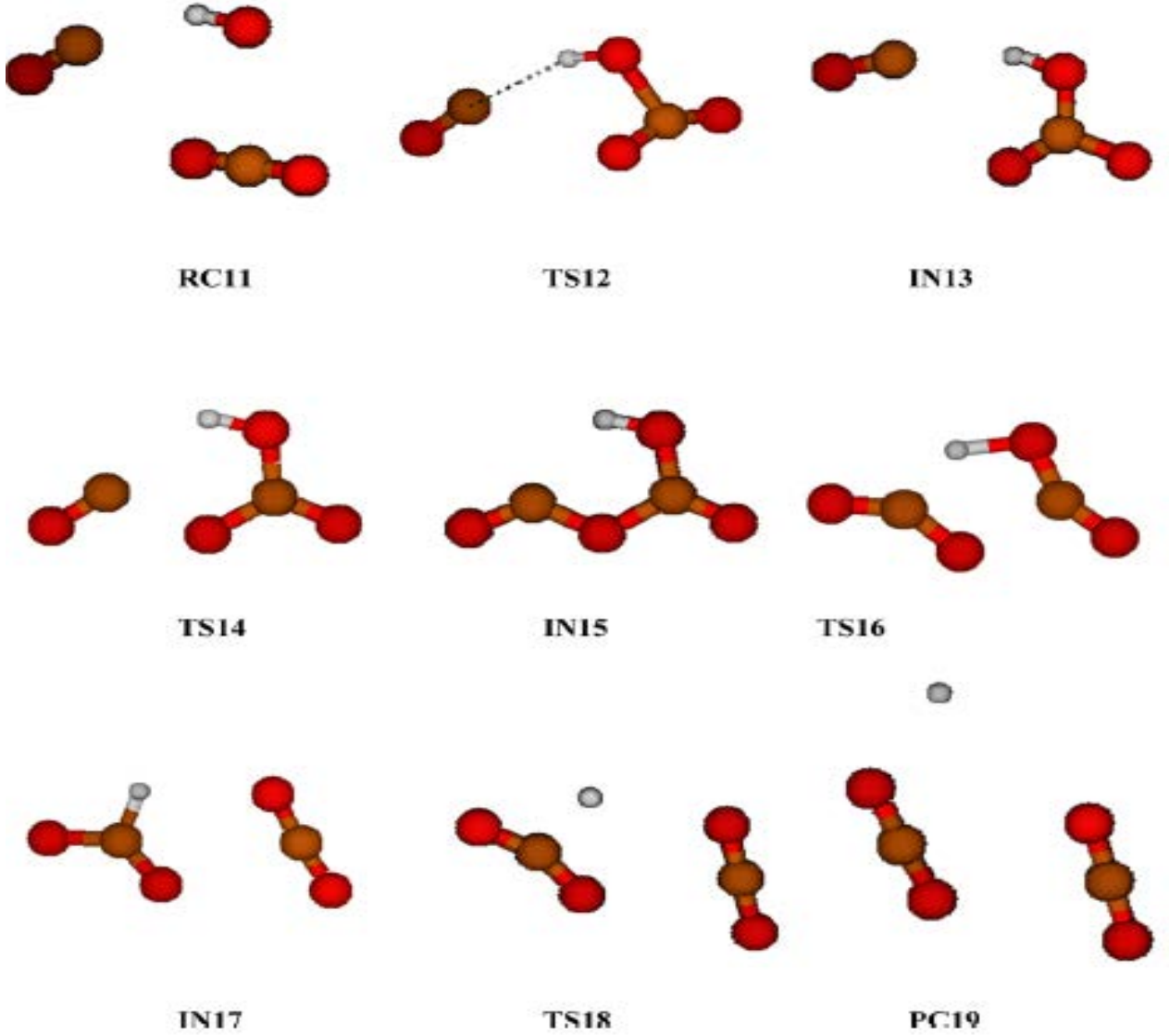


Figure 2. Relative energies (kcal/mol) of the reaction pathway shown on Scheme 1, with one covalently bound CO_2 molecule (*trans*-HOCO + CO_2 system is chosen as the reference point).

Elementary Reaction $CO+OH \rightarrow CO_2+H$ (results with covalent CO_2 addition)



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

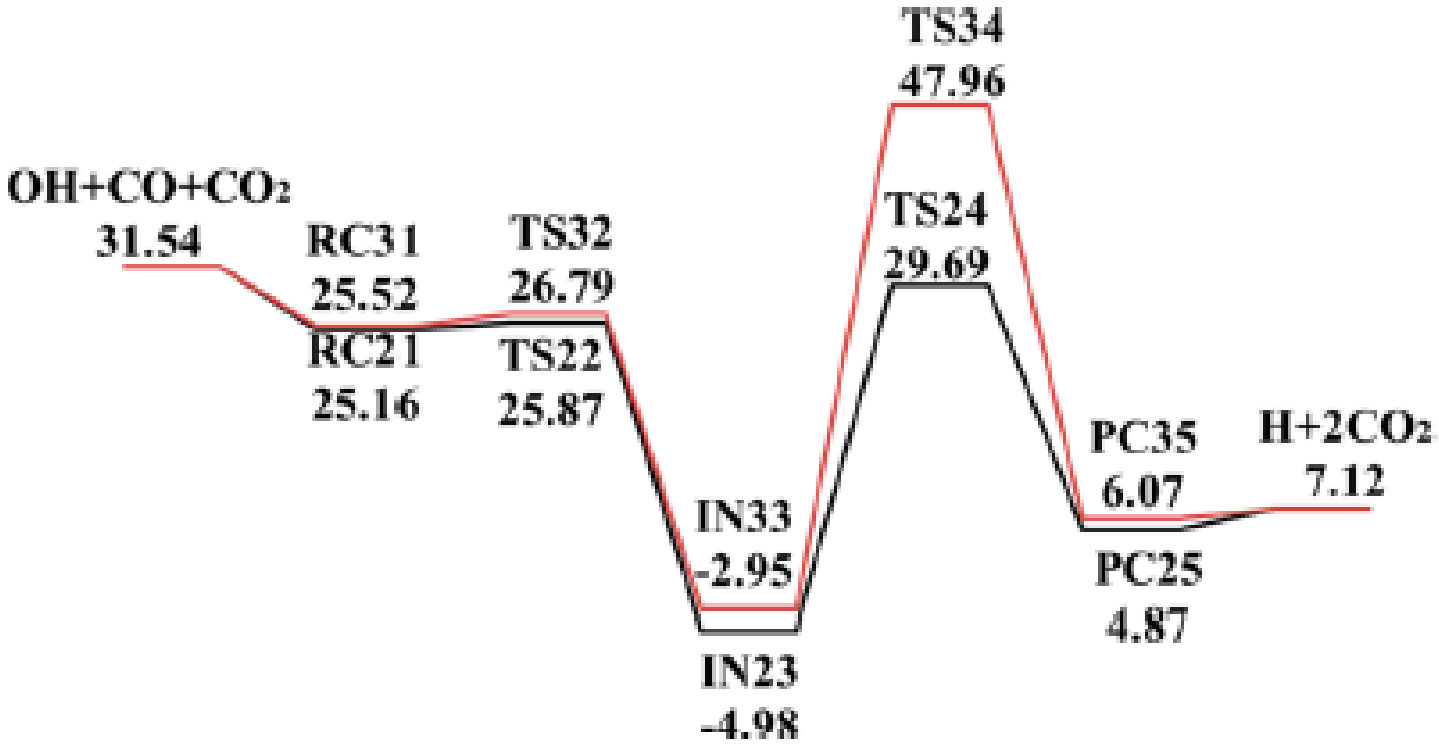
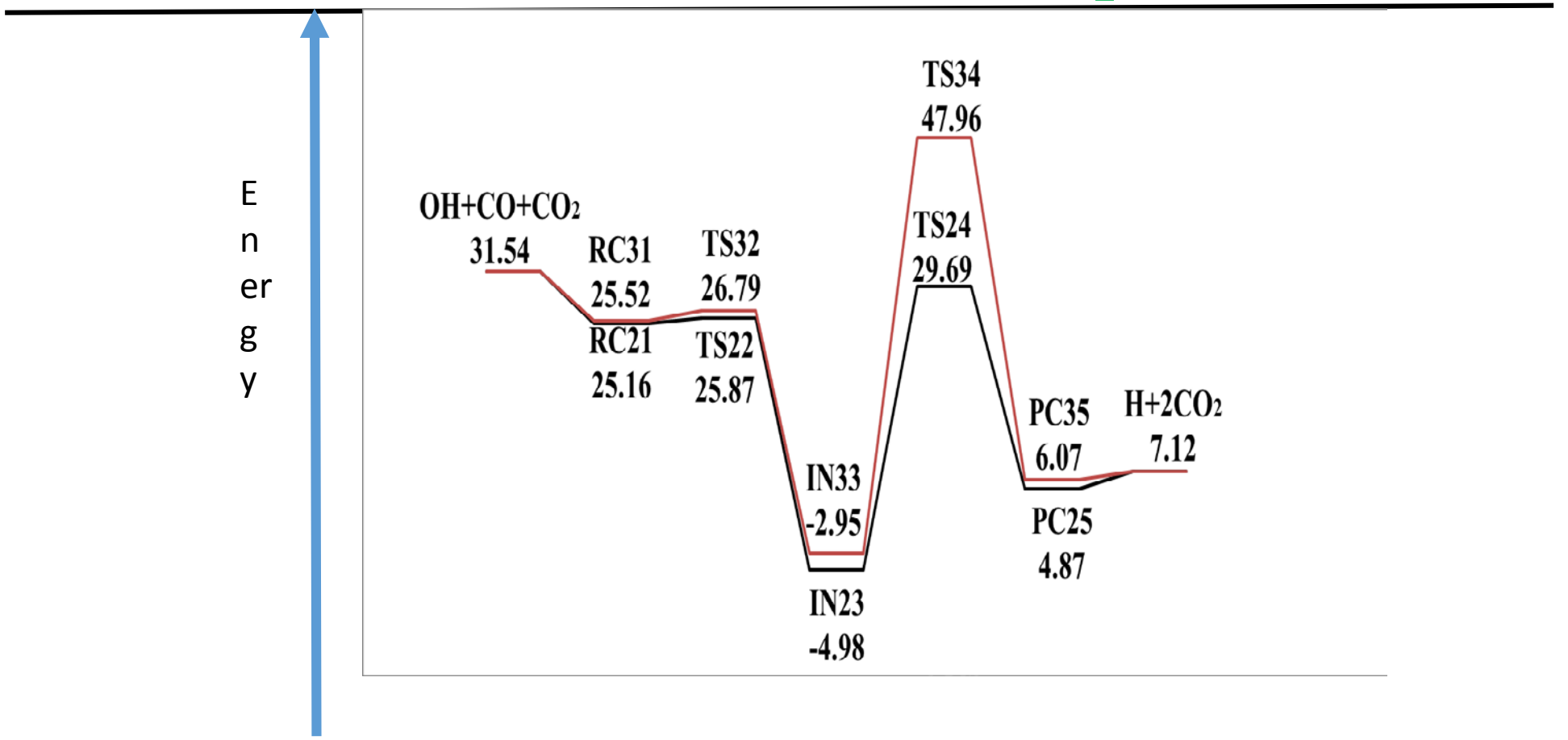


Figure 3. Relative energies (kcal/mol) of two of the reaction pathways shown shown on Scheme 2 (in black) and Scheme 3 (in red) with spectator CO_2 molecule (the *trans*-HOCO + CO_2 system is chosen as the reference point).

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



- Pathways shown for CO2 autocatalytic effect published in J. Phys Chem A- Masunov & Vasu (2016)- above work
- CO2 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 $H_2CO + HO_2 \rightarrow HCO + H_2O_2$

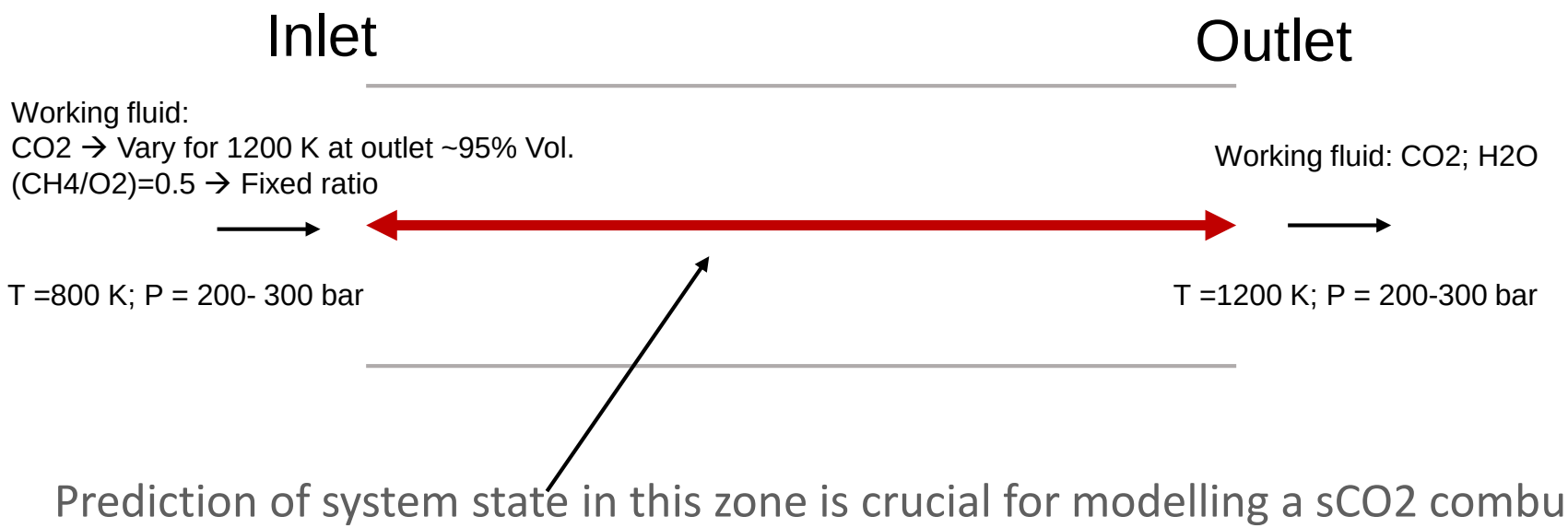
Task 5: CFD development and implementation in OpenFOAM

- Real Gas Equations of State for sCO2
- Thermal properties for sCO_2 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:



Prediction of system state in this zone is crucial for modelling a sCO2 combustor

Introduction to Equation of States

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

Ref: Joes O. Valderrama (2003)

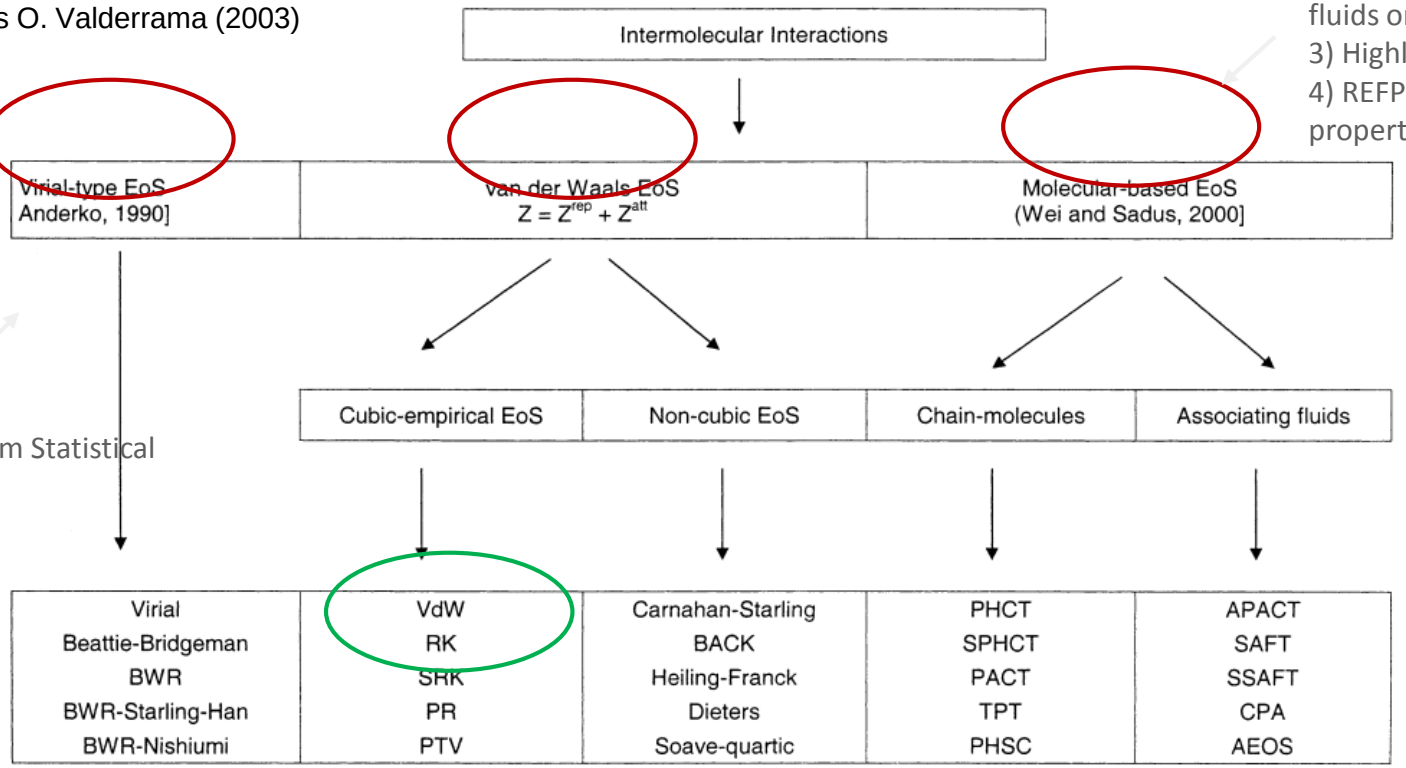


Figure 1. Classification of various type of equations of state, with a selection of equations for each group. In this classification, van der Waals EoS are those cubic and non-cubic equations that consider the compressibility factor as $Z = Z^{rep} + Z^{att}$.

Developed from Statistical Mechanics;
Very complex.

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:

H_2O; H_2; O_2; CO; CO_2; CH_3OH; C_3H_4; CH_4; C_2H_6; C_3H_8; C_3H_6

→ REFPROP is reported to be very time expensive for sCO_2 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,

$$a = \frac{0.45724\ R^2\ T^2{}_c}{P_c}$$

$$b = \frac{0.07780\ R\ Tc}{P_c}$$

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, $Z = \frac{PV}{RT}$ $\qquad Pr = \frac{P}{Pc}$

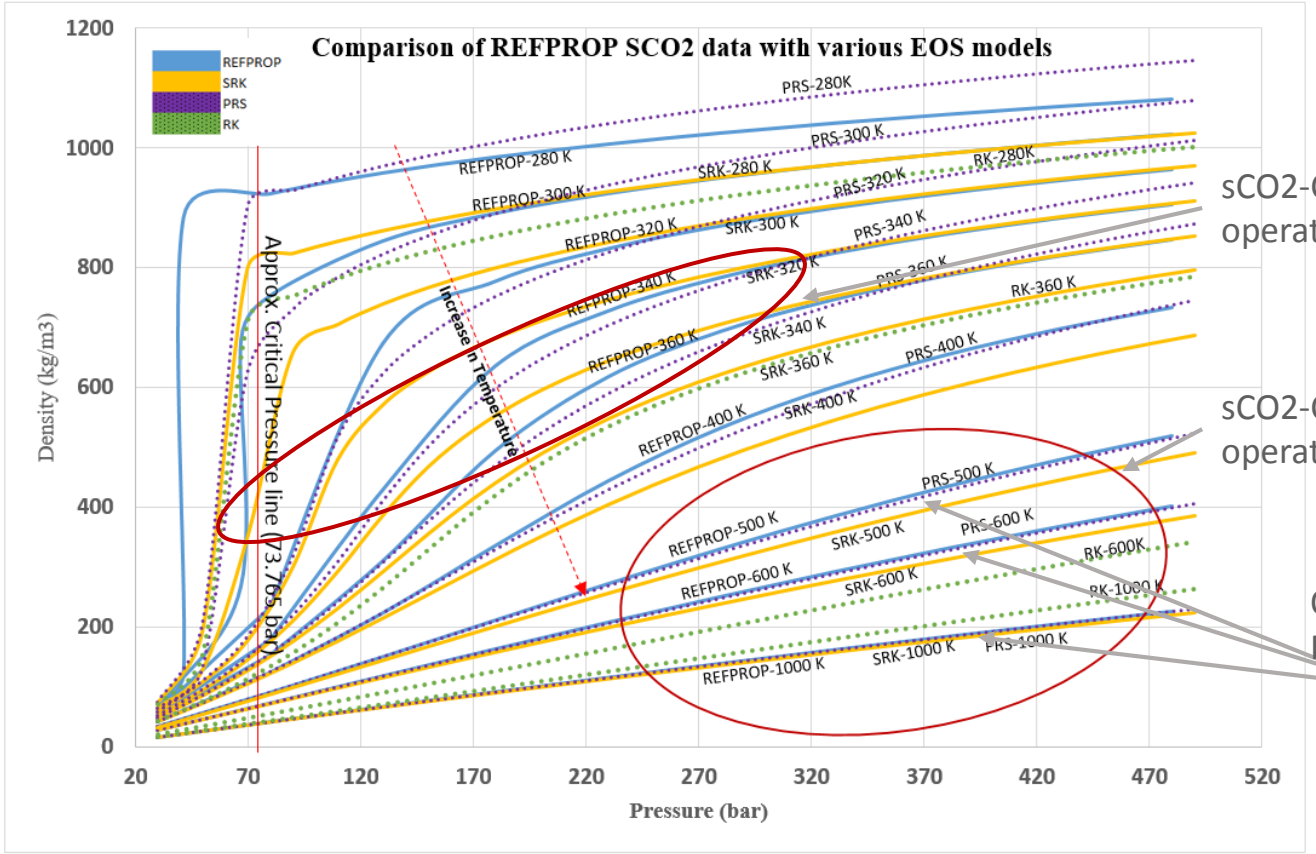
$$A = \frac{0.45724\ \alpha\ Pr}{Tr^2} \qquad Tr = \frac{T}{Tc}$$

$$B = \frac{0.07780 Pr}{Tr} \qquad \omega - Ancentric\ factor$$

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

EOS suitable for sCO2 Combustor Simulations

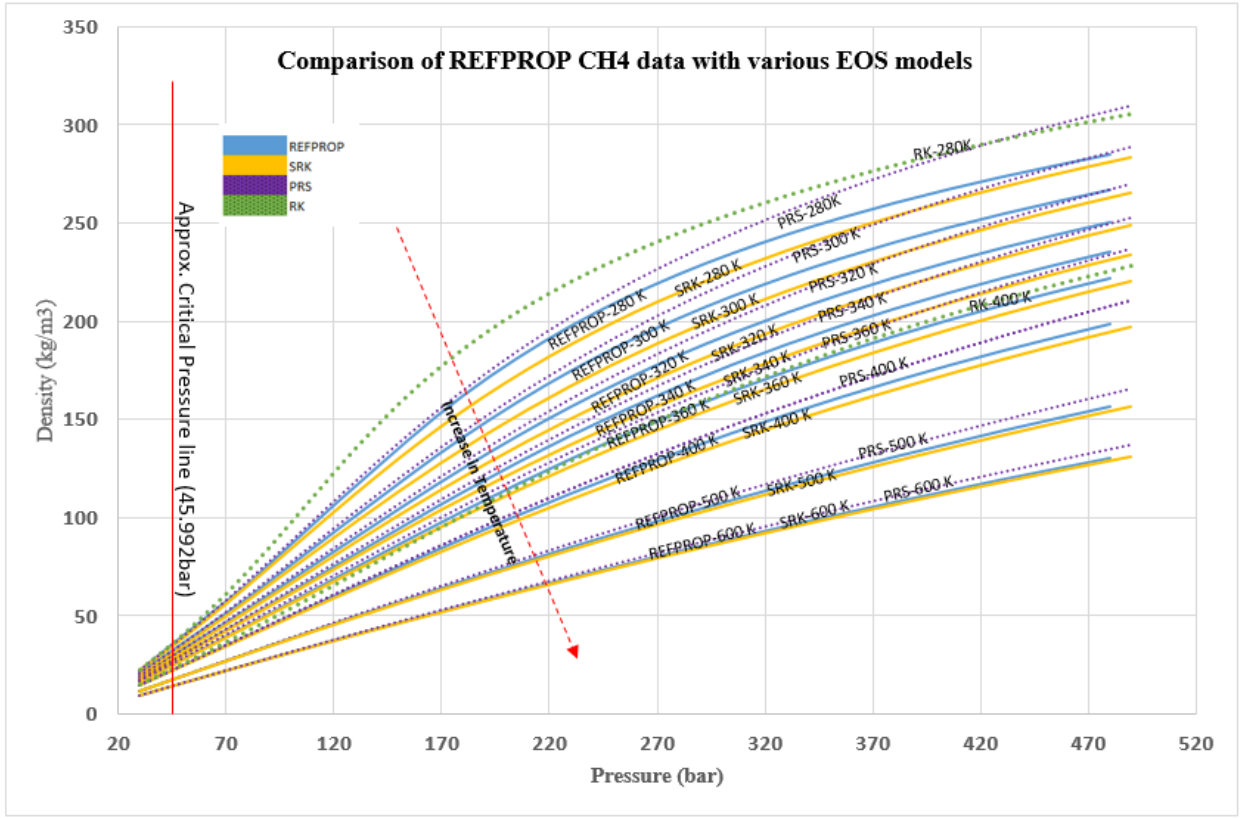
- RK (Redlick-Kwong), SRK (Soave-Redlick-Kwong) and PR (Peng-Robinson) models are compared against the REFPORP for sCO2



Note: REFPROP data for CO2 is available 1100 K only.

EOS suitable for sCO2 Combustor Simulations

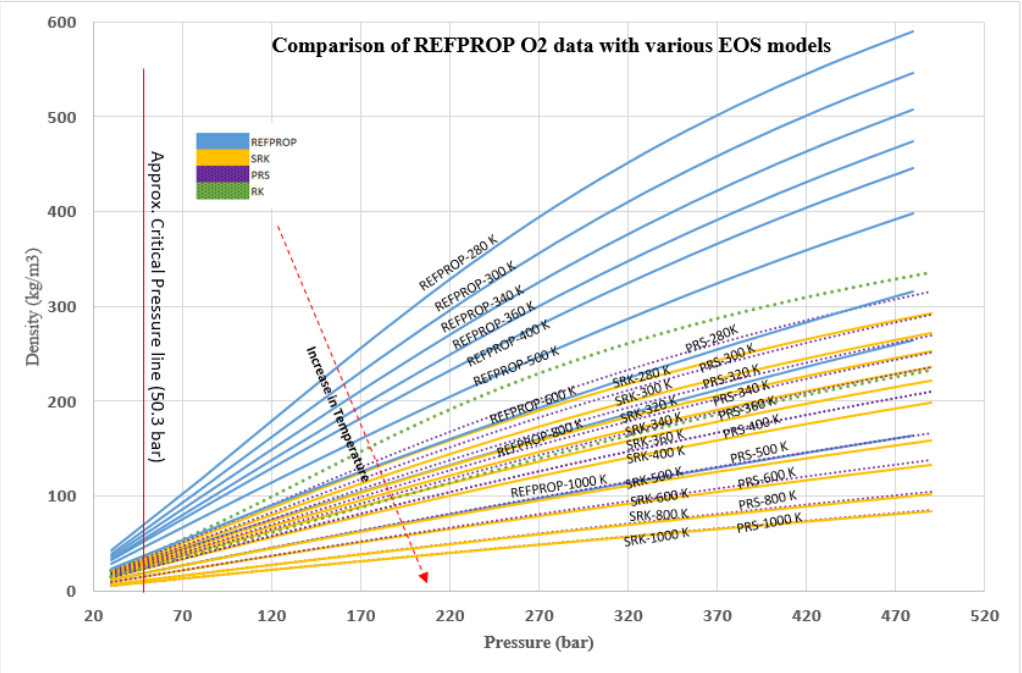
- RK, SRK and PR models are compared against the REFPORP for sCH4



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

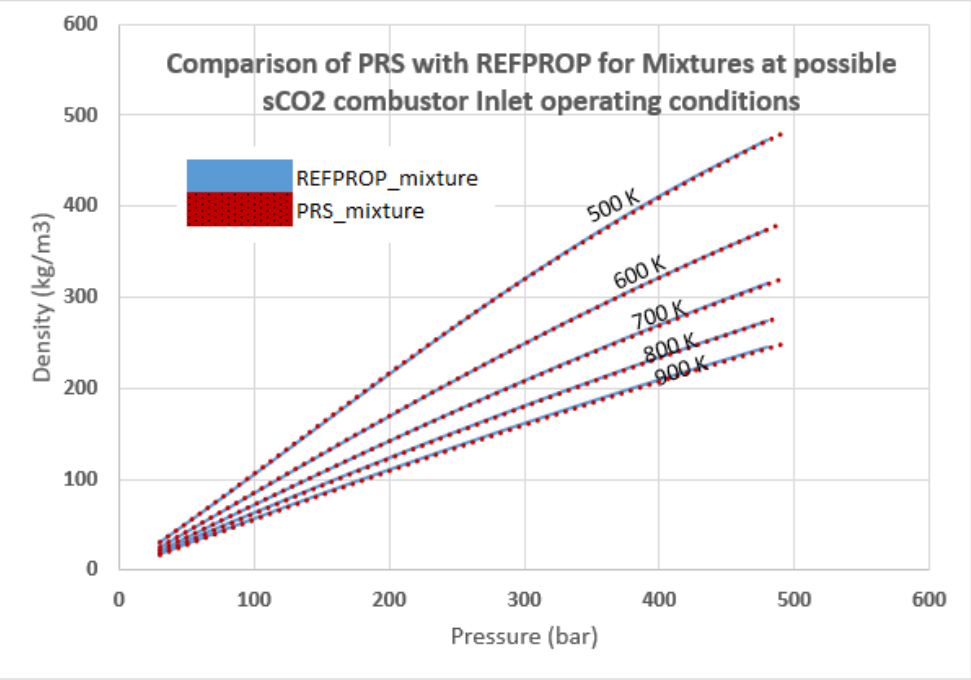


→None of the models are predicting the sO2 behavior. Possible reasons for this deviation is under investigation.

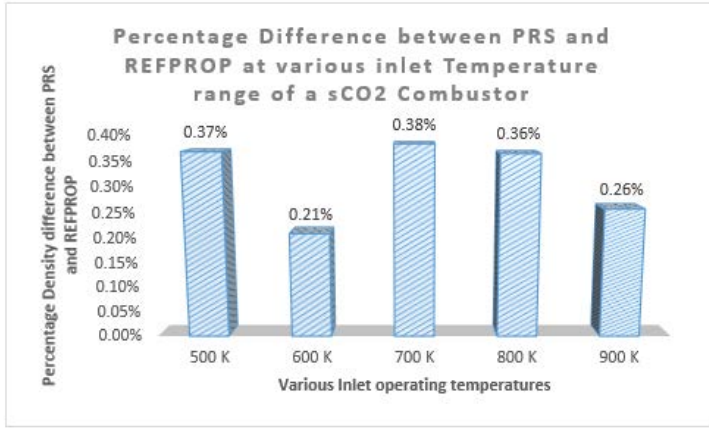
→'O2' is second largest concentration in the sCO2 combustor.

EOS suitable for sCO2 Combustor Simulations

- PR models are compared against the REFPORP mixtures properties at the Inlet of sCO2 Combustor



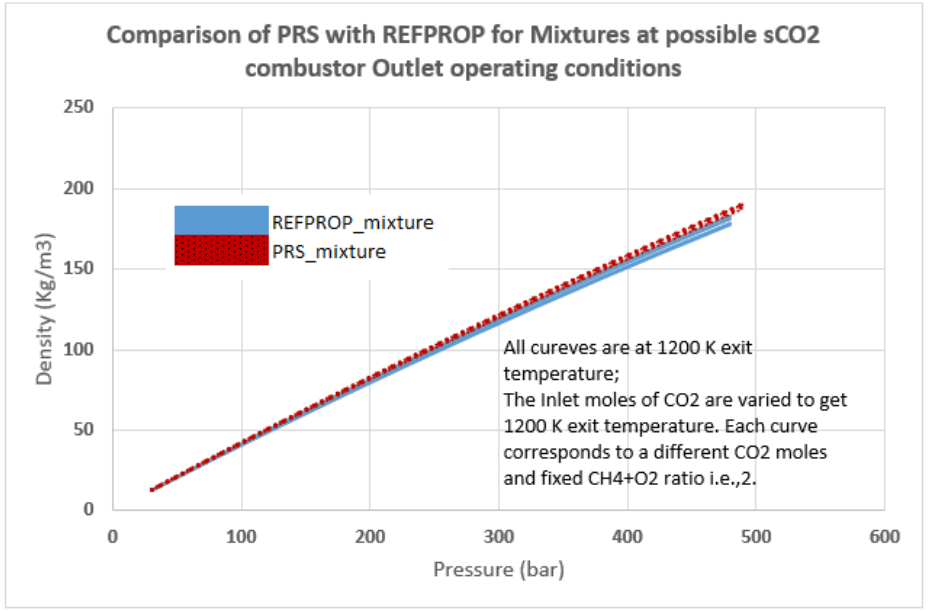
Inlet conditions		
Ratio of CO2/(CH4+O2)	Inlet Temperature	Exit Temperature
6.50	500 K	1200 K
7.42	600 K	1200 K
9.15	700 K	1200 K
11.48	800 K	1200 K
15.02	900 K	1200 K

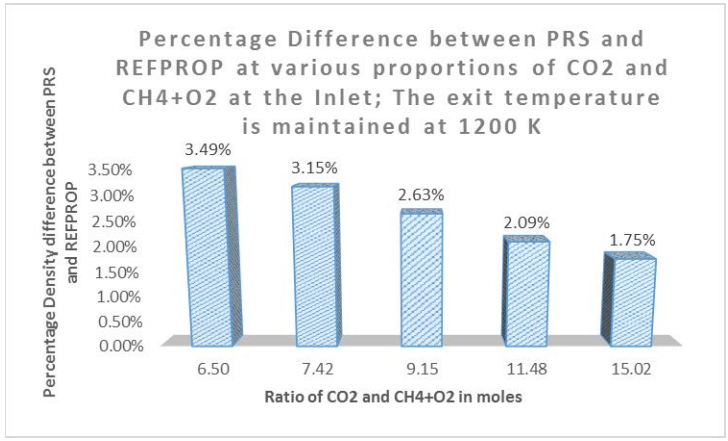


Note: The percentage differences are averaged over pressures between 30-480 bar at every temperature.

EOS suitable for sCO2 Combustor Simulations

- PR models are compared against the REFPORP mixtures properties at the Outlet of sCO2 Combustor

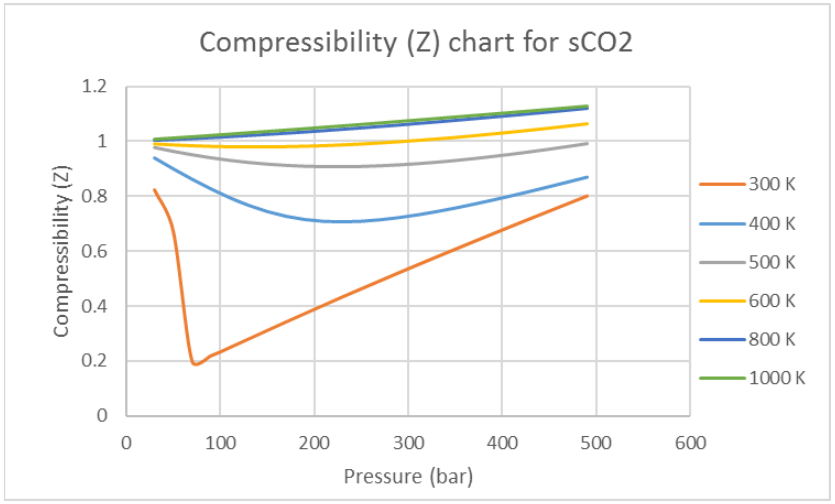


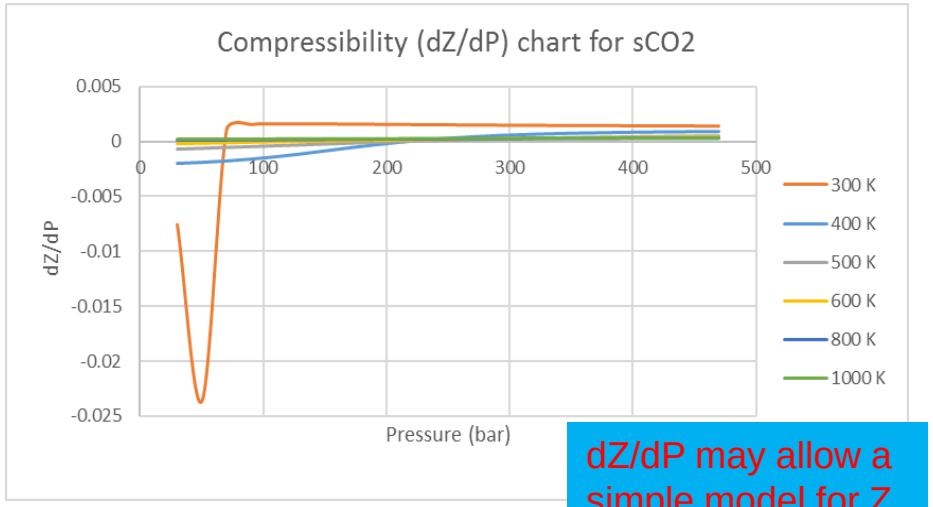


Thermal properties for sCO_2 combustor

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:

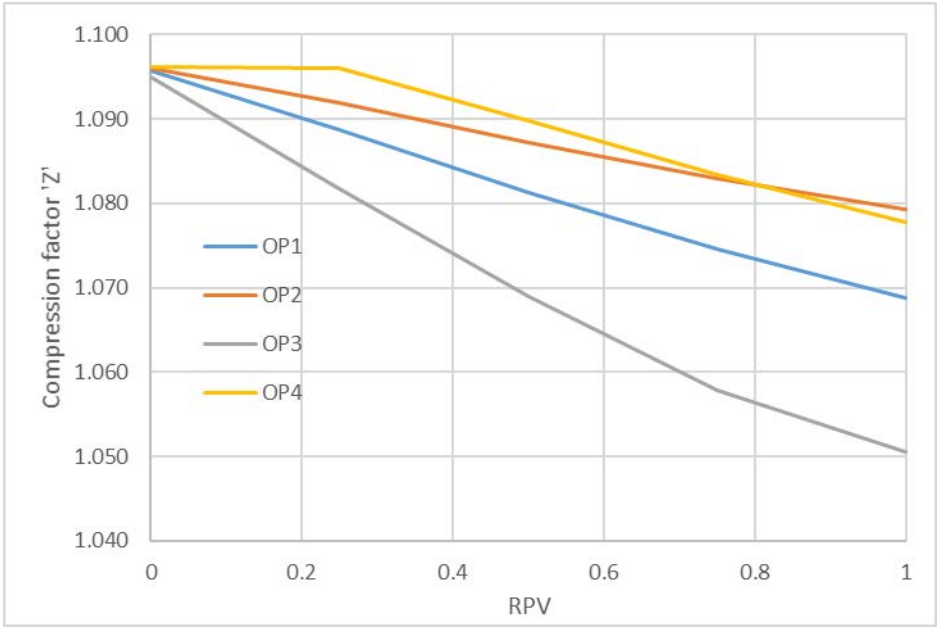
Property	Definition	Ideal Gas Case
Compressibility factor	$Z = f(T, p)$	$Z = 1$
Isothermal compressibility	$\beta_T = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T = \frac{1}{p} - \frac{1}{Z}\left(\frac{\partial Z}{\partial p}\right)_T$	$\beta_T = \frac{1}{p}$
Isobaric compressibility	$\beta_p = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p = \frac{1}{T} + \frac{1}{Z}\left(\frac{\partial Z}{\partial T}\right)_p$	$\beta_p = \frac{1}{T}$

Ref: Nikola D. Baltadjiev (2012, MIT Thesis)

More thermal properties for sCO_2 combustor

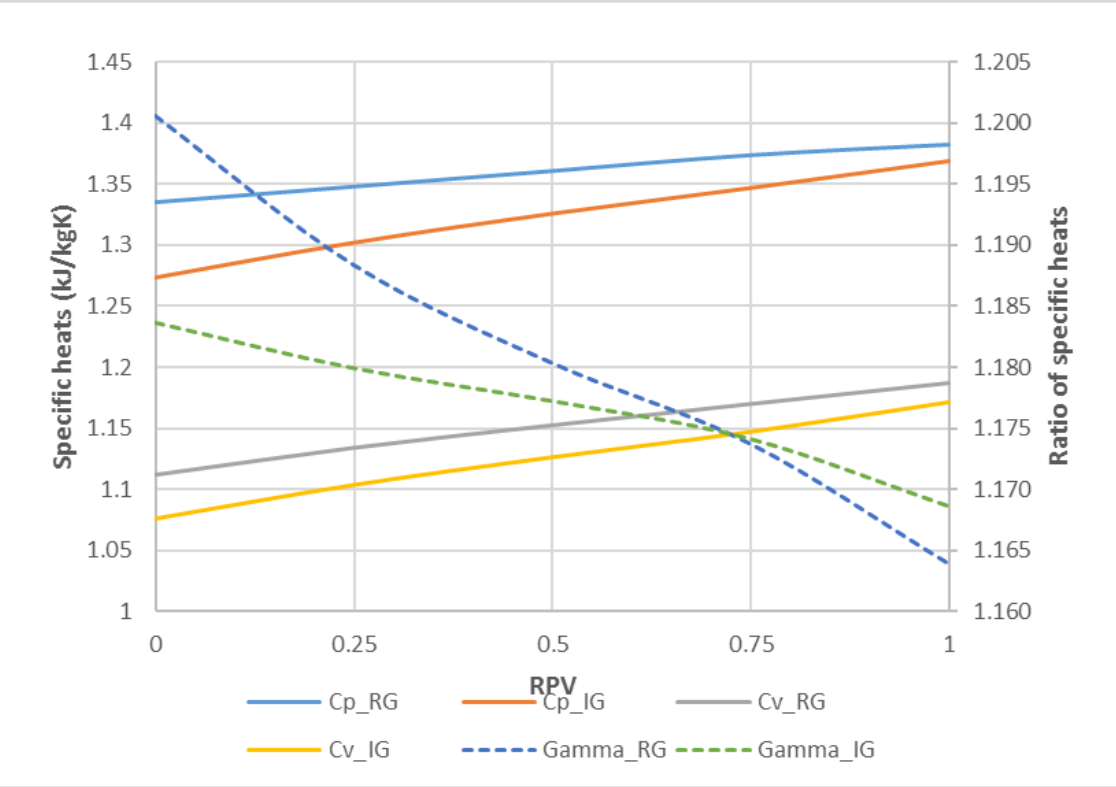
Compressibility factor ‘Z’ under various operating conditions:

Operating Condition	*What it explains?*	*Initial molar mixture and Temperature (K) ($CH_4/O_2/CO_2/T$)*
OP1	Reference Mixture	1/2/24/1000
OP2	Inlet [CO_2] increases	1/2/40/1000
OP3	Inlet [CH_4+O_2] increases	2/4/24/1000
OP4	Inlet temperature decreases	1/2/24/800



More thermal properties for sCO_2 combustor

Specific heats and ratio of specific heats:



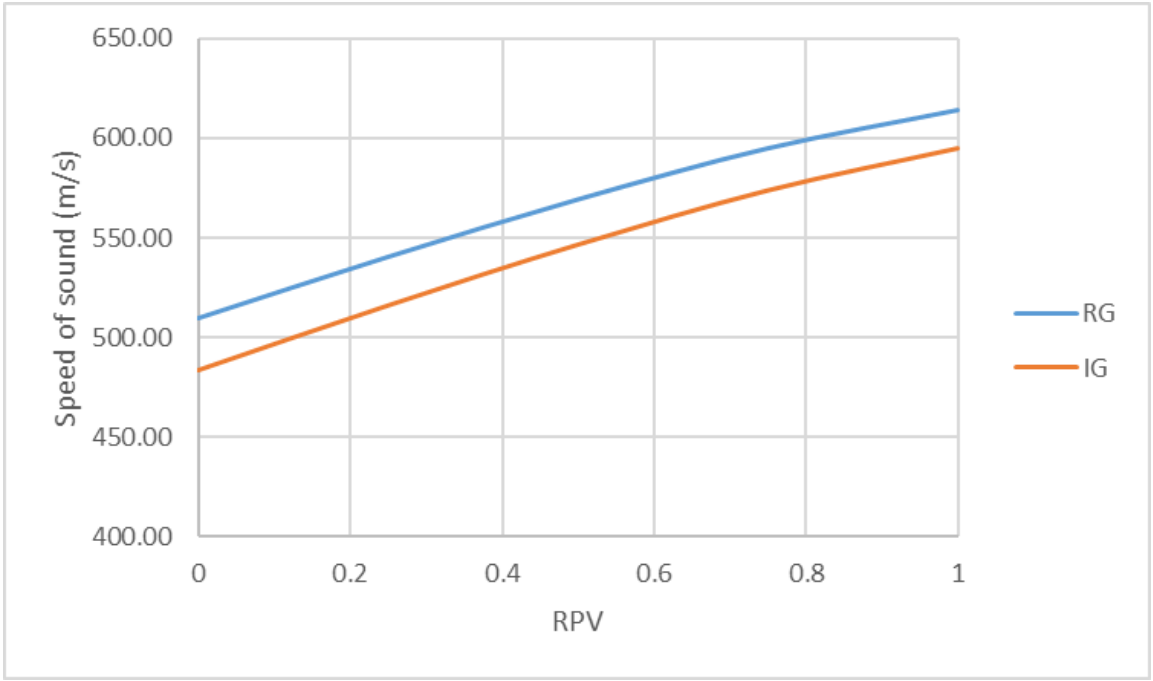
$$\Rightarrow c = \left(\frac{d\left(\frac{E}{\frac{\rho_i}{Z} V}\right)}{dT} \right)_{p \text{ or } v}$$

'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 γ ranges from 1.2-1.164 across the sCO_2 combustor.

More thermal properties for sCO_2 combustor

Speed of Sound:



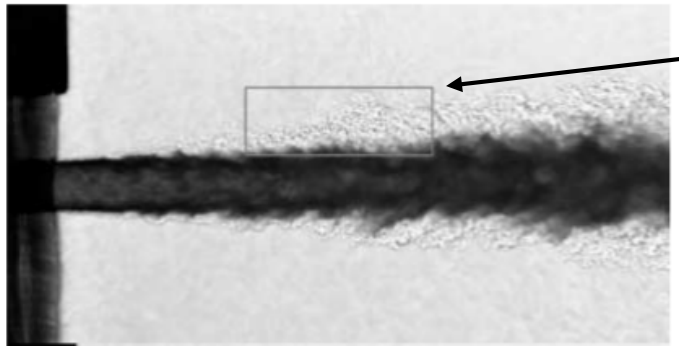
- Repulsive forces also results in increasing speed of sound by a factor $\left(\frac{\gamma}{n_s Z}\right)^{1/2}$.

CFD simulation status

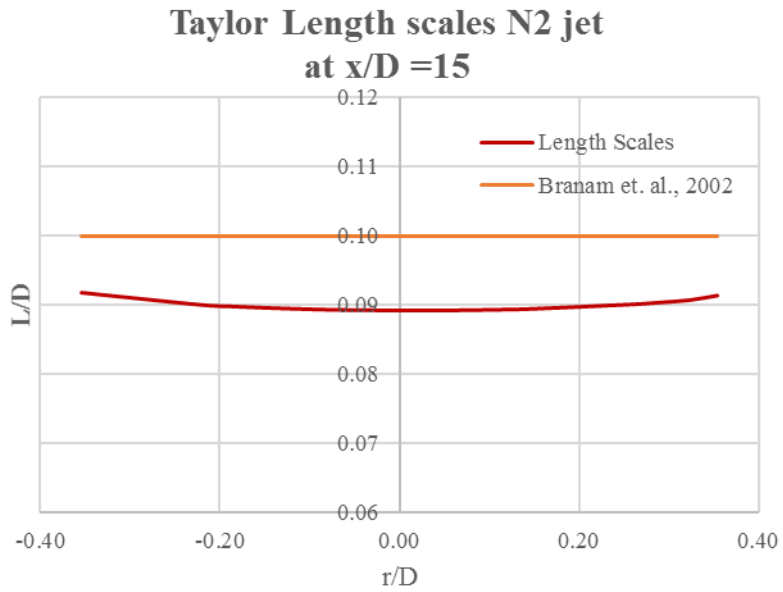
Present CFD simulation status:

Validation of supercritical N2 jet (In progress)

(R. Branam and W. Mayer, 2002)



RANS simulation



- 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?