Autoignition of CH_4 and H_2/CO in CO_2 and Ar Diluent at High Pressure Conditions

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Near Zero-Carbon Combustion Technology
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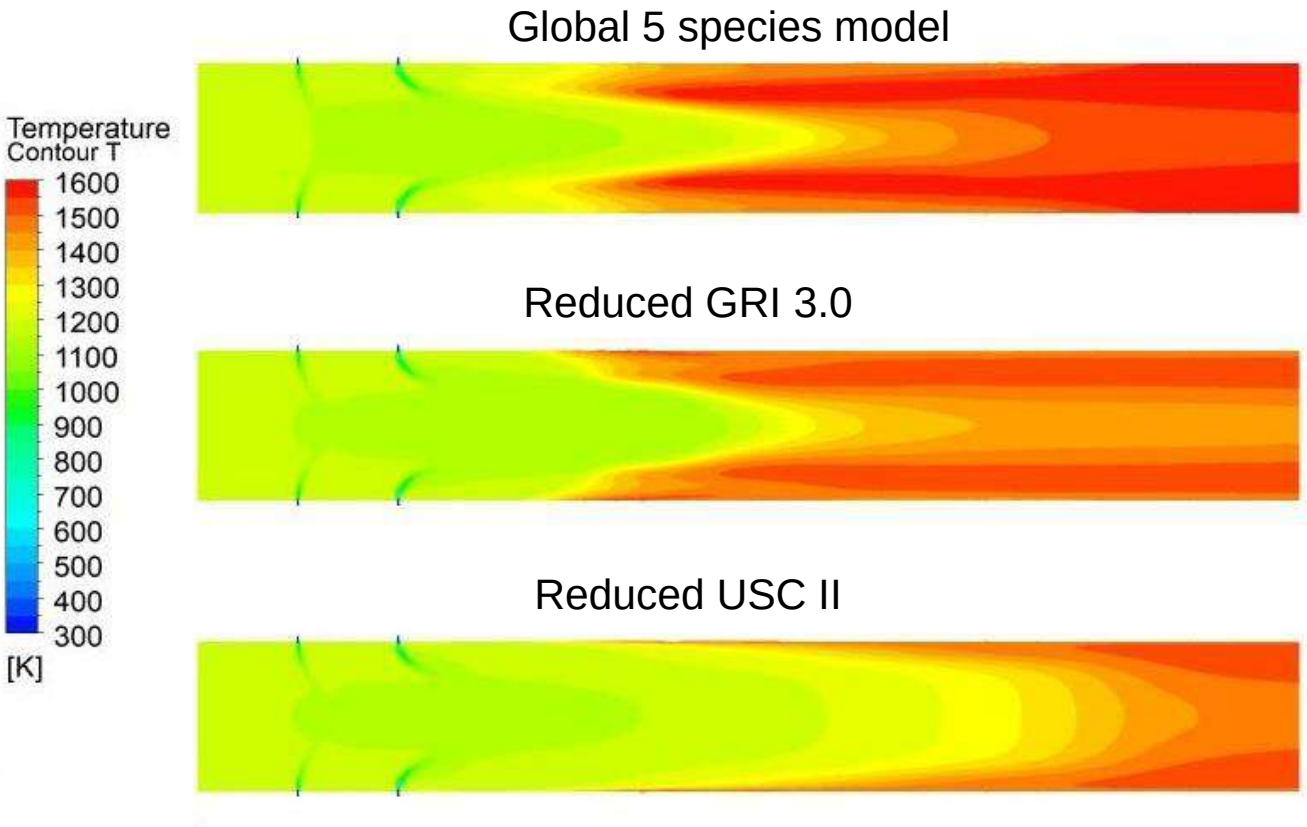
Why Should We Care about Combustion Kinetics?

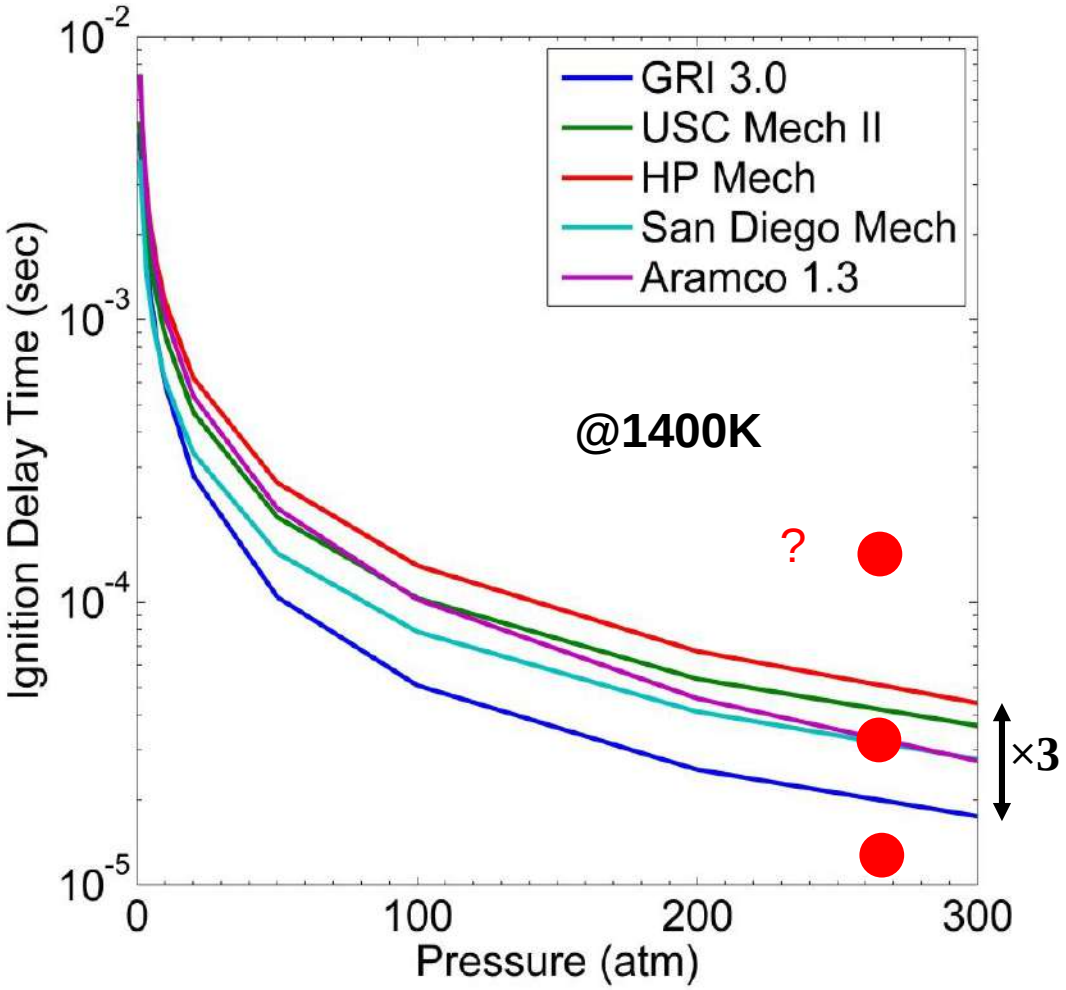
$CH_4/O_2/CO_2$ JICF reactor at 100 bar (FLUENT simulation)



Must have validated kinetic model for combustor design

Kinetic Challenges for sCO_2-fuel-O_2 Mixtures

Deviation increases with pressure



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

We simply need experimental evidence in regime of interest

Georgia Tech 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

Diaphragm section (single or double)

Eight optical windows

Contoured valve for vacuum

Single piece test section (2.1 m)

How Can We do Better?

How to measure and define τ_{ign} matters!

Large C_p of CO_2

↓

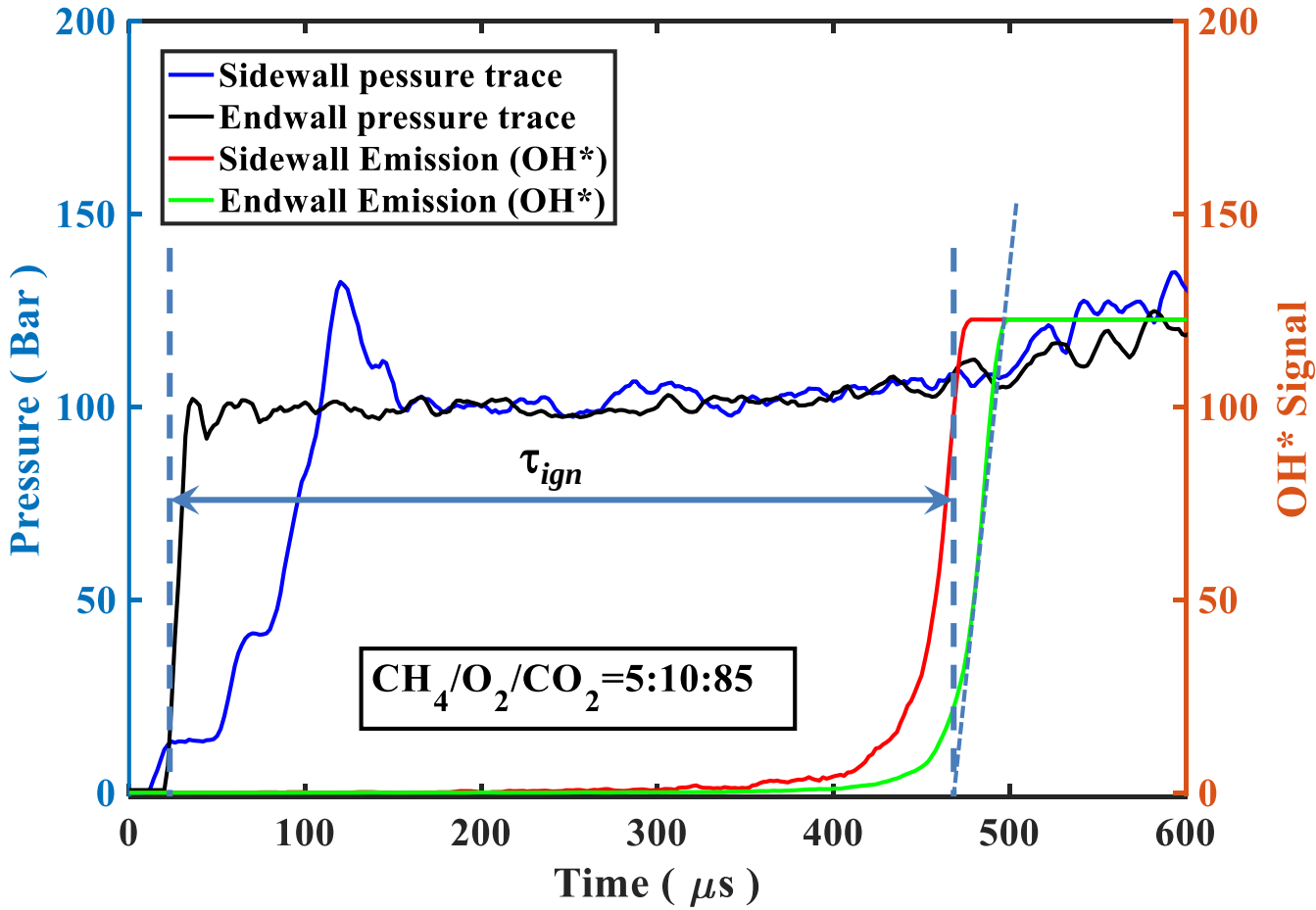
Strong shock + CO_2

↓

Large and fast growing BL

↓

Large ID helps Challenges on data interpretation



Simultaneous sidewall and endwall traces and emissions

Q: sidewall ignition event always faster than endwall

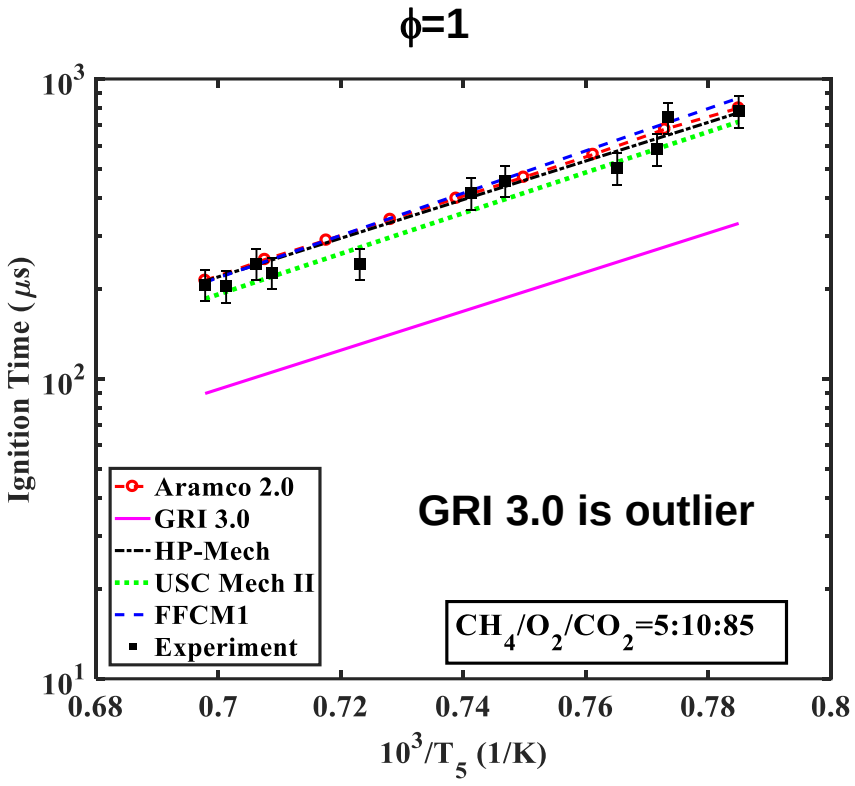
CH_4 Autoignition

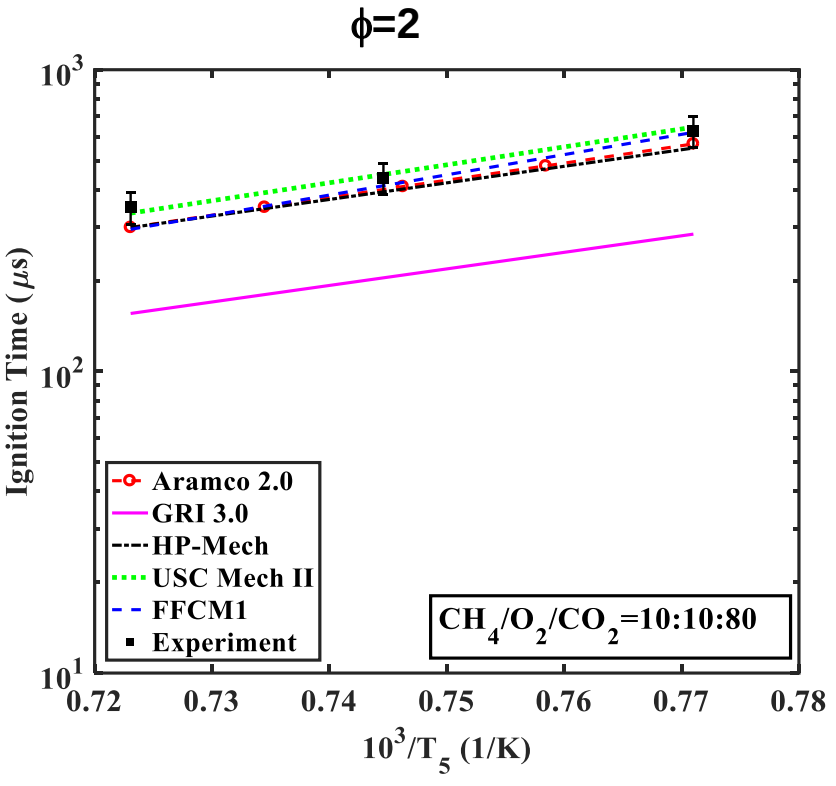
(only GT results because of time limitation)

M. Karimi, B. Ochs, Z. Liu, D. Ranjan, W. Sun, “Measurement of methane autoignition delays in carbon dioxide and argon diluents at high pressure conditions” 2019 ***Combustion and Flame***, 204, 304-319

Autoignition Delays at sCO_2 condition

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

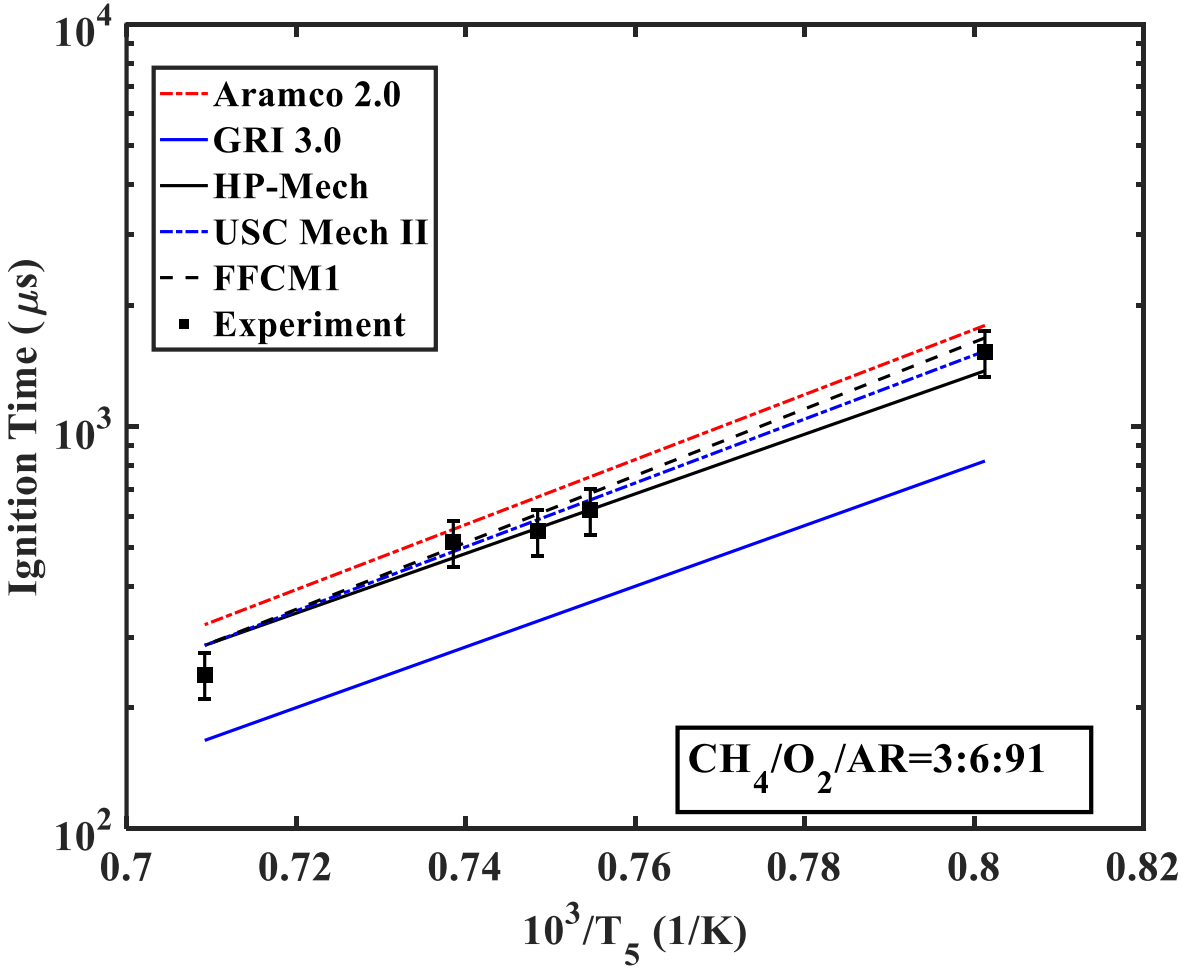




Simulation results from Aramco 2.0, USC Mech II and HP-Mech are close to each other, however GRI 3.0 predicts a significantly shorter autoignition delay, having approximately a **factor of 3 difference**

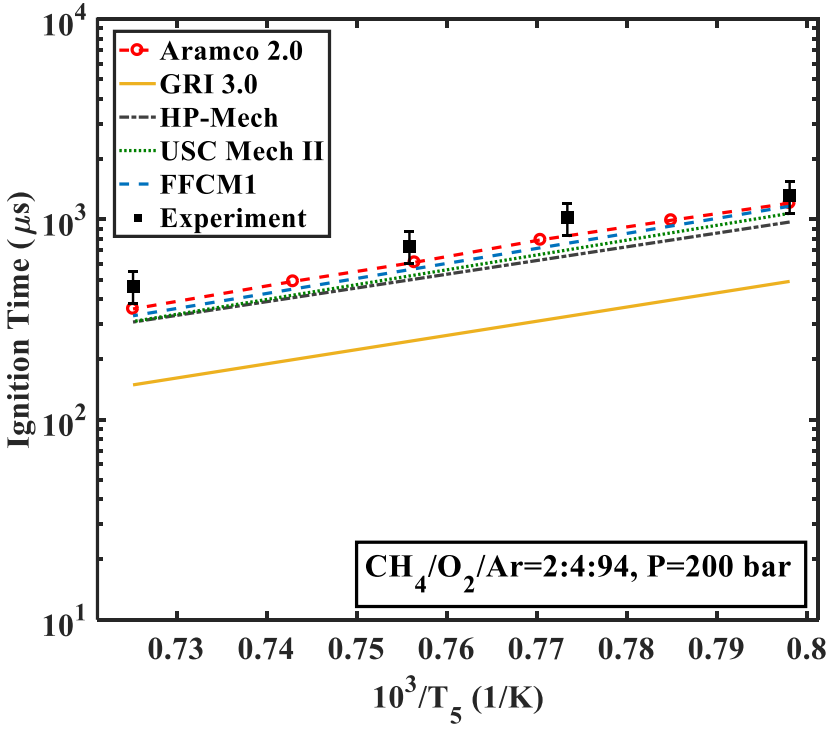
Autoignition Delays of CH_4 in Ar

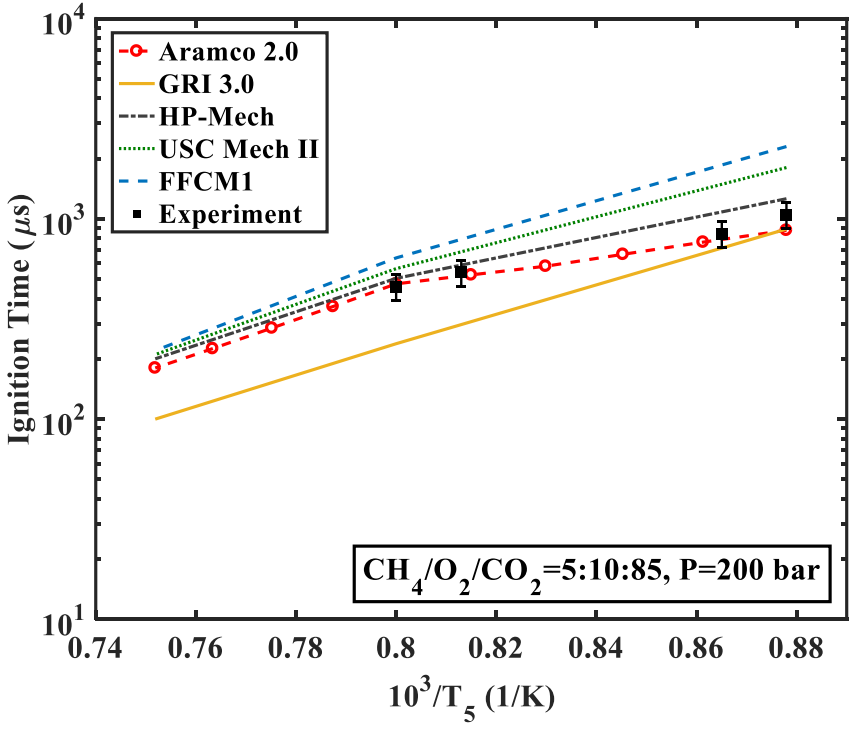
- **Pressure: 95±3 bar**, and **temperature range of 1248 to 1410 K**



Autoignition Delays of CH_4 in CO_2 and Ar

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

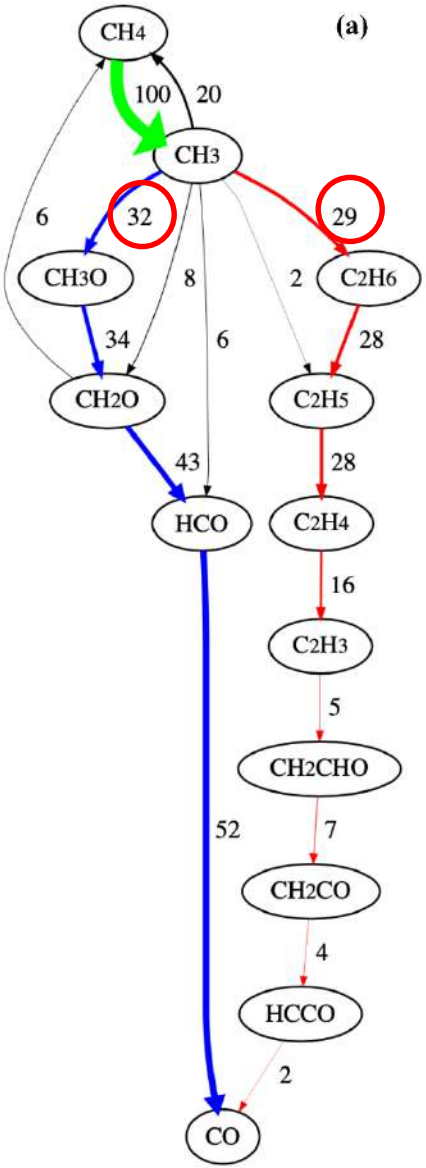




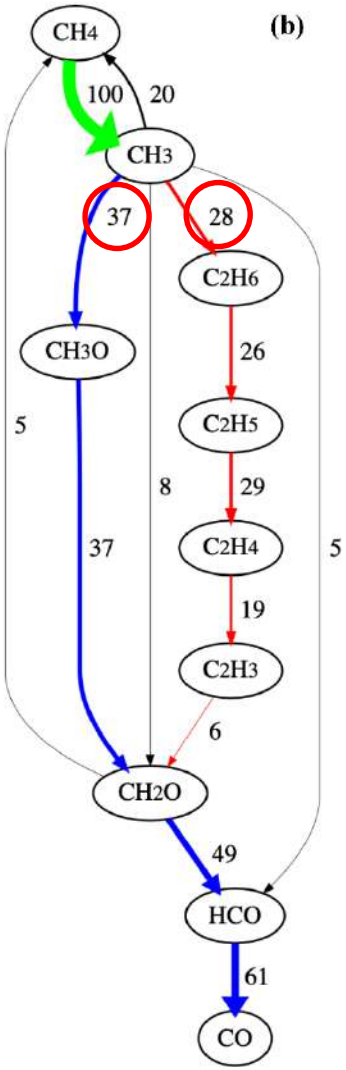
Temperature further distinguishes different kinetic models
- High T kinetics is much simpler than low T kinetics

Chemical Analysis (a brief summary)

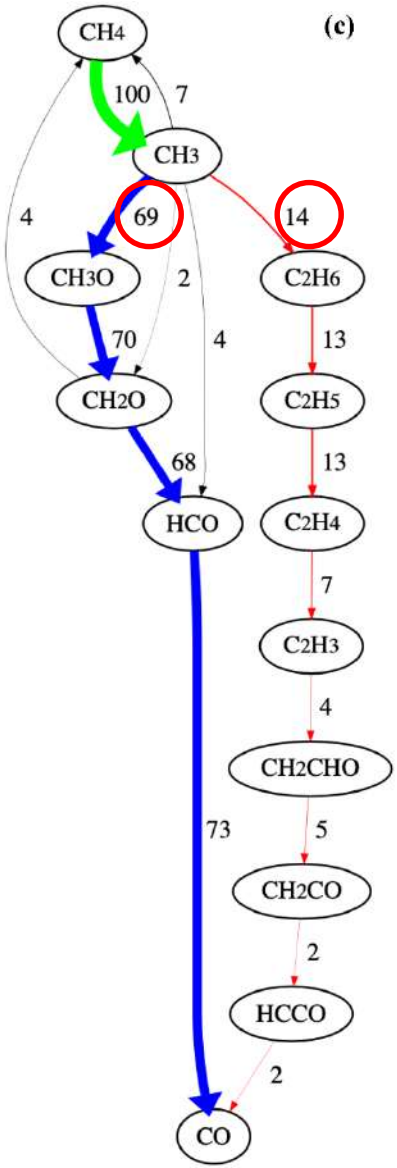
Aramco 2.0



FFCM-1



GRI 3.0

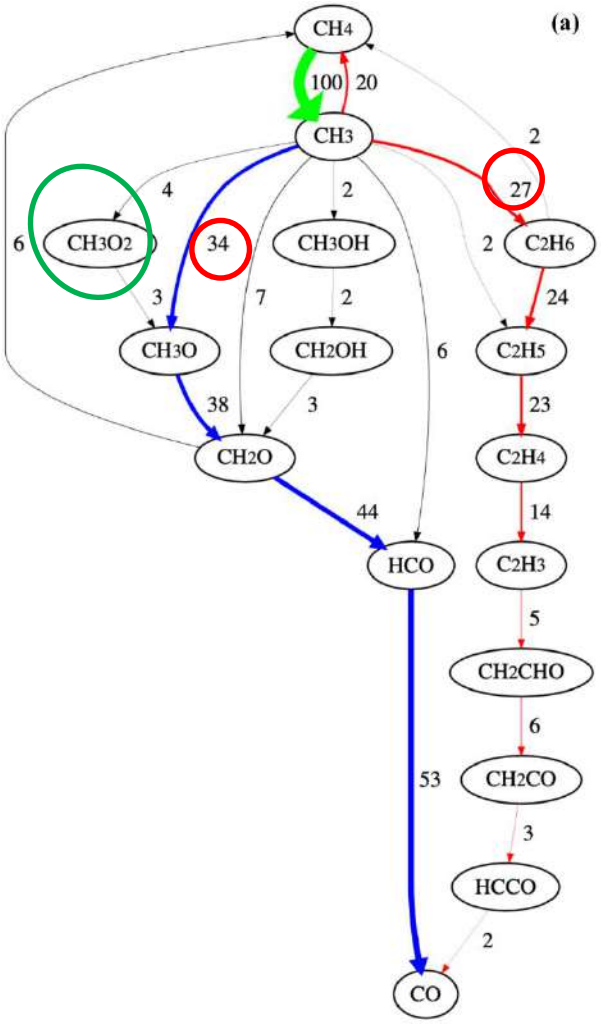


P=100 bar, T=1200 K
$CH_4/O_2/CO_2$ (5:10:85)

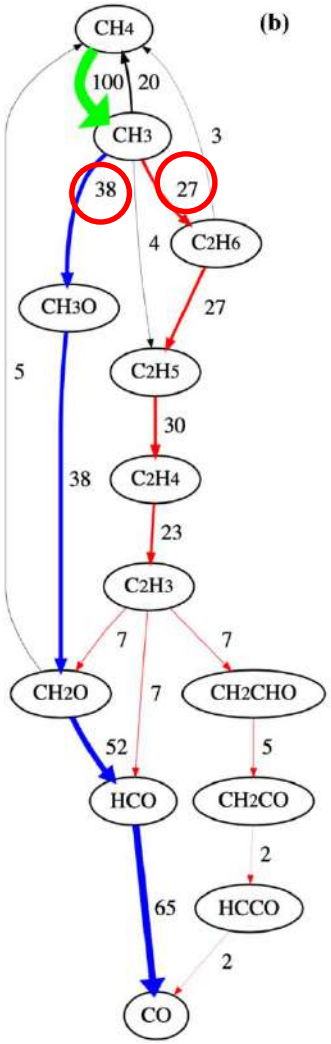
CH_4 branching ratio dictates ignition

CH_4 Reaction Pathway Analysis

Aramco 2.0

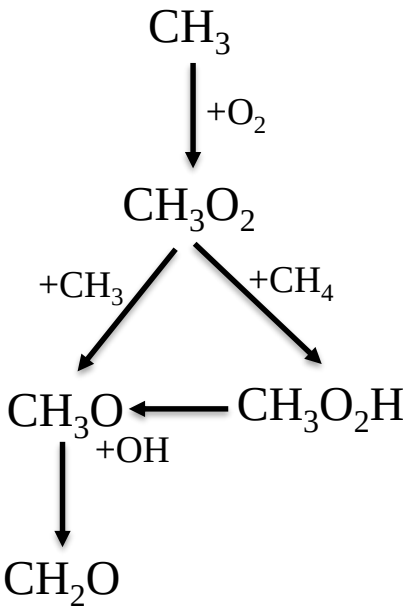


FFCM-1



P=200 bar, T=1200 K
$CH_4/O_2/CO_2$ (5:10:85)

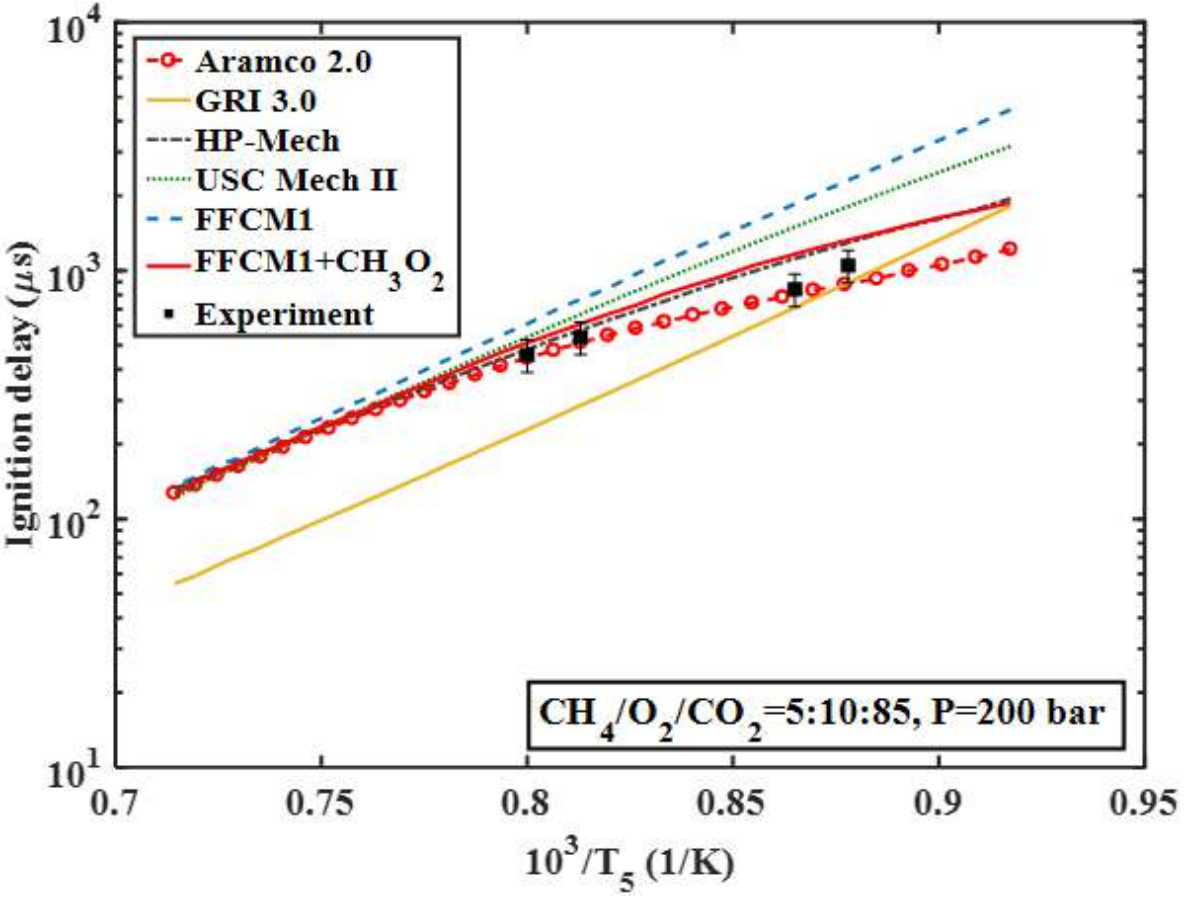
Additional pathway of CH_3 at low temperature



CH_3O_2 is NOT included in FFCM

CH_4 Autoignition Delays

Both P and T play a role



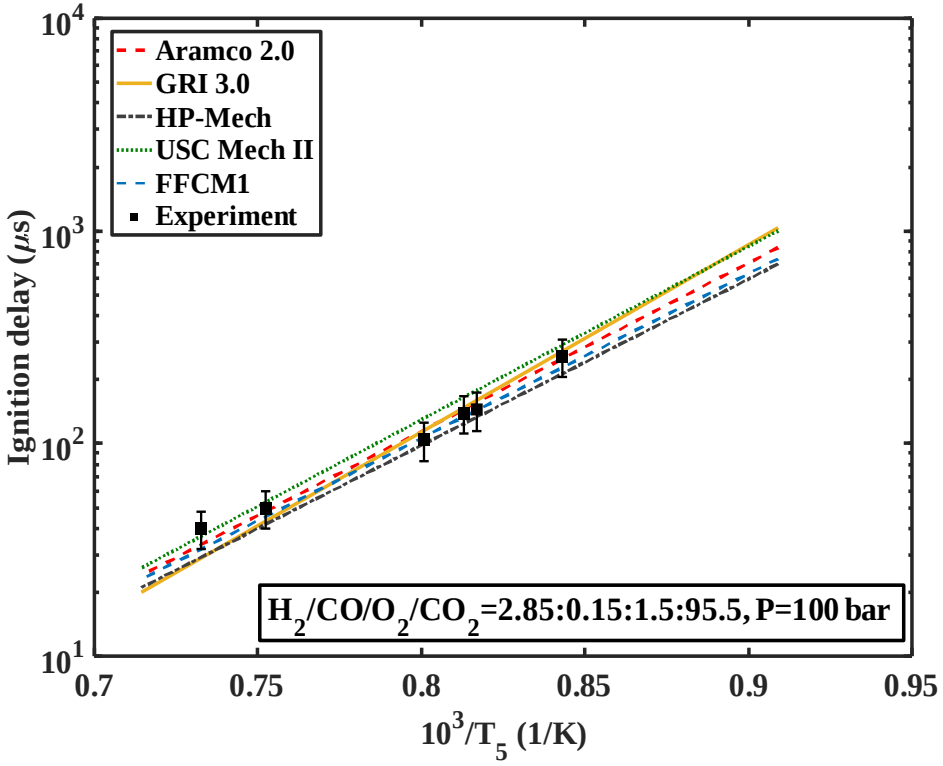
H_2/CO Mixture Autoignition

(only GT results because of time limitation)

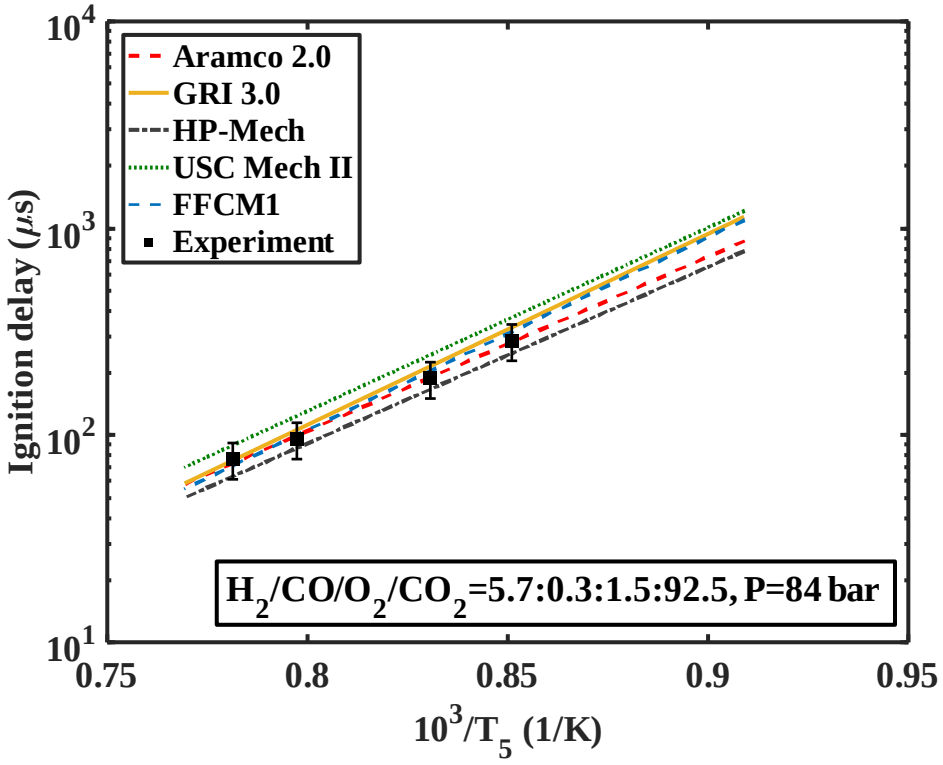
M. Karimi, B. Ochs, W. Sun, D. Ranjan, “High pressure ignition delay times of H2/CO mixture in carbon dioxide and argon diluent” 2021 *Proceedings of the Combustion Institute,* 38, 251-160

H_2/CO Mixture Autoignition

Ignition delay time of $H_2/CO/O_2/CO_2$ mixture at near 100 bar



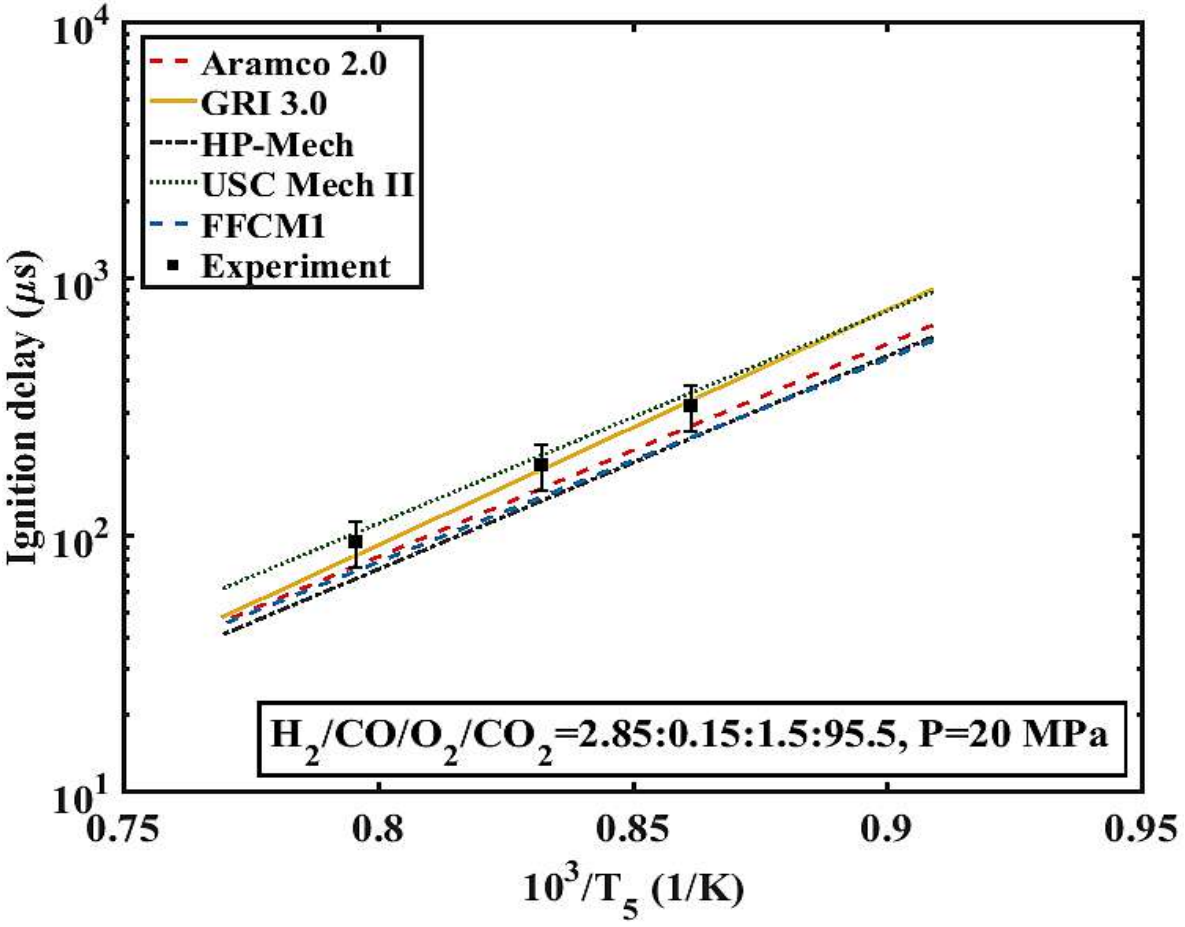
stoichiometric (Φ =1), T=1186–1365 K



Rich (Φ =2) mixtures, T=1175–1280 K

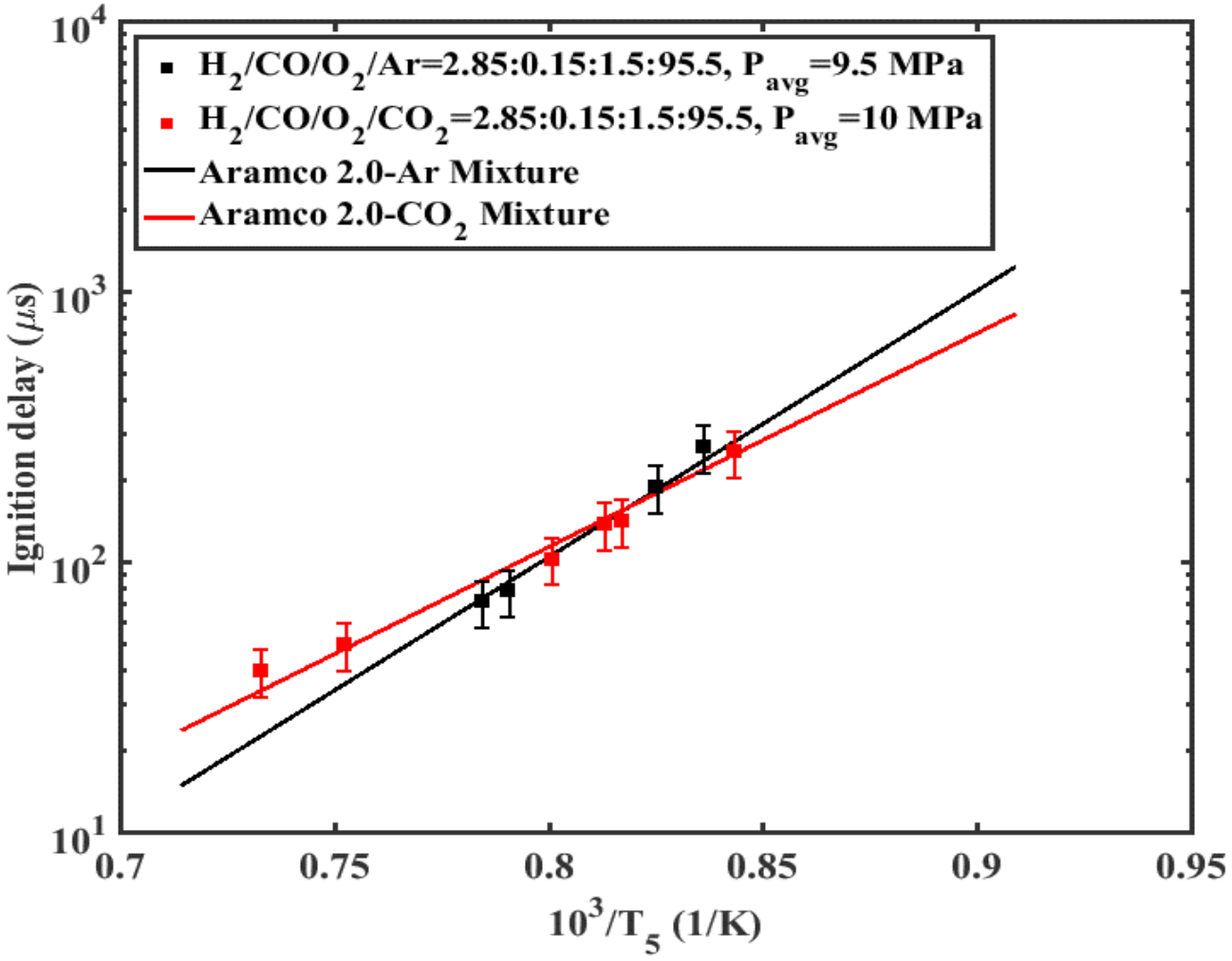
Models work well

H_2/CO Mixture Autoignition



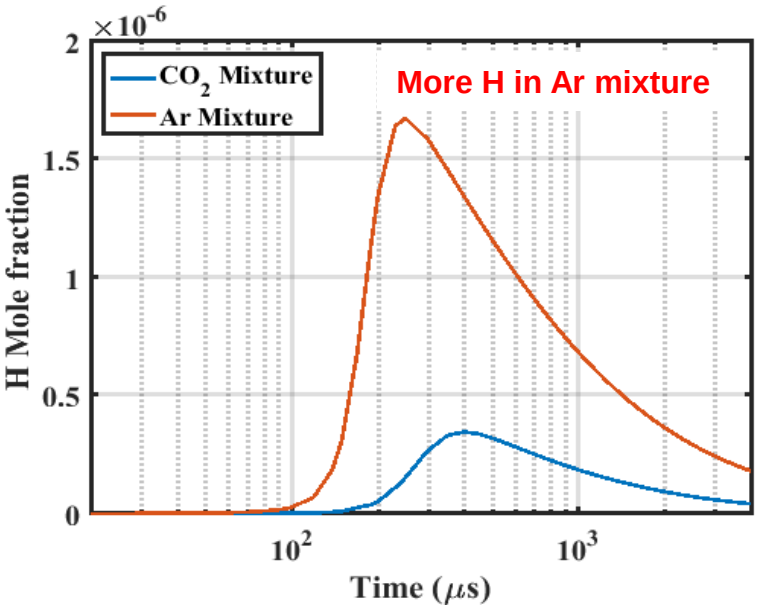
Ignition delay time of stoichiometric $H_2/CO/O_2/CO_2$ mixture at 200 bar and T=1161–1257K

H_2/CO Mixture Autoignition



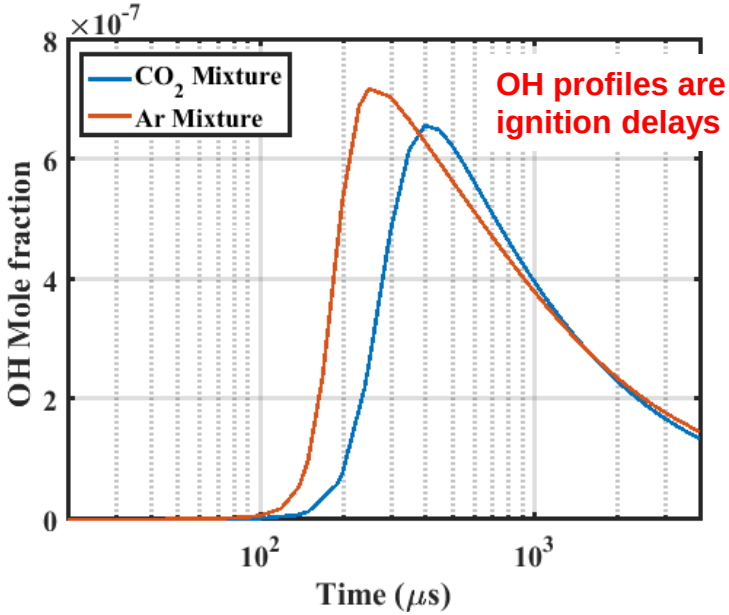
- It seems no obvious effect from diluent (Ar, CO_2) to IDTs
- But this may not be true at elementary reaction level

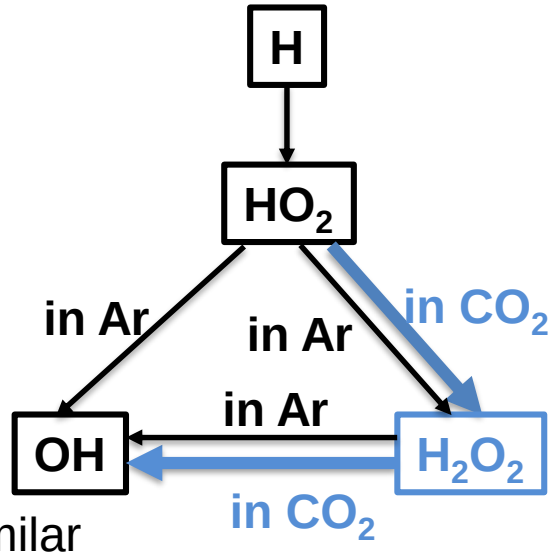
Chemical Analysis (a brief summary)



At high Pressure,
$H+O_2+M \rightarrow HO_2+M$ dominates

$H+O_2+CO_2 \rightarrow \underline{HO_2}+CO_2$ (7X faster)
$H+O_2+Ar \rightarrow HO_2+Ar$ (slower)





Similar
end results

Conclusion – CH_4

- Most kinetic models can predict CH_4 autoignitions reasonably well at sCO_2 conditions
  - GRI 3.0 is rejected
- CH_3O_2 is important at high pressure and low temperature conditions
- CO_2 has negligible chemical effect at high pressure conditions

Conclusion – H_2/CO

- Most kinetic models can predict H_2/CO autoignitions reasonably well at sCO_2 conditions

- CO_2 has chemical effect on elementary reactions. Its effect on autoignition delays is washed out (within uncertainty of expt.)

Clarification (Disclaimer)

- Conclusions are limited to autoignition chemistry only (we do not know flame properties at sCO_2 condition)
- Thermal effect (heat capacity) is eliminated in both experiments and simulations
- Real gas effect is not important in combustor if inflow is hot (away from critical T).
- Real gas effect is significant when temperature is near critical point.

Thank you! & Questions?

Acknowledgement:
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