2014 UTSR Workshop
Purdue University
October 22nd, 2014

High-pressure low-temperature ignition behavior of syngas mixtures, …et al.

A. Mansfield[a], M.S. Wooldridge[a,b]
[a]Department of Mechanical Engineering,
[b]Department of Aerospace Engineering,
University of Michigan, Ann Arbor, 48109

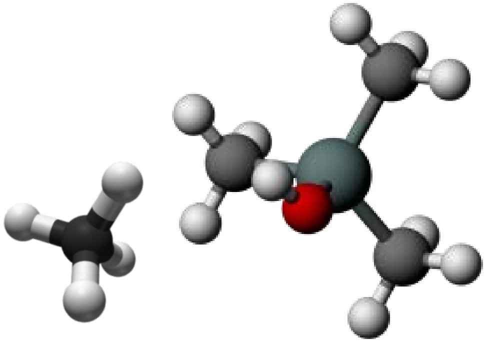
Acknowledgements

The authors acknowledge the generous financial support of the Department of Energy, National Energy Technology Laboratory via the University Turbine Systems Research Program, Award number DE-FE0007465, and the Department of Mechanical Engineering at the University of Michigan.

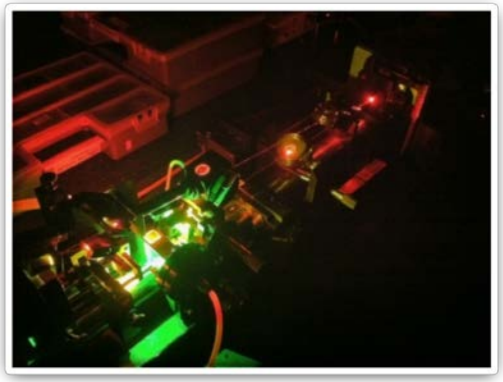
Projects

1. High-pressure, low-temperature ignition behavior of syngas mixtures

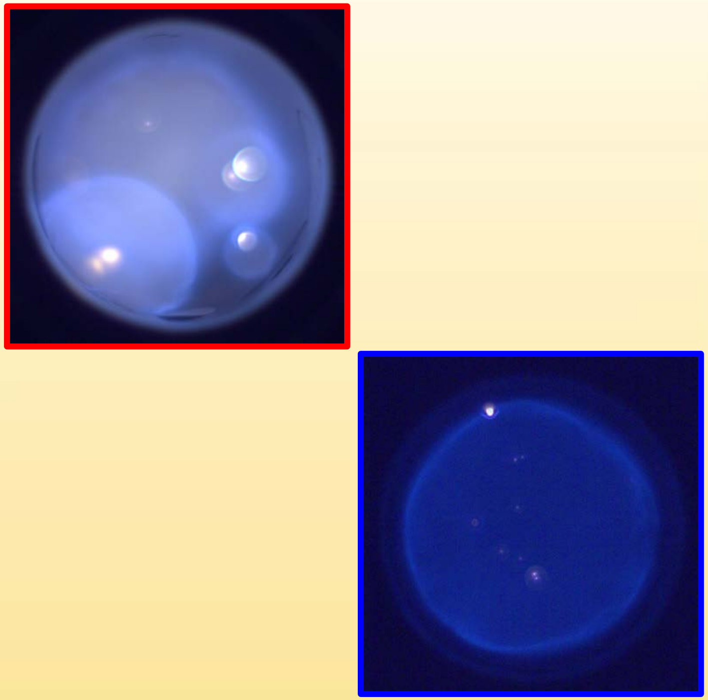
2. Effect of impurities on syngas combustion



3. Experimental study of OH time histories during syngas auto-ignition



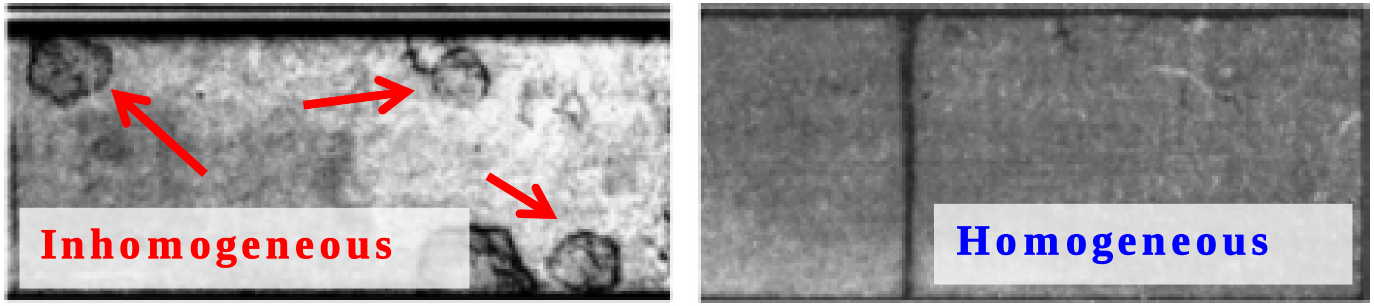
High-pressure low-temperature ignition behavior of syngas mixtures



Published as, A.B. Mansfield, M.S. Wooldridge, Comb. and Flame 161 (2014) 2242-2251

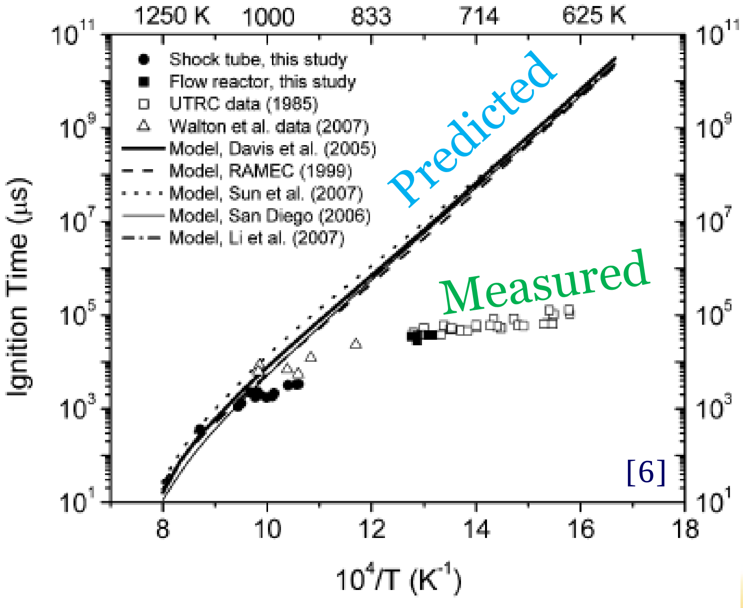
Motivation

- Few studies of auto-ignition behaviors: syngas/H_2 [7-11]



[9]

- Inhomogeneous behavior → unpredicted decreases in τ_{ign} [5]

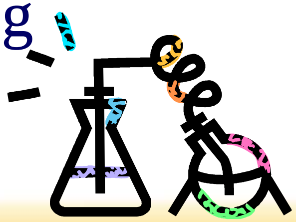


[6]

Objectives and Approach

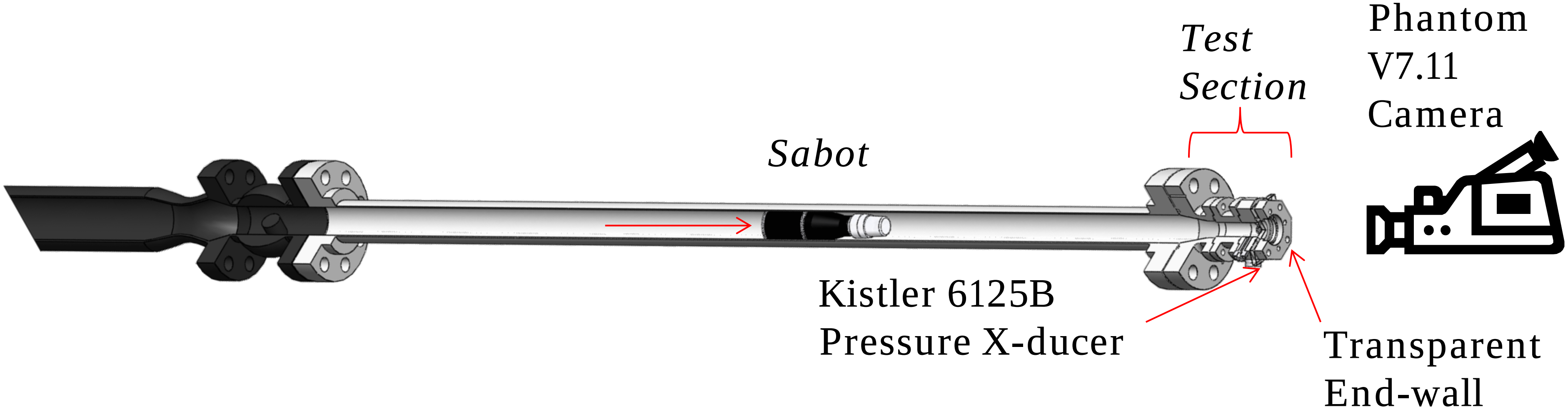
1. Where do certain auto-ignition behaviors happen?
2. Can we predict them?
3. How does it affect accuracy of typical homog. modeling?

- *University of Michigan – Rapid Compression Facility*
- Combine results with previous; map as f(P,T,φ)
- Identify strong ignition limit, compare to predictions
- Compare τ_{ign} to predictions from typical 0-D modeling



Methods: Experimental & Computational

University of Michigan – Rapid Compression Facility



Test Section

Phantom V7.11 Camera

Sabot

Kistler 6125B Pressure X-ducer

Transparent End-wall

Measurements

Transient bulk pressure & Axial high-speed images

Conditions

Pressure ~ 3, 5, 10, 15 atm, Temp. ~ 950-1150 K

φ = 0.1 & 0.5, H_2:CO = 0.7, ~Air Dil. With N_2 (CO_2, Ar)

Computations

CHEMKIN 0-D homogeneous reactor and flame speed calculator, Li 2007 mechanism* with A-factor uncertainty ($H+O_2 = OH+O$ & $H+O_2(+M)=HO_2(+M)$)

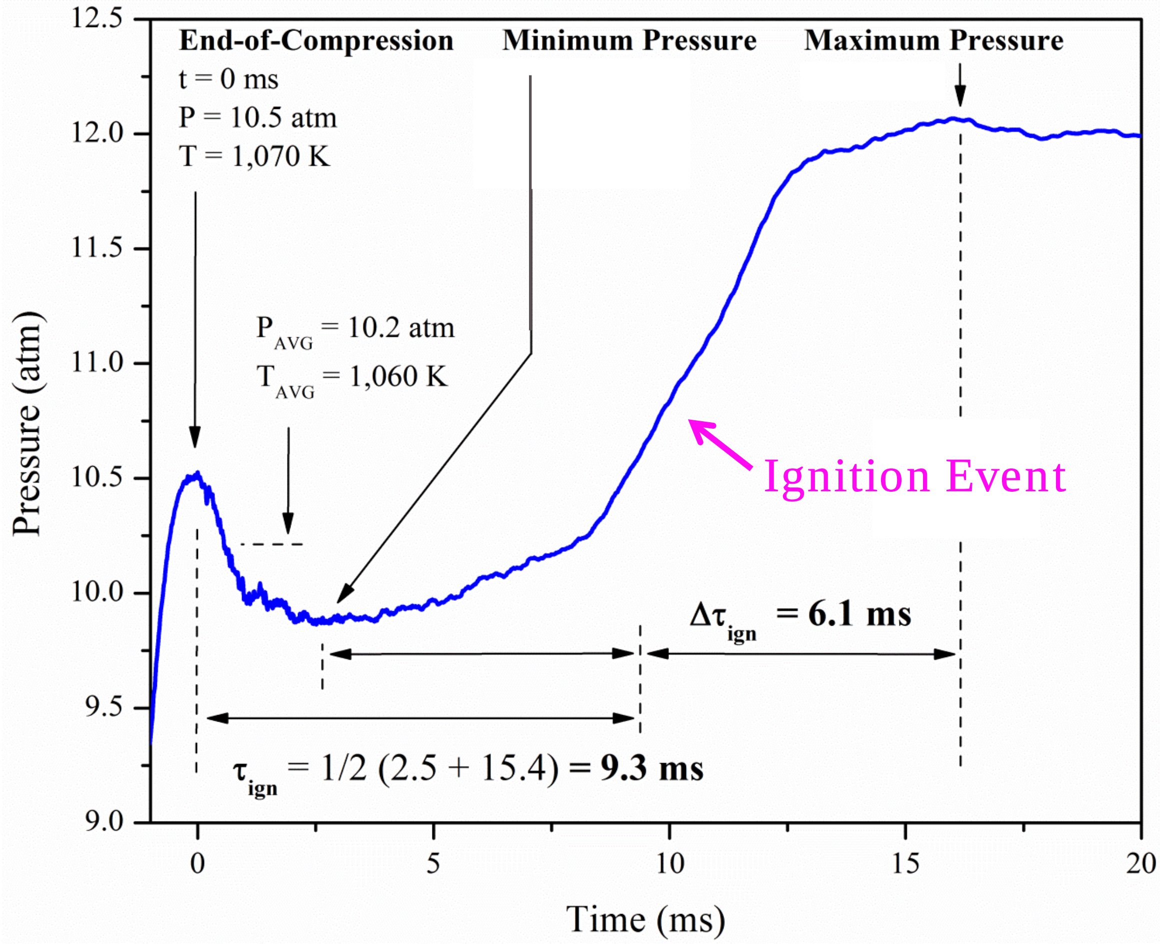
---

*J. Li, Z. Zhao, A. Kazakov, M. Chaos, F.L. Dryer, J.J. Scire, Int. J. Chem. Kinet. 39 (2007) 109–136

Typical Pressure Time History

P(t)

Homog. Ignition, ($\varphi = 0.1$)

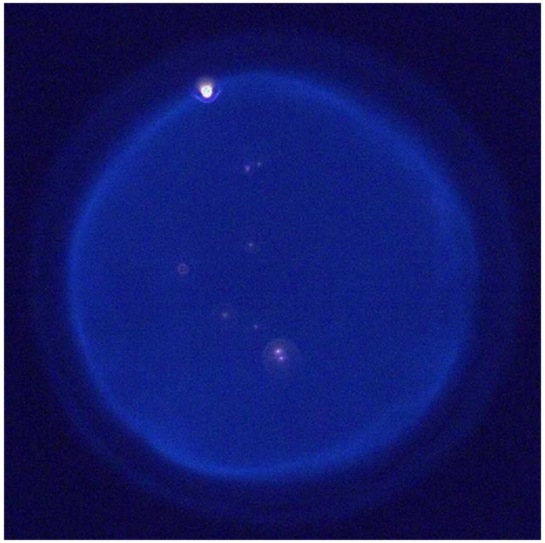


For each experiment:

1. Assigned state (P,T)
2. Calculated $\tau_{ign} \pm\Delta$
3. Classified auto-ign. behavior

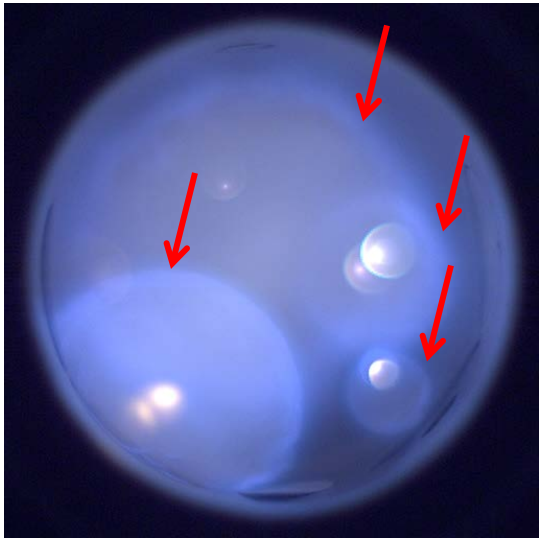
Typical High Speed Imaging

Homogeneous



(P = 3.3 atm, T = 1043 K, φ = 0.1)

Inhomogeneous

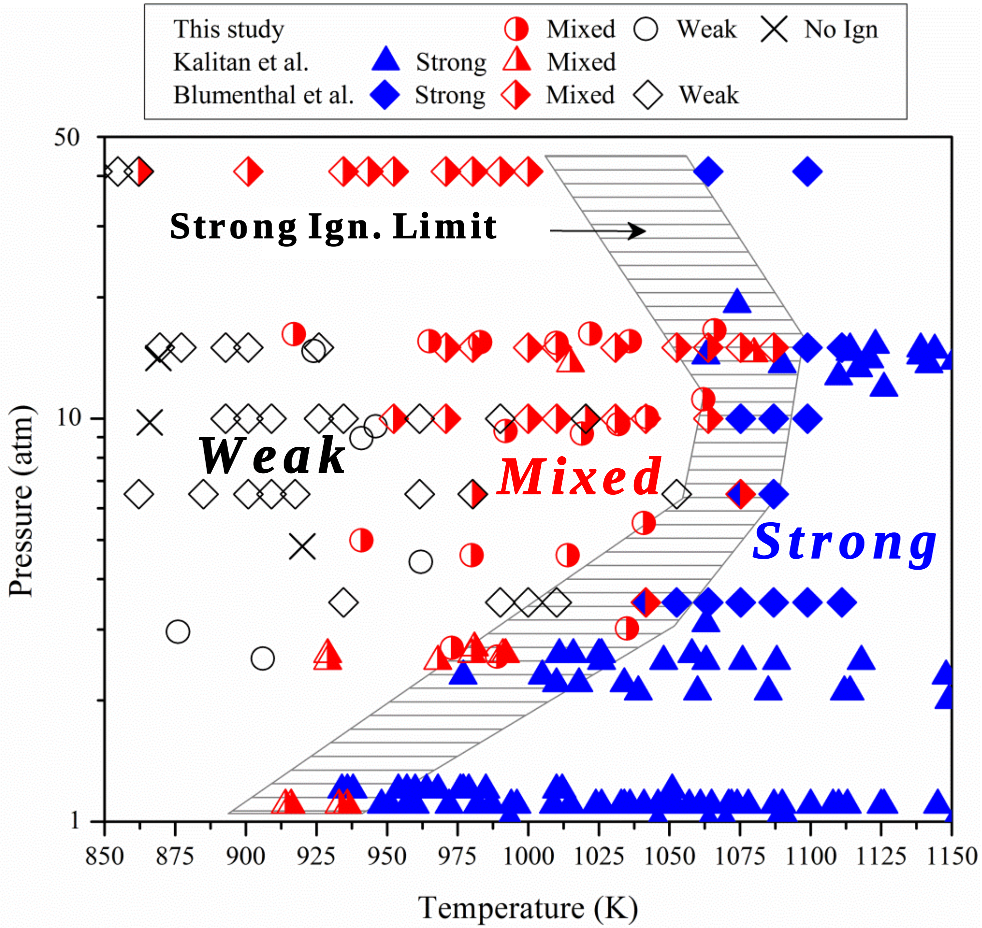


(P = 9.2 atm, T = 1019 K, φ = 0.5)

Ignition Classification	**Imaging Characteristics**	**Auto-Ignition Behavior**
Strong	Spatially uniform only	Homogeneous
Weak	Flame-like structures only	Inhomogeneous
Mixed	Flame-like structures → spatially uniform in unburned	Inhomogeneous → homogeneous

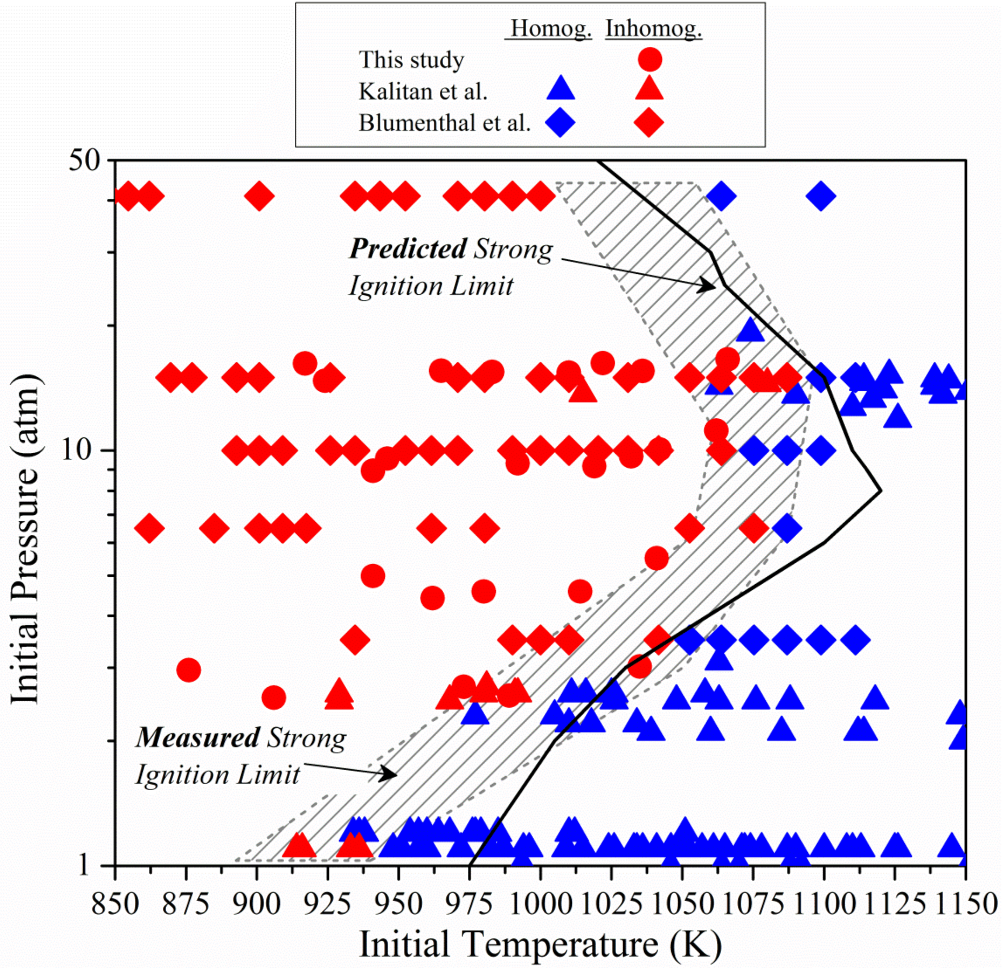
- Re-classified previous results [7-11]

Ignition Behavior Map, φ = 0.5



- Excellent agreement across devices, mixture variations
  - Strong ignition limit identified; Function of φ, P, T
    - First comprehensive integrated mapping

Prediction: Sankaran Criterion

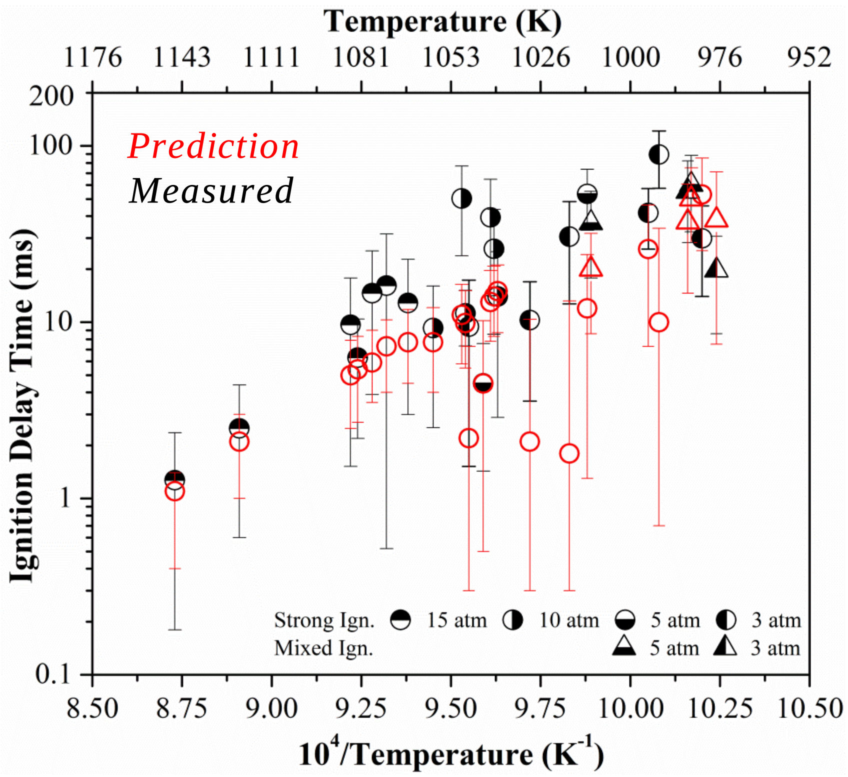


- Criterion captures strong ign. limit, both φ, all P,T
  - First application to experimental data

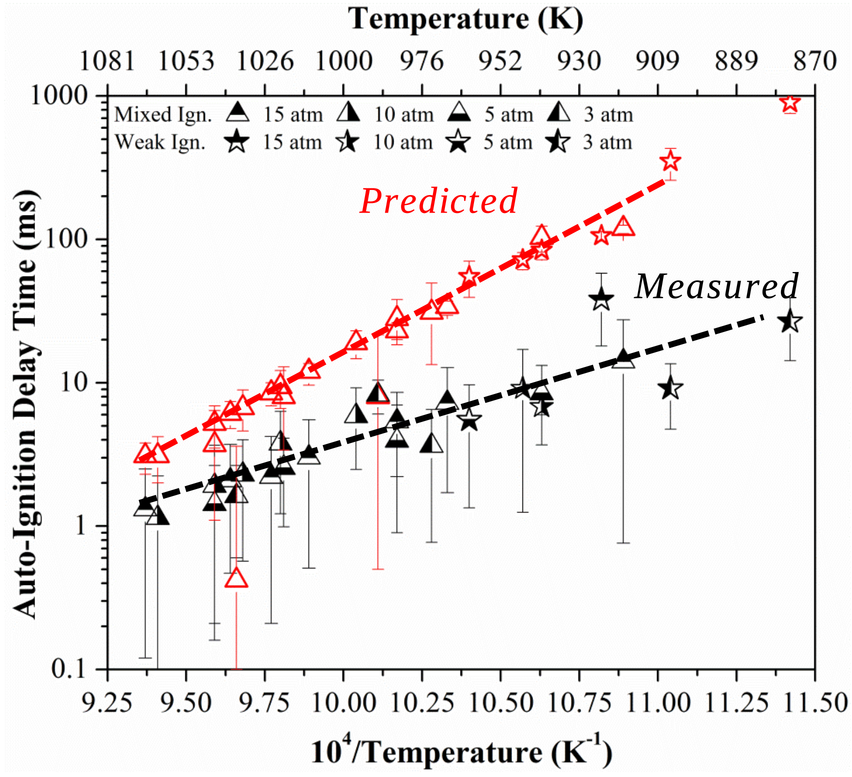
➢ *A priori* prediction, from basic modeling (τ, s_L^0)!

Behaviors and model accuracy

φ = 0.1

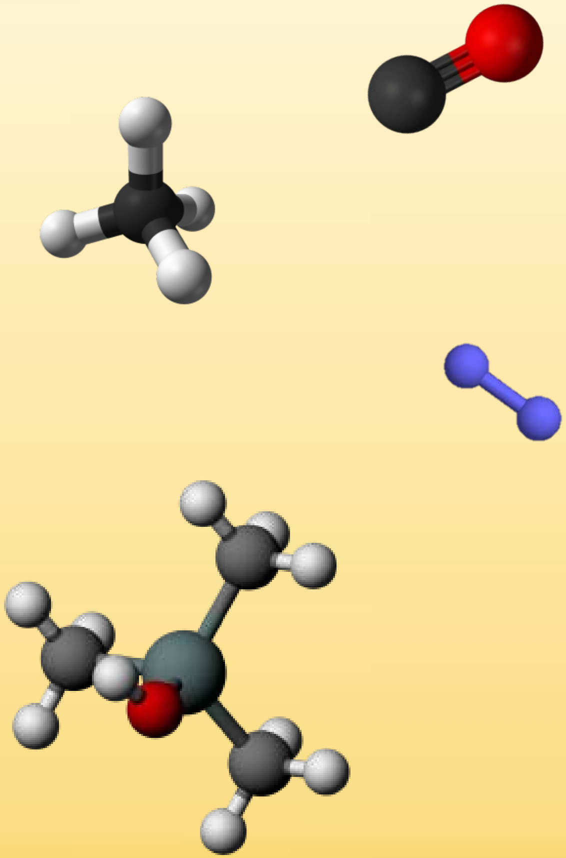


φ = 0.5

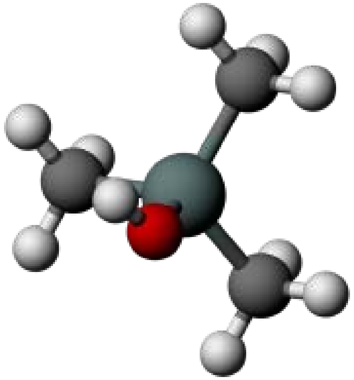


- φ = 0.1: Excellent agreement, regardless of ign. behavior
- φ = 0.5: Poor agreement, worse as T ↑, all inhomog. Behavior
- Inhomogeneous behavior correlated to modeling error

The effects of impurities on syngas combustion

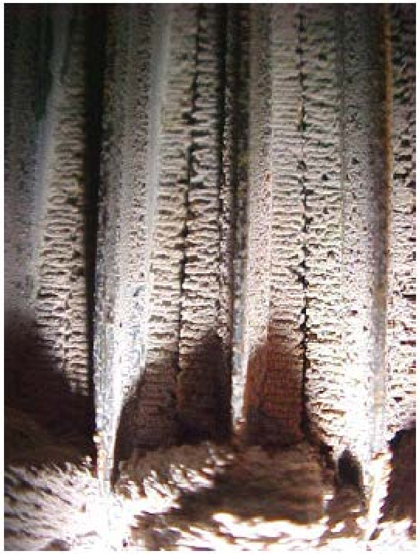


Background



- Numerous impurities in real syngas, with significant impacts on reactivity [15-21]

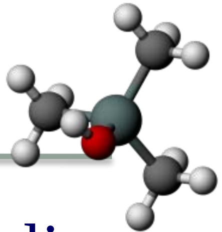
- Particular concern for **Organic Si** species
  - Silanols, Siloxanes increasing in concentration in landfill-based syngas [13]
  - Known to foul; effects on combustion?
  - SiH_4 has marked effect on H_2, likely also the case for syngas [25, 28]



[Pierce, 2005]

Project Objectives and Approach

1. Effect of Trimethylsilanol (**TMS**) on syngas reactivity.
   - Unstudied impurity related to commonly found Si-species in landfill-based syngas



- Compare ignition times to predictions from typical modeling
- Use model to interpret and analyze observations

P ~ 5 & 15 atm, T ~ 1010 – 1110 K

φ = 0.1, ~Air Dil. with N_2 (CO_2, Ar)

(1) syngas: 30% H_2, 70% CO

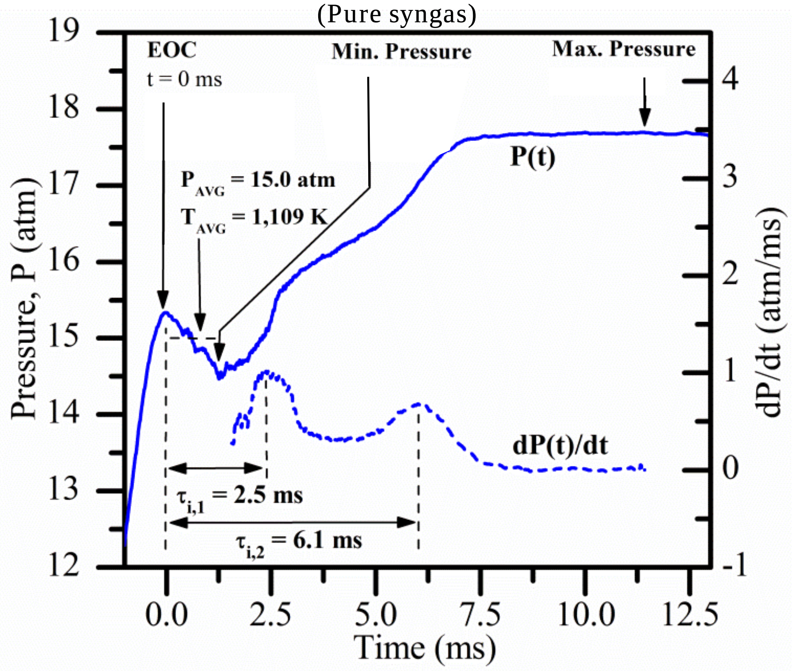
(2) syngas + 10ppm TMS

(3) syngas + 100ppm TMS

Results: Typical Pressure Time Histories

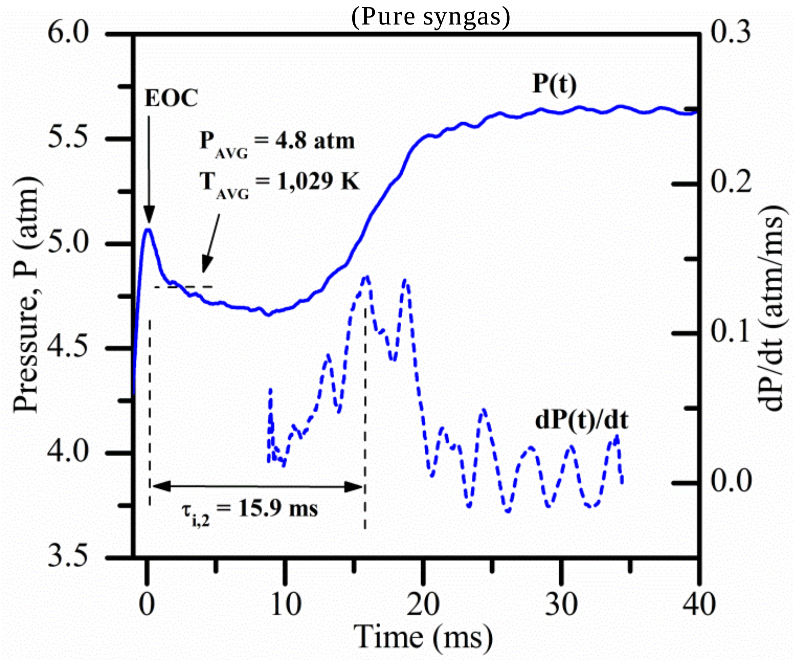
15 atm

Two-step ignition



5 atm

One-step ignition

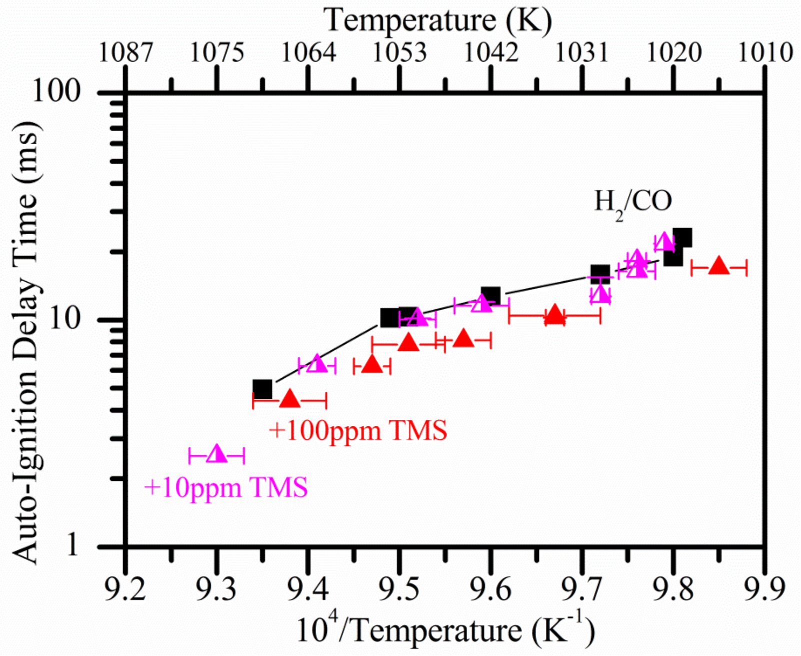


- 2-step ignition never before reported
- Modeling trends indicate worse for higher P, more CO

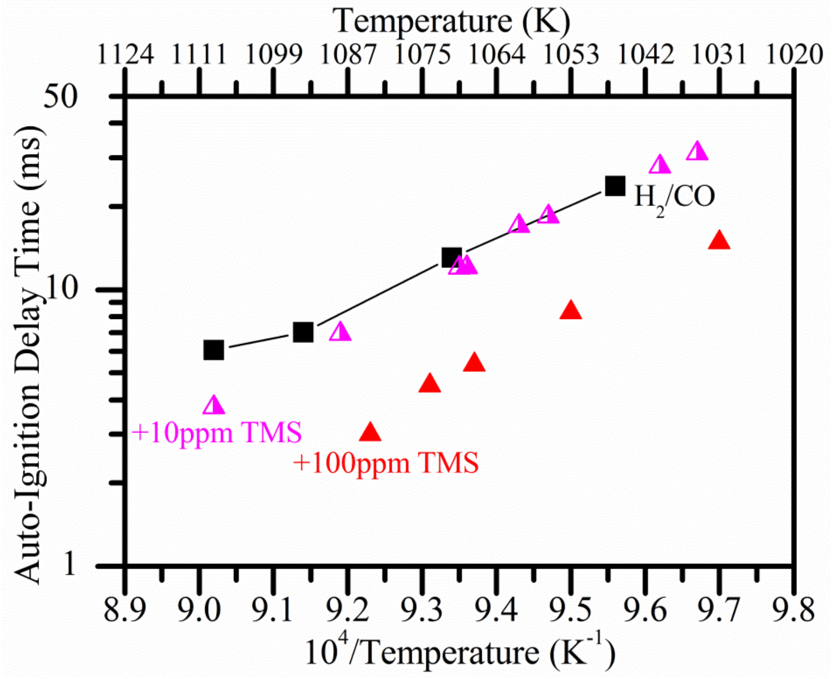
- For each experiment, assigned:
  - Thermo. State (**P**,**T**) , $\boldsymbol{\tau_{ign,\,2}}$ and $\boldsymbol{\tau_{ign,\,1}}$ (if 2-step)
  - Sources of uncertainty: direct meas. and post-processing filters

Results: $\tau_{ign,2}$

5 atm



15 atm



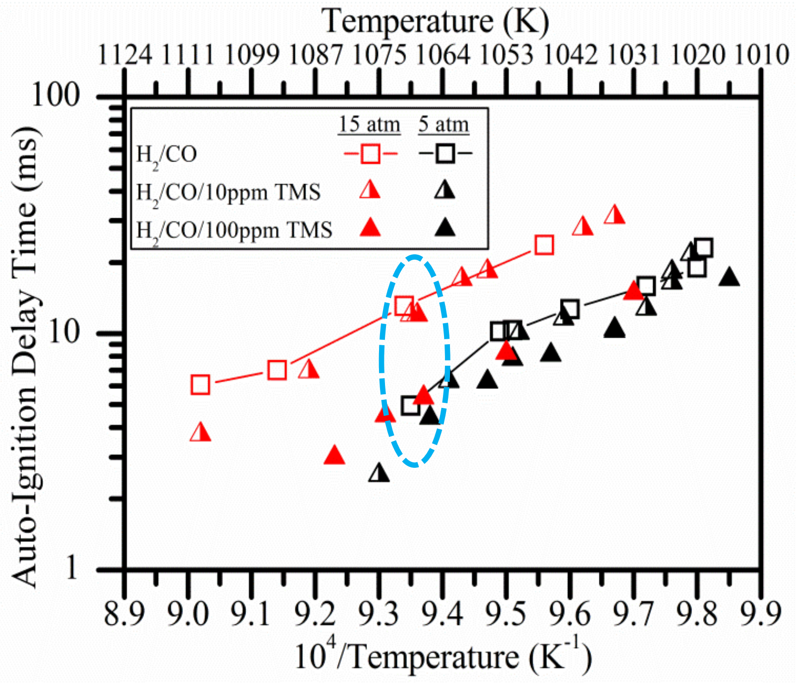
- 10 ppm TMS ~ negligible
- 100ppm TMS decrease by ~**20-30%**

- 10 ppm TMS ~ negligible?
- 100ppm TMS decrease by ~**50-70%**

➢ TMS effect consistent and drastically promoting at 100 ppm!

Results: TMS and P Dependence

$\tau_{ign,2}$



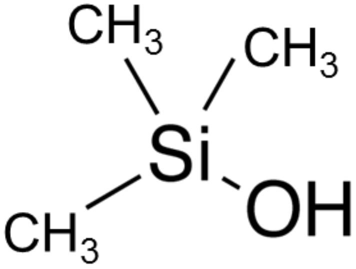
- 100ppm TMS virtually eliminates P dependence
- Suggests TMS effect is on HO_2/ H_2O_2 chemistry: supported by modeling
- Very similar effects seen for another Si compound, SiH_4 , in H_2 [petersen][mclain]
- Dangerous trend for Si species? Warning for future syngas with more Si

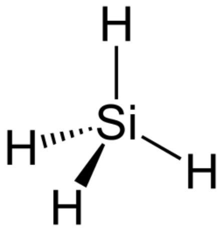
<u>Syngas</u>

- 5 to 15 atm → ~ 100% increase in $\tau_{i,2}$

<u>Syngas + 100ppm TMS</u>

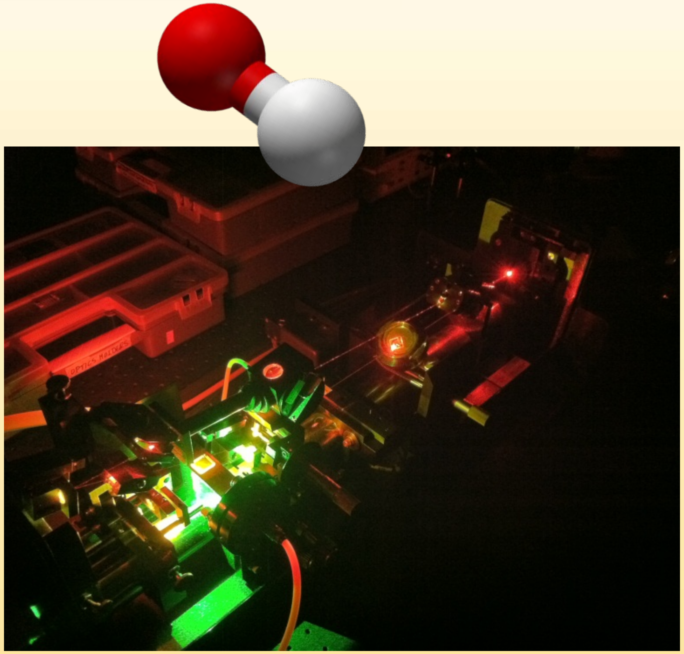
- 5 to 15 atm → ~ negligible increase



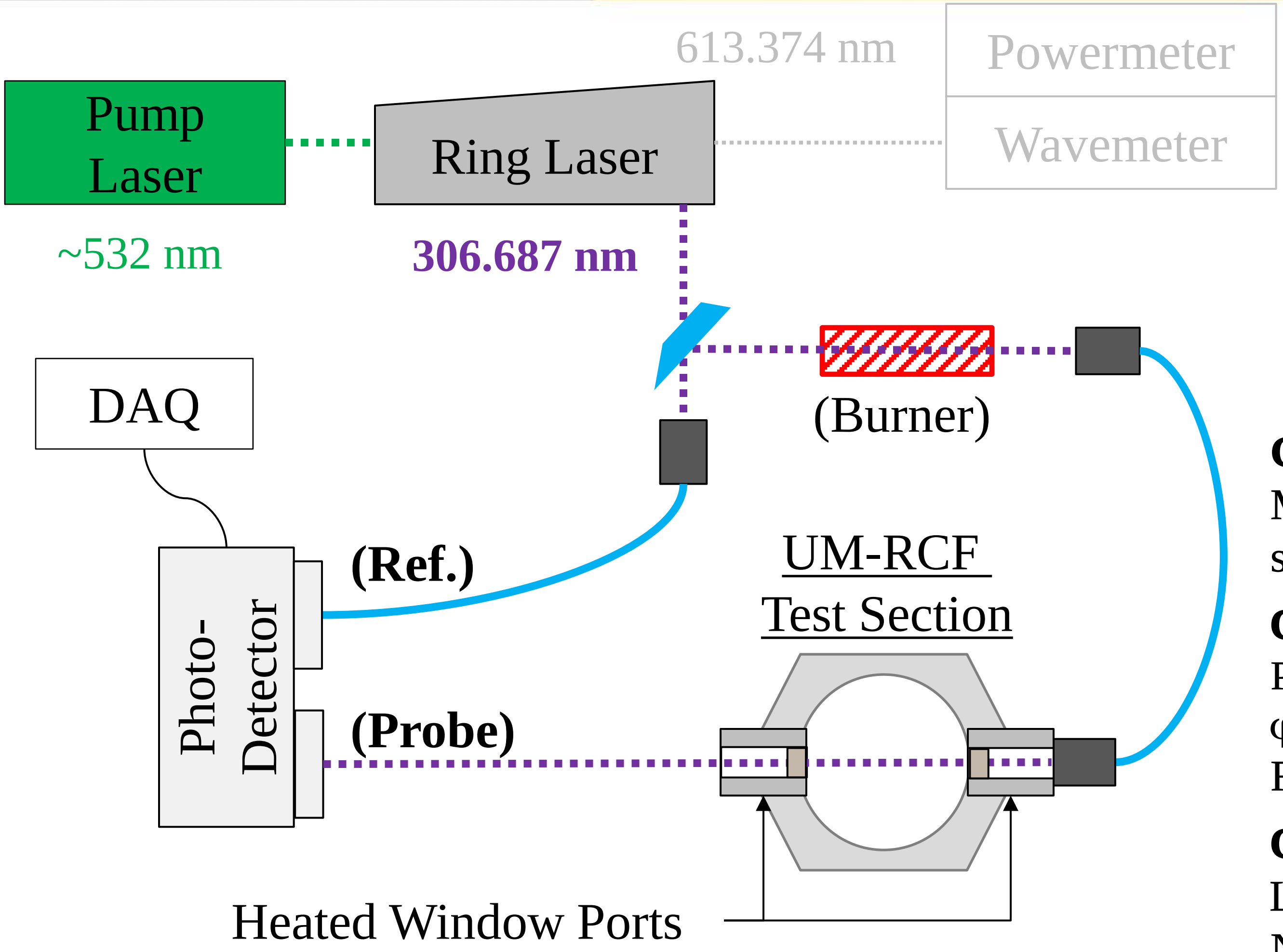


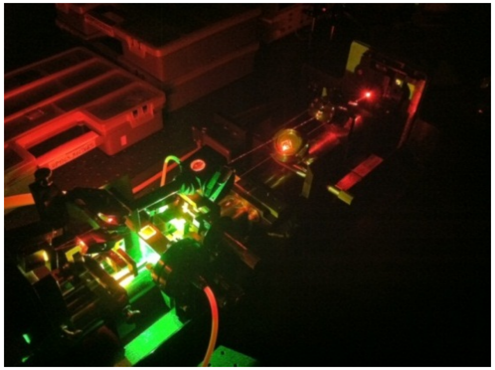
Molecule images:
http://en.wikipedia.org/wiki/

Experimental study of OH time histories during syngas auto-ignition



New OH Laser Absorption System





Goal

Measure $\chi_{OH}(t)$ during syngas auto-ignition.

Conditions

P ~ 5 atm, T ~ 1000-1090 K

φ = 0.1, ~Air Dil., N_2 (Ar)

Fuel: 30% H_2, 70% CO

Computations

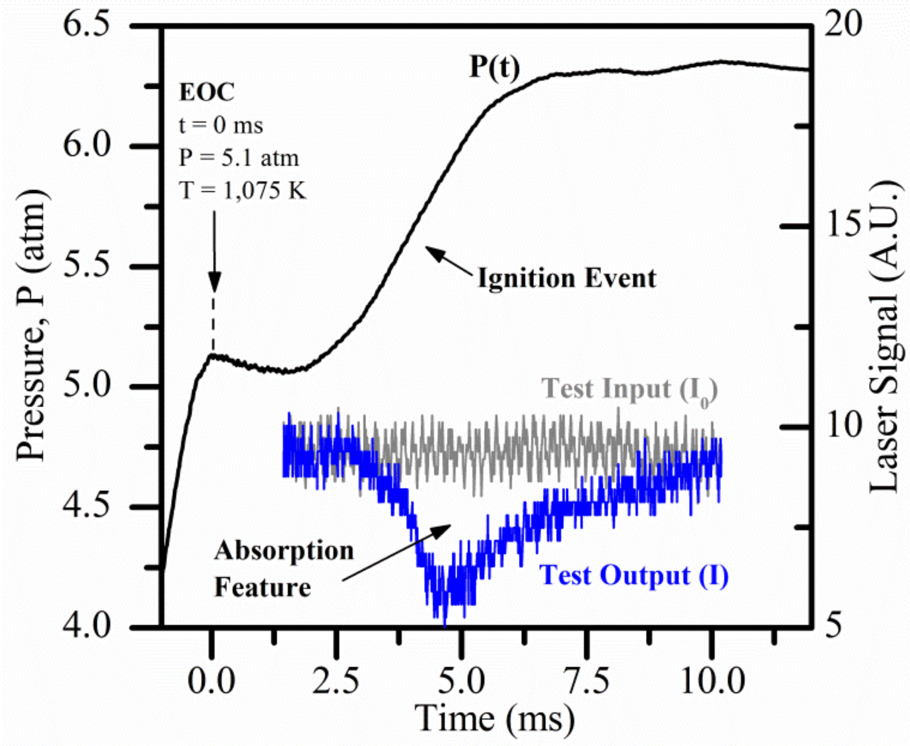
Li 2007 mech.

NUIG 2013 mech. [19]

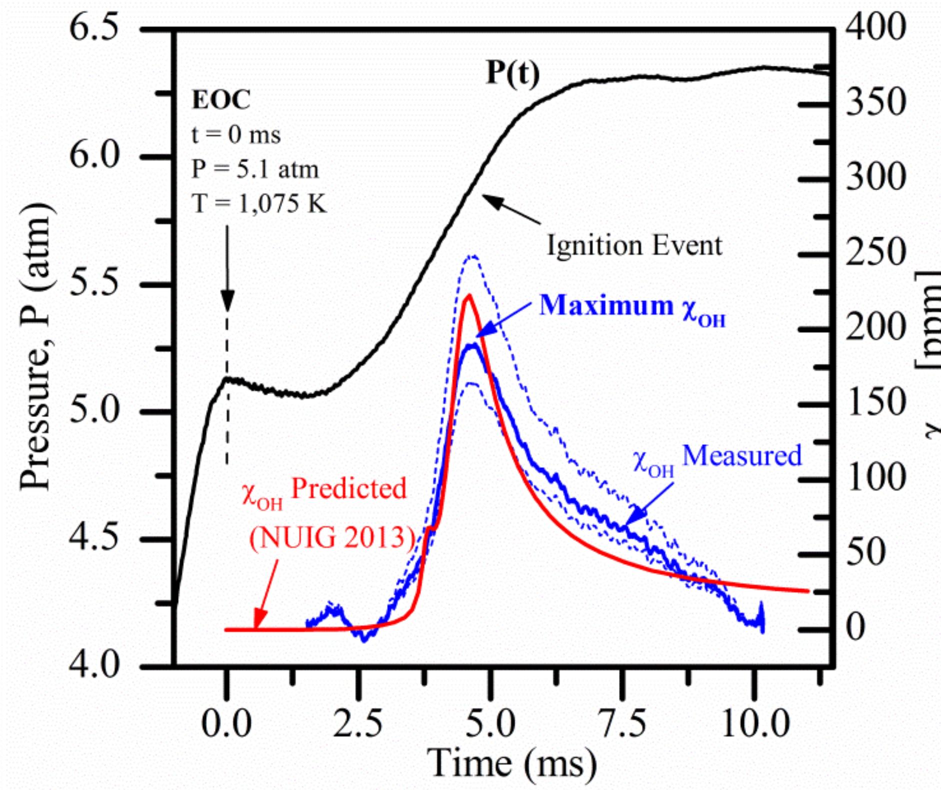
- Low precision targets dominate (τ_{ign}, s_L^0) available kinetic data
- Important O, OH, H radical data very limited for H_2 (high-T, low-P, ultra dilute) [29], unstudied for syngas

Typical χ_{OH} time history

Raw Signals



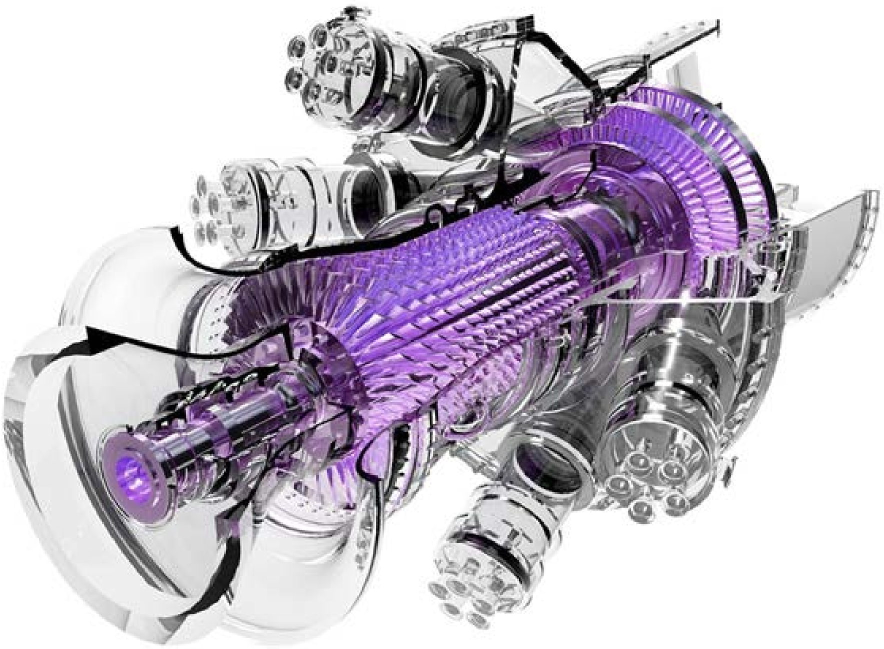
$\chi_{OH}(t)$

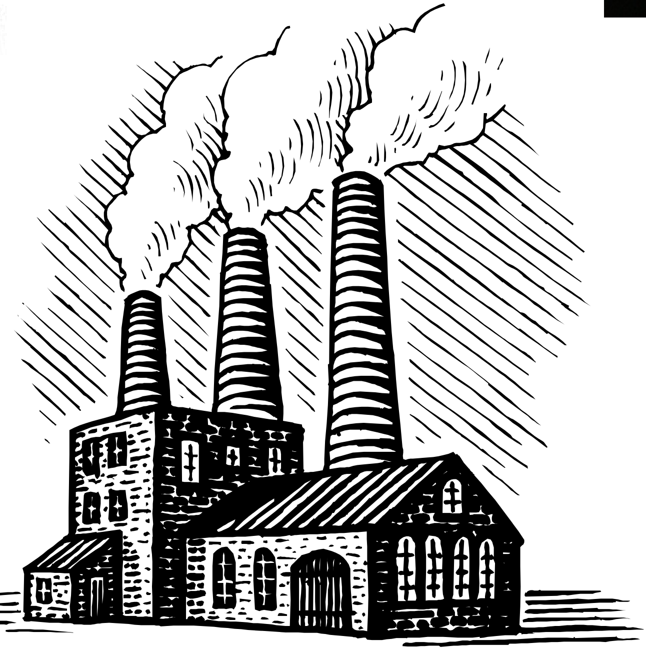


- Clear absorption feature
- Excellent agreement between measured and predicted $\chi_{OH}(t)$
- Interrogation of multiple features possible (magnitudes, slopes), to improve chemical kinetics

Thank you!

Questions/Comments?





http://www.netl.doe.gov/research/coal/energy-systems/turbines

References

- [5] Chaos, Marcos, and Frederick L. Dryer. "Syngas combustion kinetics and applications." *Combustion Science and Technology* 180, no. 6 (2008): 1053-1096.
- [6] Petersen, Eric L., Danielle M. Kalitan, Alexander B. Barrett, Shatra C. Reehal, John D. Mertens, David J. Beerer, Richard L. Hack, and Vincent G. McDonell. *Combustion and flame* 149, no. 1 (2007): 244-247.
- [7] Voevodsky V, Soloukhin R. On the mechanism and explosion limits of hydrogen-oxygen chain self-ignition in shock waves. Symp Combust 1965:279–83.
- [8] Meyer JW, Oppenheim A. K. On the shock-induced ignition of explosive gases. Symp Combust 1971;13:1153–64.
- [9] Blumenthal R, Fieweger K, Komp K. Self-ignition of H_2-air mixtures at high pressure and low temperature. Proc. 20th ISSW, World Sci., 1996, p. 935–40.
- [10] Kalitan DM, Mertens JD, Crofton MW, Petersen EL. Ignition and Oxidation of Lean CO / H 2 Fuel Blends in Air. J Propuls Power 2007;23:1291–303.
- [11] Walton SM, He X, Zigler BT, Wooldridge MS. An experimental investigation of the ignition properties of hydrogen and carbon monoxide mixtures for syngas turbine applications. Proc Combust Inst 2007;31:3147–54.
- [13] Rasi S, Lehtinen J, Rintala J. Determination of organic silicon compounds in biogas from wastewater treatments plants, landfills, and co-digestion plants. Renew Energy 2010;35:2666–73.
- [15] Glarborg P. Hidden interactions—Trace species governing combustion and emissions. Proc Combust Inst 2007;31:77–98.
- [16] Pierce J. Siloxane Quantification, Removal, and Impact on Landfill Gas Utilization Facilities. 8th Annu. LMOP Conf. Proj. Expo, 2005.
- [17] Mathieu O, Deguillaume F, Petersen EL. Effects of H_2S addition on hydrogen ignition behind reflected shock waves: Experiments and modeling. Combust Flame 2013;161:23–36.
- [18] Mathieu O, Kopp MM, Petersen EL. Shock-tube study of the ignition of multi-component syngas mixtures with and without ammonia impurities. Proc Combust Inst 2012;34:3211–8.
- [19] Mathieu O, Petersen EL, Heufer A, Donohoe N, Metcalfe W, Curran HJ, et al. Numerical Study on the Effect of Real Syngas Compositions on Ignition Delay Times and Laminar Flame Speeds at Gas Turbine Conditions. J Eng Gas Turbines Power 2013;136:011502.
- [20] Mueller M, Yetter R, Dryer F. Kinetic modeling of the $CO/H_2O/O_2/NO/SO_2$ system: Implications for high pressure fall off in the SO_2+ O (+ M)= SO_3 (+ M) reaction. Int J C 2000;32:317–39.
- [21] Mueller M, Yetter R, Dryer F. Flow reactor studies and kinetic modeling of the $H_2/O_2/NO_x$ and $CO/H_2O/O_2/NO_x$ reactions. Int J Chem Kinet 1999;31:705–24.

- [25] Petersen E, Kalitan D, Rickard MA. Reflected Shock Ignition of $SiH_4/H_2/O_2/Ar$ and$SiH_4/CH_4/O_2/Ar$ Mixtures. J Propuls Power 2004;20:665–74.
- [28] McLain, Allen G., Casimir J. Jachimowski, and R. Clayton Rogers. *Ignition of SiH4-H2-02-N2 behind reflected shock waves*. Vol. 2114. National Aeronautics and Space Administration, Scientific and Technical Information Branch, 1983.
- [29] Burke, Michael P., Marcos Chaos, Yiguang Ju, Frederick L. Dryer, and Stephen J. Klippenstein. "Comprehensive H_2/O_2 kinetic model for high-pressure combustion." *International Journal of Chemical Kinetics* 44, no. 7 (2012): 444-474.

BACKUP SLIDES

Strong Ign. Limit Prediction

We mapped the strong ignition limits
…can we predict their location *a priori*?

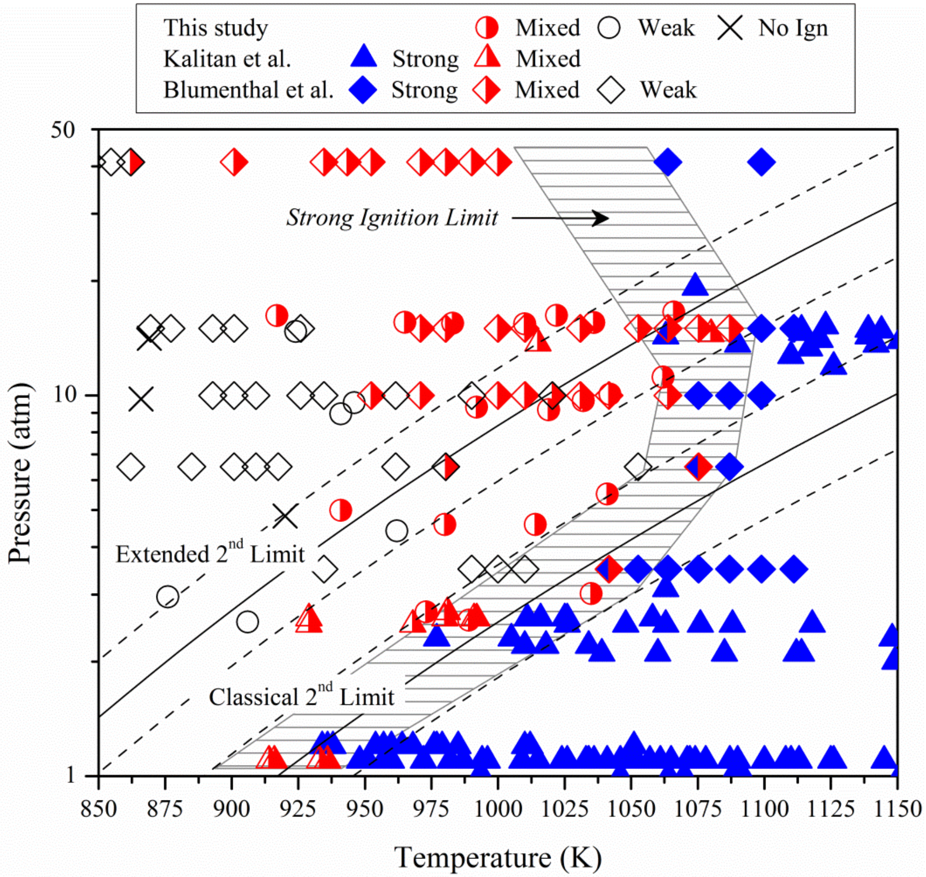
- **Previous attempts** (800 – 1300K, < 3 atm)
  - 2nd explosion limit; Voevodsky and Soloukhin, 1965
  - Thermal sensitivity, $(d\tau_{ign}/dT)_p$; Meyer and Oppenheim, 1971

- **New method here, based on computational work**
  - *Sankaran Criterion*; Sankaran, Im, Hawkes, Chen, 2005

$$s_L^0(P,T,\dots) = u_{prop}(P,T,\dots) \rightarrow \text{ strong ignition limit}$$

Distributed thermal gradients
drive local prop. fronts ➡ $u_{prop} = \left(\frac{d\tau_{ign}}{dT}\frac{dT}{dx}\right)^{-1}$

H_2/O_2 2nd Explosion Limits



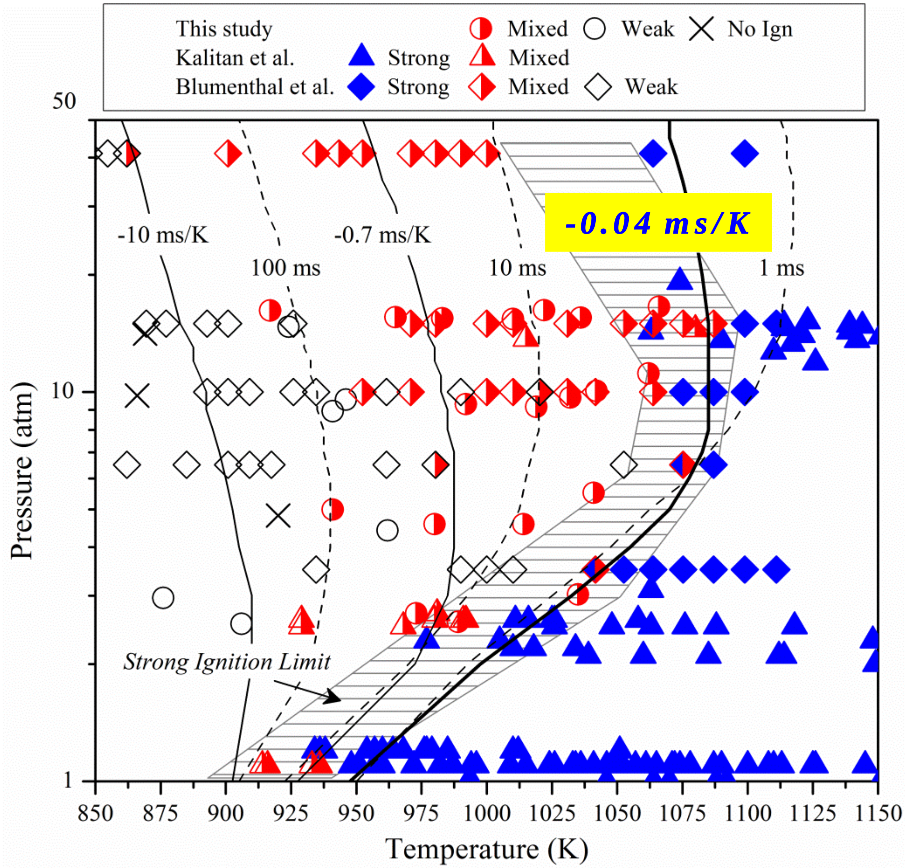
Extended 2nd limit

Classical 2nd limit

- P < 5 atm: explosion limits ~ capture strong ign. limit
- P > 5 atm: Poor correlation

➢ Chemistry is important, but its not the whole story

Thermal sensitivity, $(d\tau_{ign}/dT)_p$

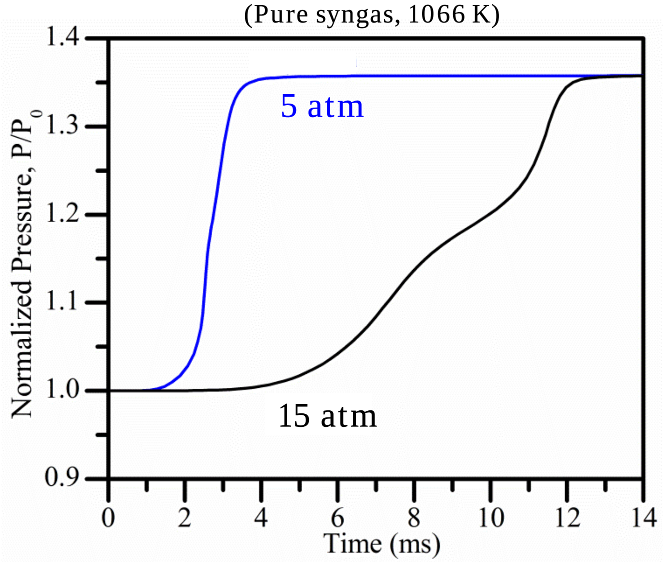


- P < 5 atm: Crit. iso-contour captures strong ign. limit
- P > 5 atm: OK agreement, not quite

➢ Improvement, but not purely predictive; need to *find* critical value

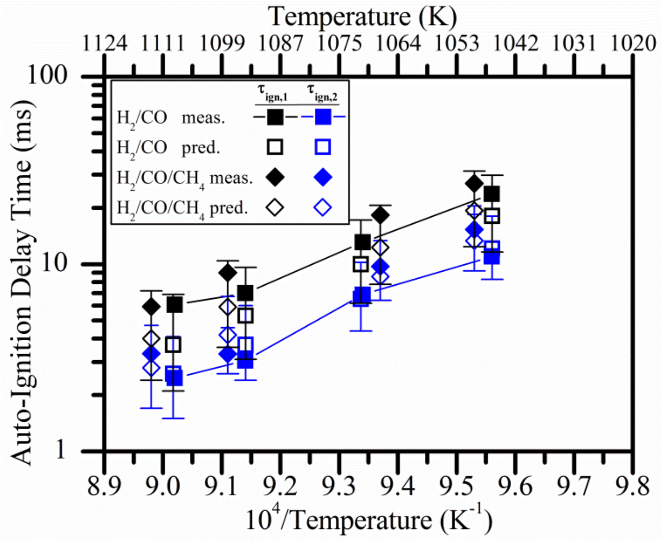
Measurements v. Model Predictions

Predicted P-t history

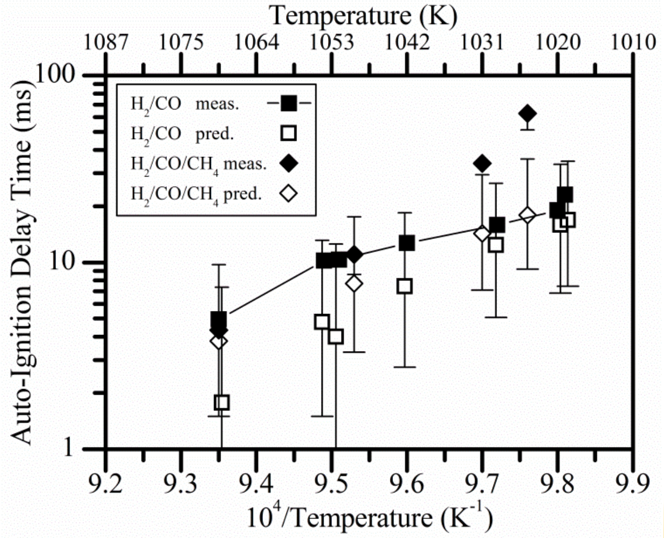


- Modeling accurately predicts 2-step ignition at 15 atm, 1-step 5 atm
- $\tau_{ign,1\ \&\ 2}$ **predictions in excellent agreement** for both P, syn. & syn. + CH_4
- System well represented by Li 2007 mech. and CHEMKIN homog. reactor model

15 atm



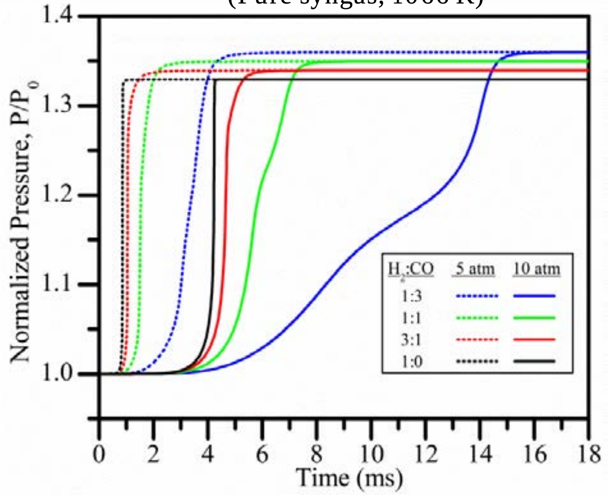
5 atm



Discussion: Why 2-step Ignition?

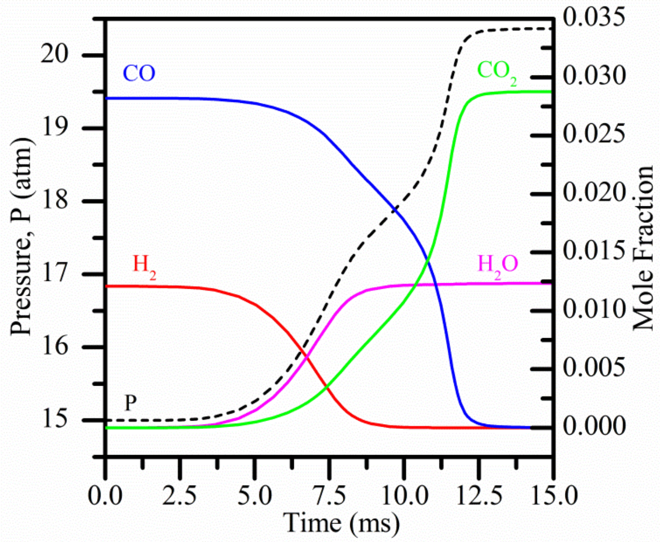
Predicted P-t trends

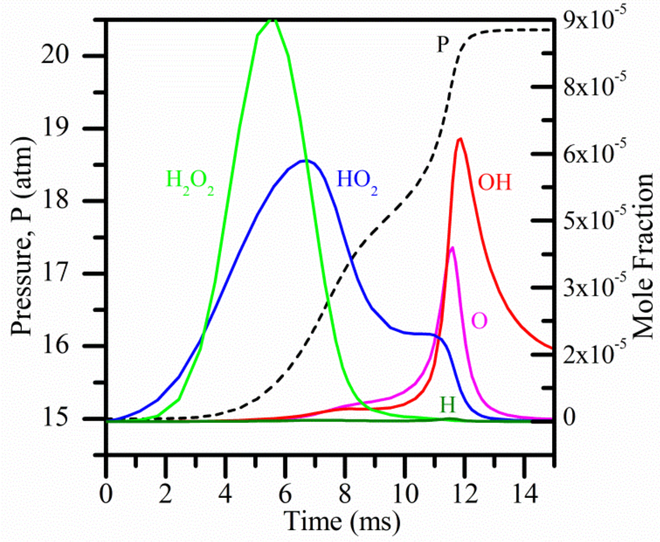
(Pure syngas, 1066 K)



- 2-step behavior minimal at 5 atm, pronounced at 15 atm for high χ_{CO}

Predicted χ_i-t history





(Pure syngas, 15 atm, 1066 K)

Why 2-step ignition?

(ROP and sensitivity analysis)

- $CO + OH = CO_2 + H$ dominates
- OH lag after step 1, H_2 exhausted
- $H + O_2 = OH + O$ v. $H + O_2(+M) = HO_2(+M)$
- Explains P and H_2:CO (T_{step1}) dependence

Discussion: Why promoting effect of TMS?

- Can't investigate directly…
- Jachimowski & McLain and Petersen:
  - SiH_4 in H_2 disrupts formation and/or enhances consumption $\mathbf{HO_2}$
- Simulated these effects using current model with Li 2007 mechanism
  - $H + O_2(+M) = HO_2(+M)$ $(A \times 10^{1,-1,-3})$
  - $HO_2 + HO_2 = H_2O_2 + O_2$ $(A \times 10^{1,-2})$

- Trends of increased reactivity and lowered pressure dependence replicated, but smaller magnitude
- HO_2 interaction likely part of TMS effect
- Good qualitative agreement with other Si-base impurity, SiH_4