Brief Comments on Ignition Delay Characteristics

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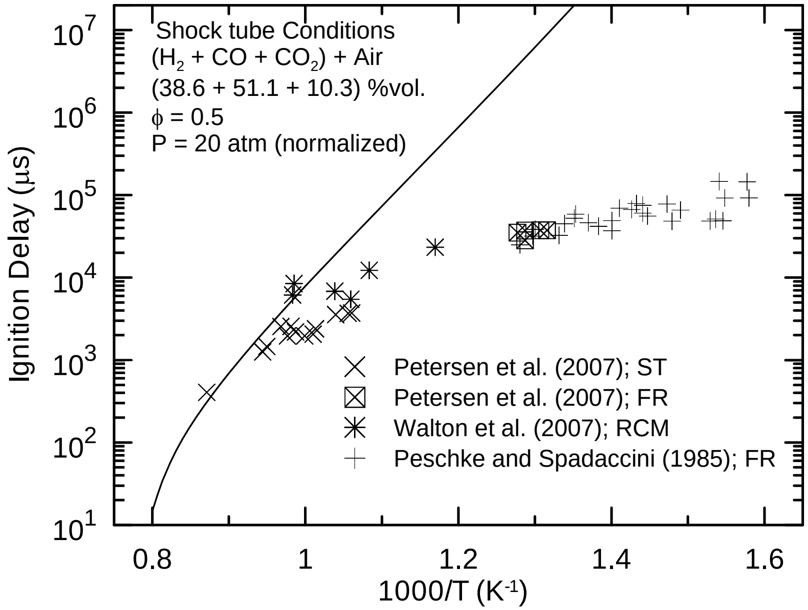
The “Troubling Observation”

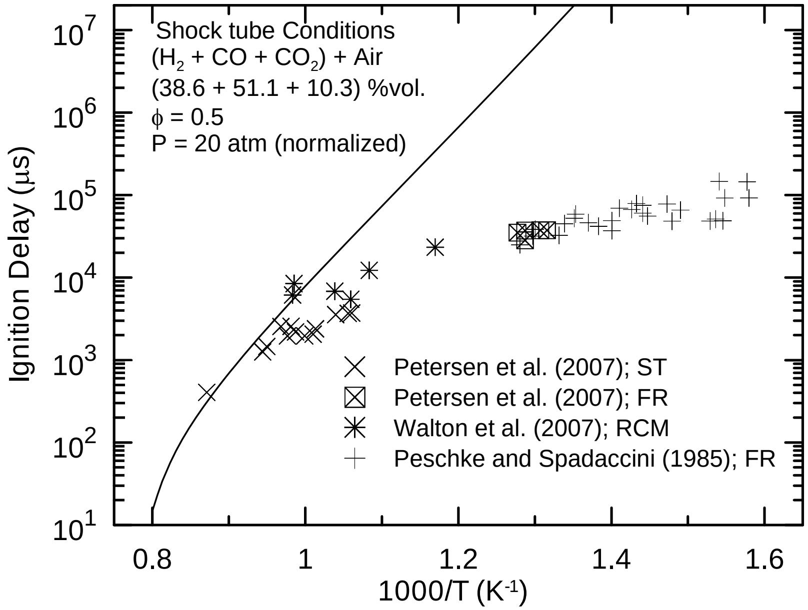


From Petersen et al. Combust Flame (2007)

- Order-of-magnitude differences between “model predictions” and experiments for all gas phase kinetic models presently in the literature for conditions at temperatures below ~1200 K
- Data from various venues, including shock tubes, flow reactors, and rapid compressions machines “appear to be consistent with one another”.
- Concerns raised that chemical kinetic model parameters/reactions may need revision.
- CO only adds three additional elementary reactions to the hydrogen oxidation mechanism.

- “Trends observed for high-pressure low-temperature syngas ignition are not specific to the presence of CO, but to hydrogen” (Yetter, 1985).

The “Troubling Observation”



From Petersen et al. Combust Flame (2007)

*Do we really know the hydrogen – oxygen kinetic mechanism with reasonable predictive accuracy? **Yes, we know it sufficiently well!***

*Are the existing kinetic models really constrained by the above experiments? **No, only indirectly!***

*Can the experiments be modeled as homogeneous kinetic observations? **No!***

- Order-of-magnitude differences between “model predictions” and experiments for all gas phase kinetic models presently in the literature for conditions at temperatures below ~1200 K
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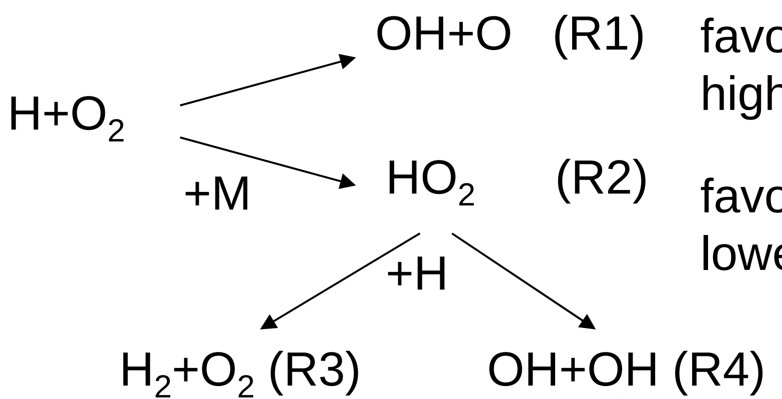
- “Trends observed for high-pressure low-temperature syngas ignition are not specific to the presence of CO, but to hydrogen” (Yetter, 1985).
- *Has similar behavior been observed in H_2 systems? (**Yes**!)…and for a very long time!*
- *Syngas ignition is strongly driven by H_2/O_2 kinetics !*

The Impacting Parameters

- *Kinetics!* (Reactive radical initiation, and radical pool growth)
  - Radical Initiation - How are radicals first generated?
    - ***Very difficult to generate the first radical for H_2, CH_4, but not for large hydrocarbons as the fuel!***
      - *Thermal decomposition very slow, direct reactions with O_2 slow and not well quantified*
  - Radical chain propagating reactions e.g. $H_2+OH = H_2O + H$
    - ***These reactions are very exothermic, accelerating the rate of reaction by raising the reaction temperature.***
  - Radical Chain Branching , e.g. $H+O_2 = OH + O$
    - ***These reactions control the rate of growth of the radical pool***
  - Radical Termination e.g. $H+OH+M = H_2O + M$
    - *Pseudo Termination* – $H+O_2+M = HO_2+M$ (if HO_2 does not regenerate more active radicals on a comparable time scale)
    - ***These reactions temper radical pool growth rate***
  - ***The net of chemical branching and termination must exceed a critical branching condition to lead to an exponential growth of the radical pool***
  - Temperature/pressure dependence of the individual reaction rates.
- *Heterogenous Ignition* (Thermal center development and transition). Depend on:
  - Heat release rate accompanying the overall reaction chemical rate
  - Energy density of the reacting media (diluent, oxidizer, fuel, pressure)
  - *Fluid dynamical characteristics, boundary conditions of the experimental venue.*
    - Turbulent fluctuations, heat loss, inhomegenieties, etc.

Effect of Pressure on Critical Chain Branching

- The fate of H radicals reacting with molecular oxygen:



$H+O_2 \rightarrow OH+O$ (R1) favored at lower pressures and higher temperatures

$H+O_2 \xrightarrow{+M} HO_2$ (R2) favored at higher pressures and lower temperatures

$HO_2 \xrightarrow{+H}$ H_2+O_2 (R3) / $OH+OH$ (R4)

- HO_2 paths are active on an appropriate time scale at high P's and T's
  - R1/R2 competition still a major factor in pressure dependence of critical branching.
  - Other HO_2 reactions modify termination by (R2) and result in reduced branching through (R1) required to reach critical condition ("extended second explosion limit").

$$\frac{k_3+k_4}{2k_3}\frac{2k_1}{k_2[M]}<1 \longrightarrow$$ Chain-carrying (slow)

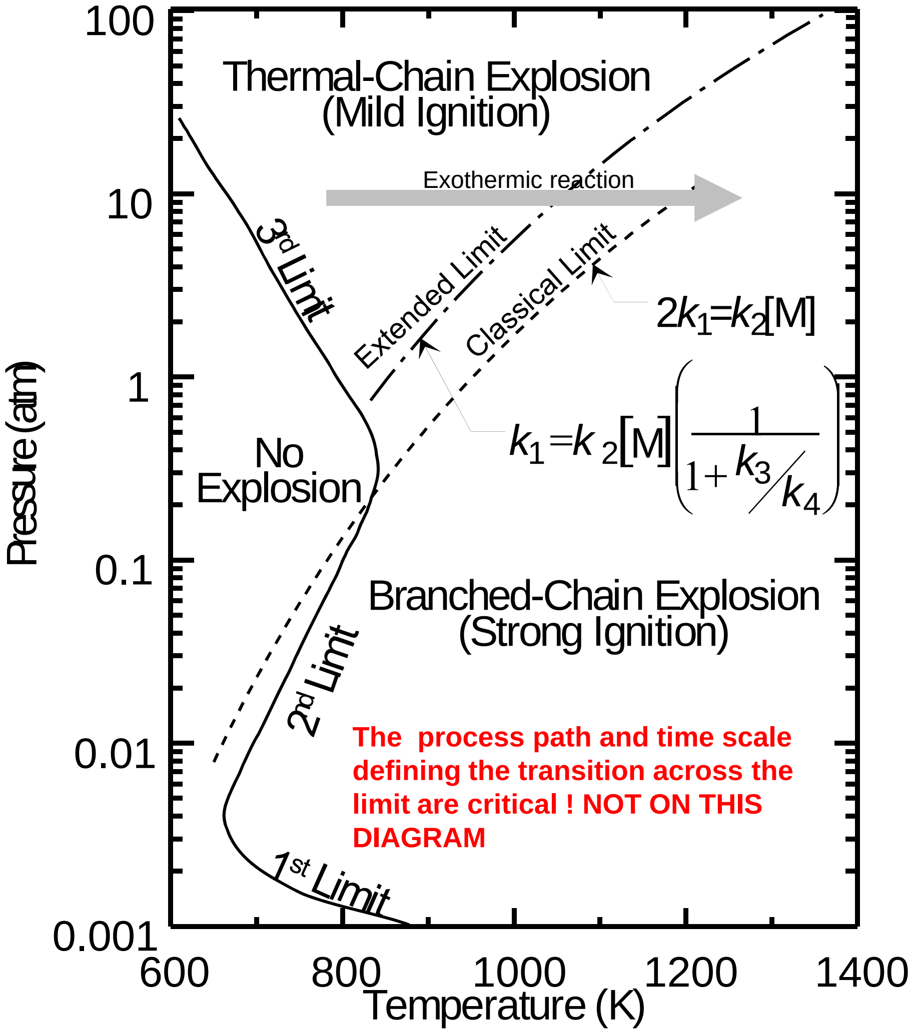
$$\frac{k_3+k_4}{2k_3}\frac{2k_1}{k_2[M]}>1 \longrightarrow$$ Chain-branching (fast)

  - Observed in flow reactor and counter-flow ignition studies.

1. M.A. Mueller, T.J. Kim, R.A. Yetter, F.L. Dryer, Int. J. Chem. Kinet. 31 (1999) 113–125.
2. X.L. Zheng, C.K. Law, Combust. Flame 136 (2004) 168–179.

Explosion Limits and Ignition Delay Properties

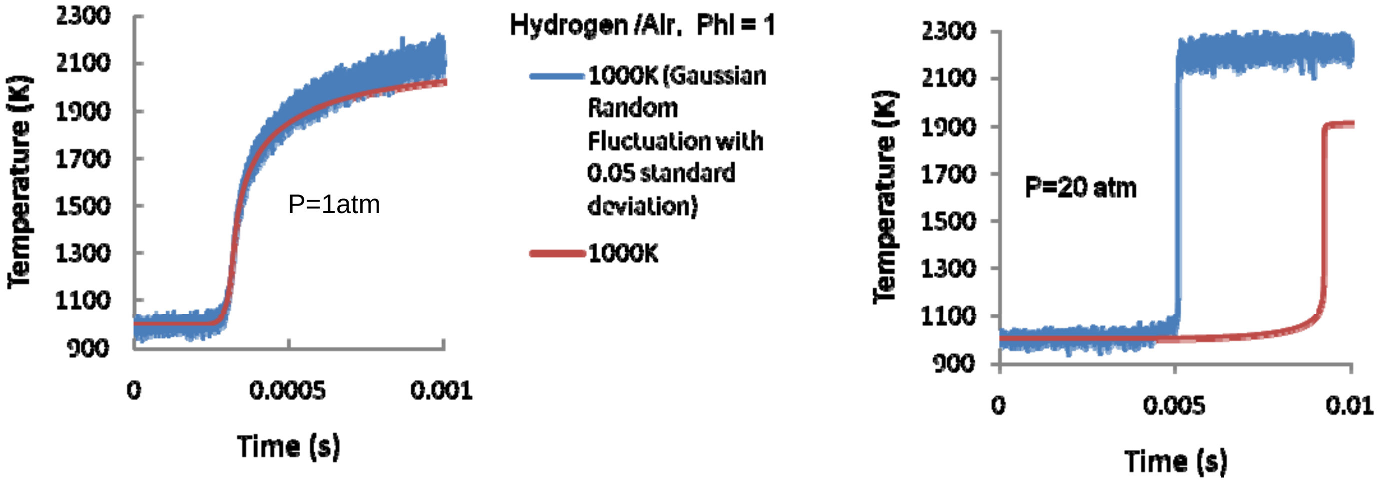
- For the same pressure, the extended second limit results in reduced "termination" from HO_2 reactions and critical branching occurs at lower temperature for the same pressure.
- The reduction in termination is dependent on rate constants of reactions that have significant uncertainties (k_3, k_4).
- Other species added to hydrogen oxidation can affect the rates of branching and termination and shift the pressure and temperature at which chemical branching becomes dominant in the oxidation.
- Instability analysis of this system shows highly sensitive region along the extended limit location boundary (Yetter et al.,1991).



The process path and time scale defining the transition across the limit are critical ! NOT ON THIS DIAGRAM

R.A. Yetter, H. Rabitz, and R.M. Hedges, Int. J. Chem. Kin. 23 (1991) 251-278.

Turbulent Fluctuation Effects on Ignition Delay



Comparison of ignition delay at constant pressure and with a fluctuating pressure (Gaussian random pressure fluctuation of 5% of mean) using detailed kinetic model of Li et al (2004). Temperature fluctuation generated by polytropic expression.

Result gives only 2% decrease in ignition delay at 1 atm pressure, but a 47% decrease at 20 atm

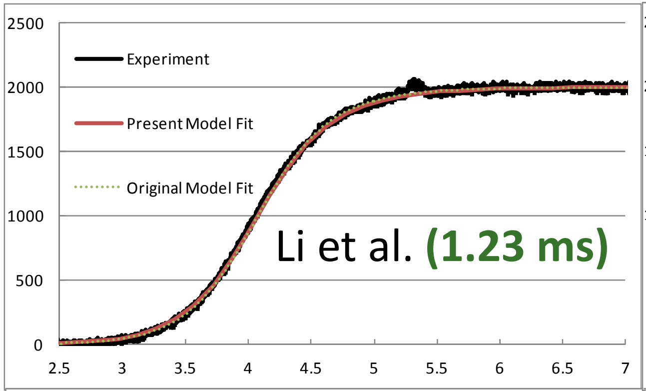
The difference occurs because Mild ignition limit is near ~ 1100 K at 20 atm and at about 928 K at 1 atm.

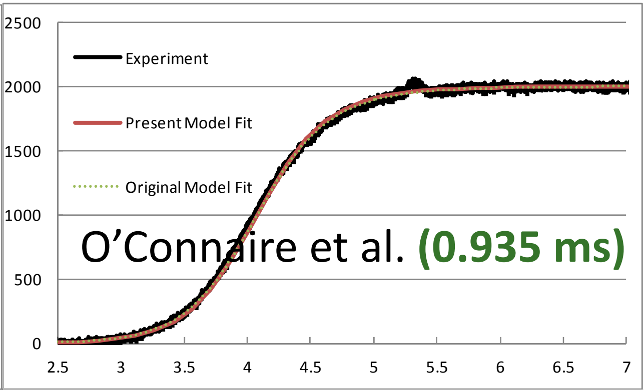
Calculations by T. Farouk 10/12/2010, Princeton

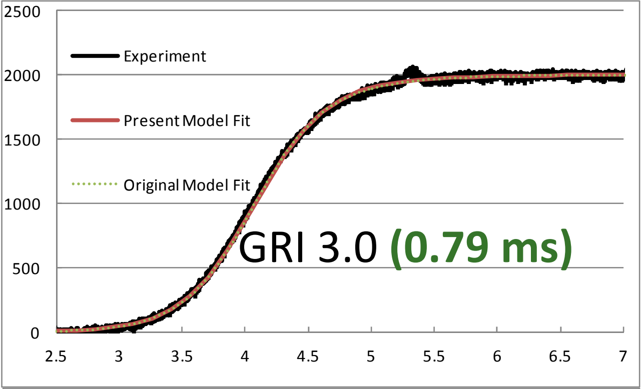
Impurities Can Modify Chemical Induction Behavior

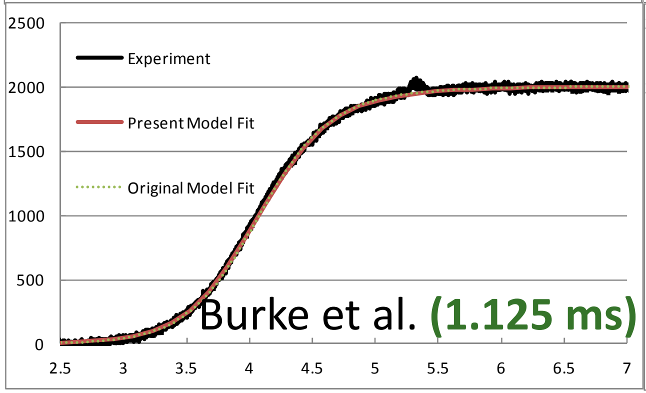
1100 K, 1.95 atm F. Dryer, F. Haas, J. Santner, T. Farouk and M. Chaos, Prog. En. Combust. Sci. 44 (2014)19-39

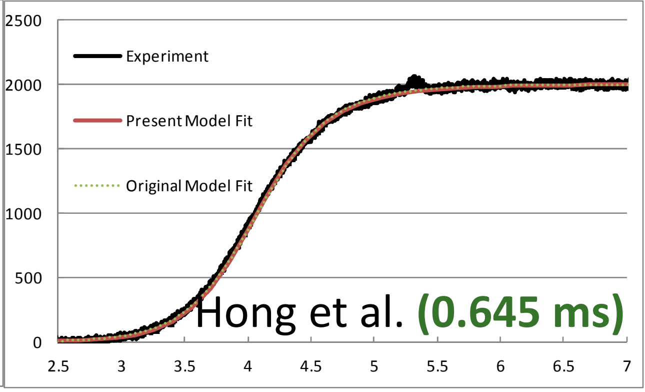
1) Black Line – experimental measurement
2) Green Line – Original Authors' Model Fit with ***(model dependent)*** **1.1 ppb H atom spiking**
3) Red Lines – Alternative Model Fits with model dependent time shifts **(denoted in blue)**

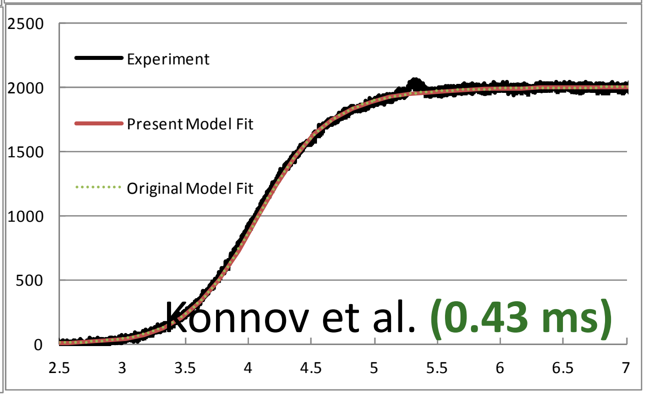










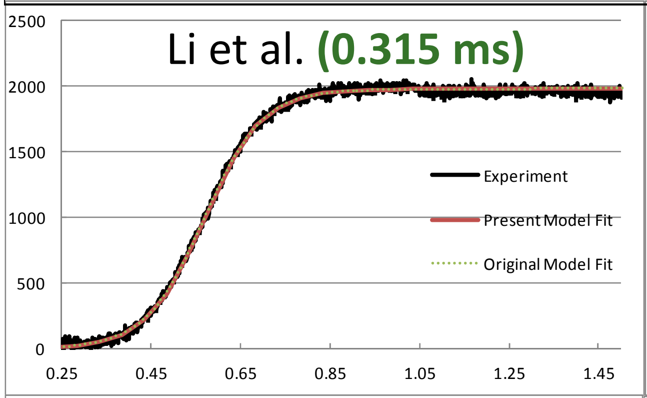


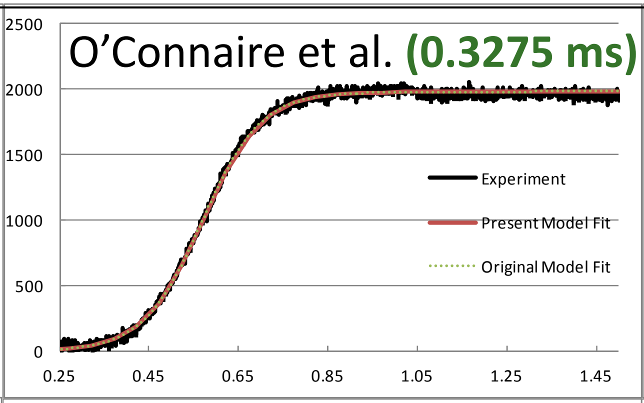
Simulations for adiabatic, CONV process using kinetic model indicated with kH+O2=O+OH adjusted for red line fits. Additional Experimental/Modeling Details in Hong et al. (2011). Y-axis: mole fraction H2O (ppm); X-axis: time (ms)

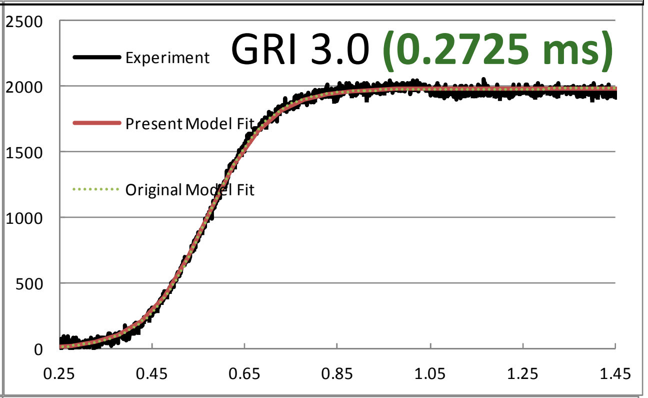
Impurities Can Modify Chemical Induction Behavior

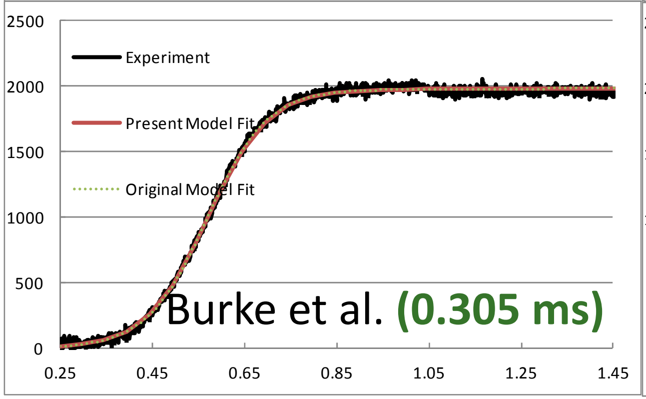
1472 K, 1.83 atm F. Dryer, F. Haas, J. Santner, T. Farouk and M. Chaos, Prog. En. Combust. Sci. 44 (2014)19-39

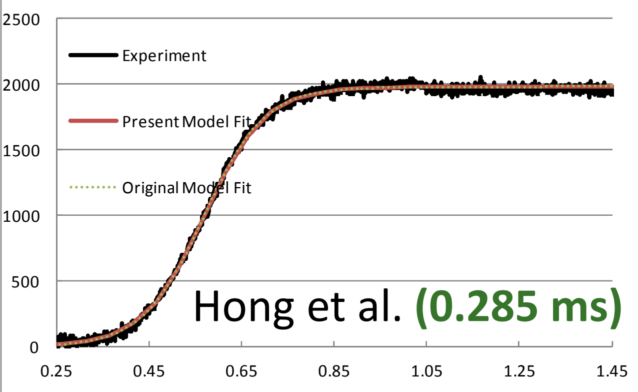
1) Black Line – experimental measurement
2) Green Line – Original Authors' Model Fit with ***(model dependent)*** **350 ppb H atom spiking**
3) Red Lines – Alternative Model Fits with model dependent time shifts **(denoted in blue)**

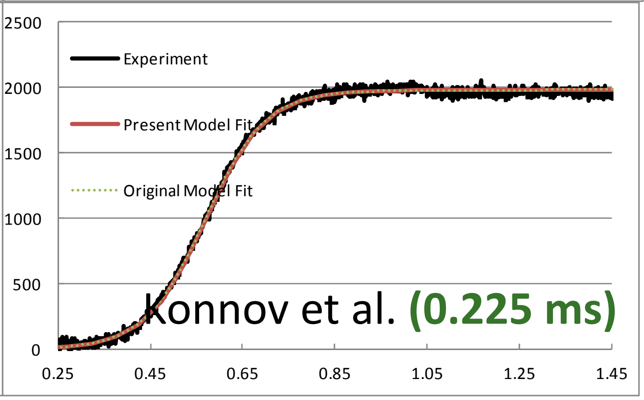












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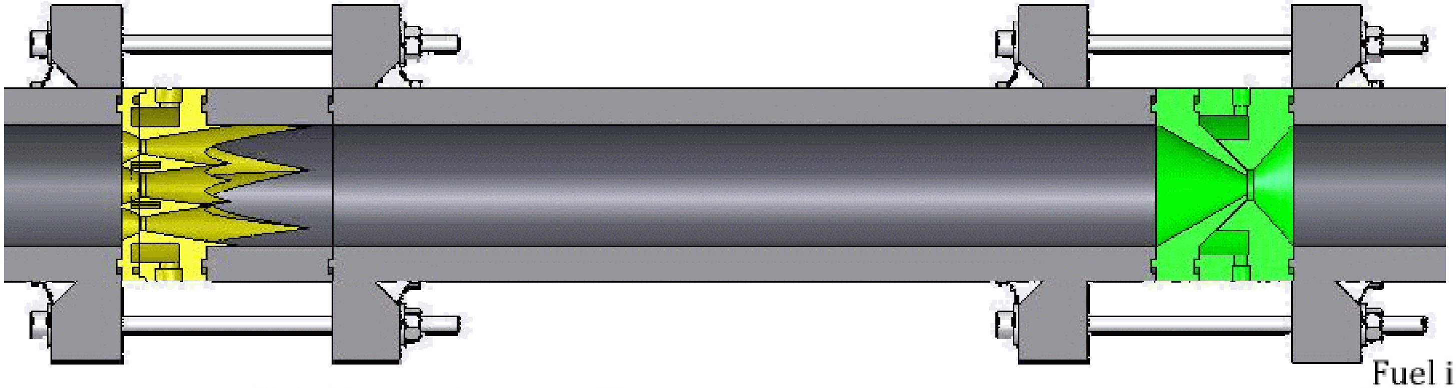
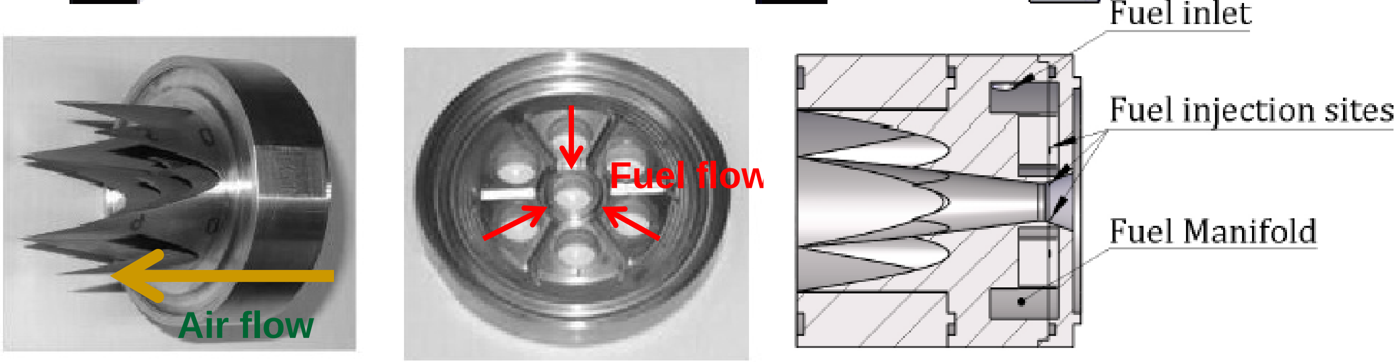
Flow Tube Mixer Designs Affect Ignition Delay

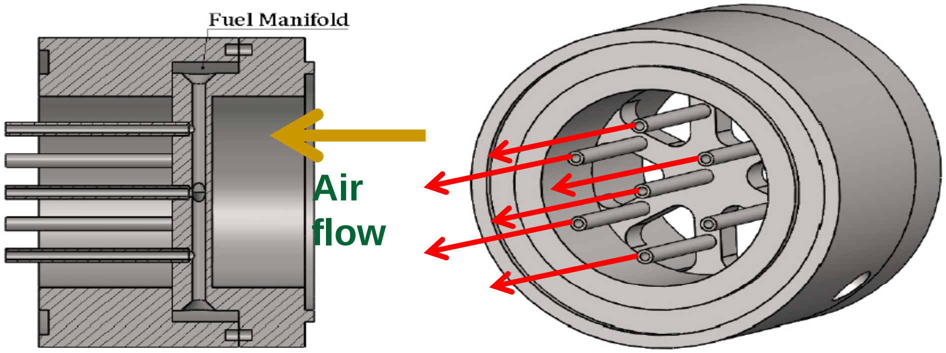


Radial Injection Mixer Design used by all Prior Flow Tube Studies (UTRC, UCI, PSU)

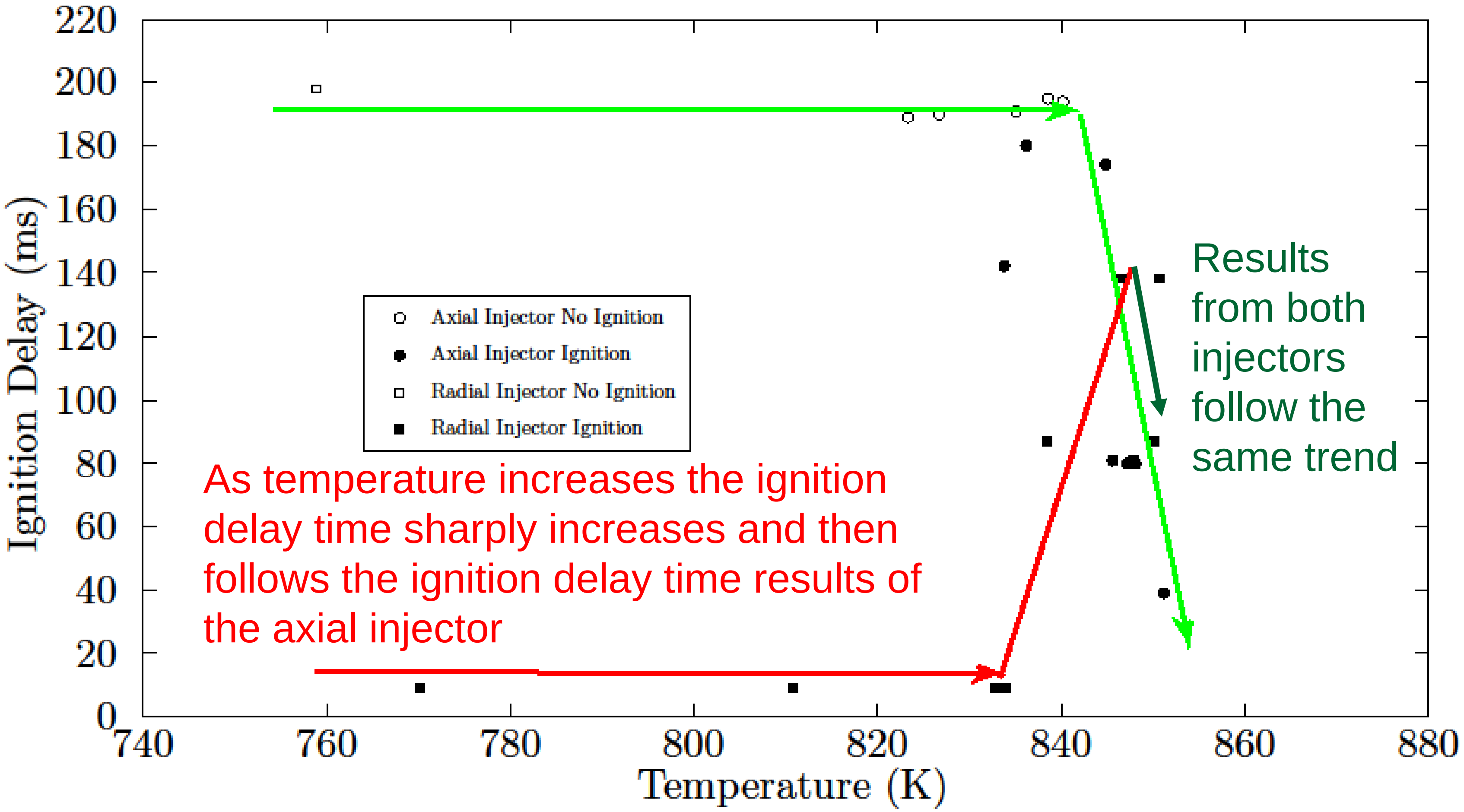


R.J. Santoro, DOE Grant # DE-NT0000752 (2012)

Axial Injection Mixer Design substituted by Santoro (PSU)



Ignition Delay Times: Axial Injector Compared to Radial Injector

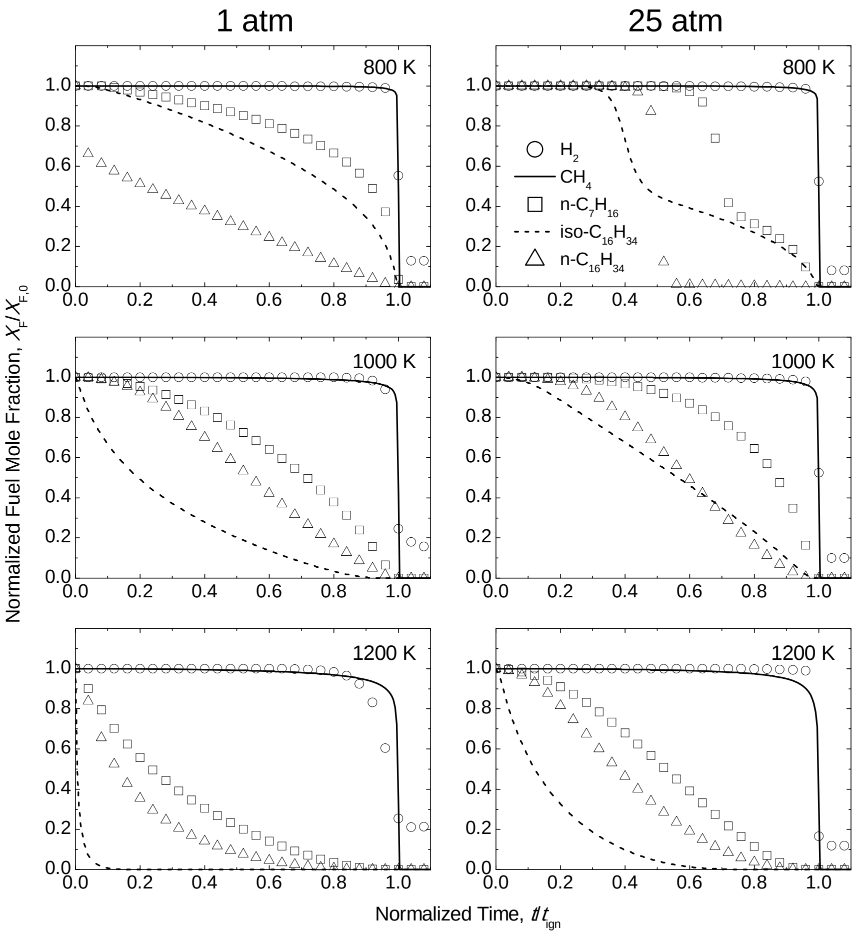


As temperature increases the ignition delay time sharply increases and then follows the ignition delay time results of the axial injector

Results from both injectors follow the same trend

R.J. Santoro, DOE Grant # DE-NT0000752 (2012)

Ignition Delay Properties for Fuels at Different P and T



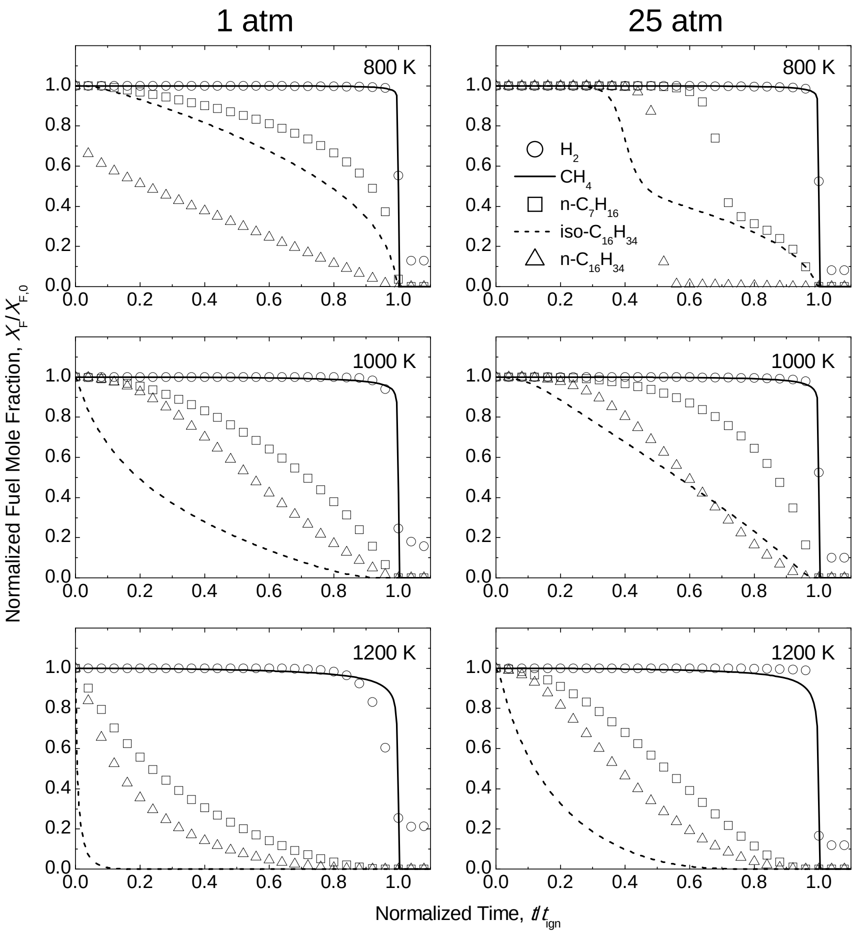
Very little fuel is consumed prior to ignition for H_2, CH_4

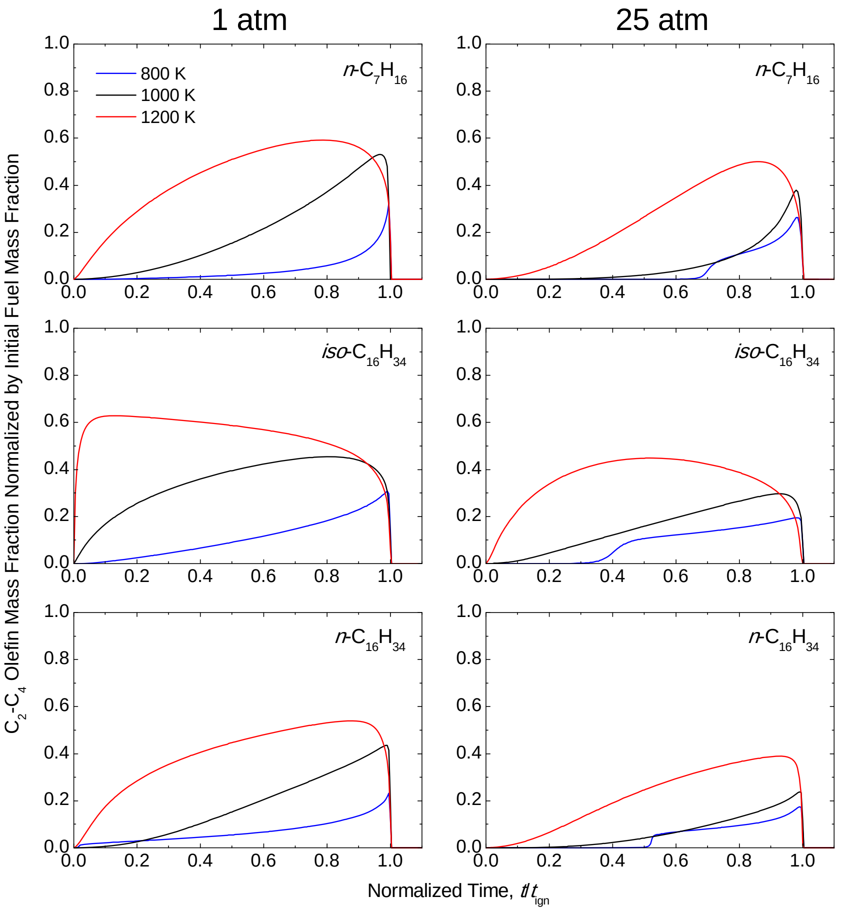
Fuel is entirely converted to small olefins, CO for large hydrocarbon with major heat release at the ignition delay condition resulting primarily from CO Olefin, CO oxidation, see right frame, next slide

Here the “ignition delay is defined by the inception of rapid heat release rate. Computed fuel profiles during ignition of stoichiometric fuel/air mixtures at isochoric conditions are plotted v reaction time normalized by the ignition delay.

F.L. Dryer , Proc Combust Ins. (2014) In press

Ignition Delay Properties for Fuels at Different P and T



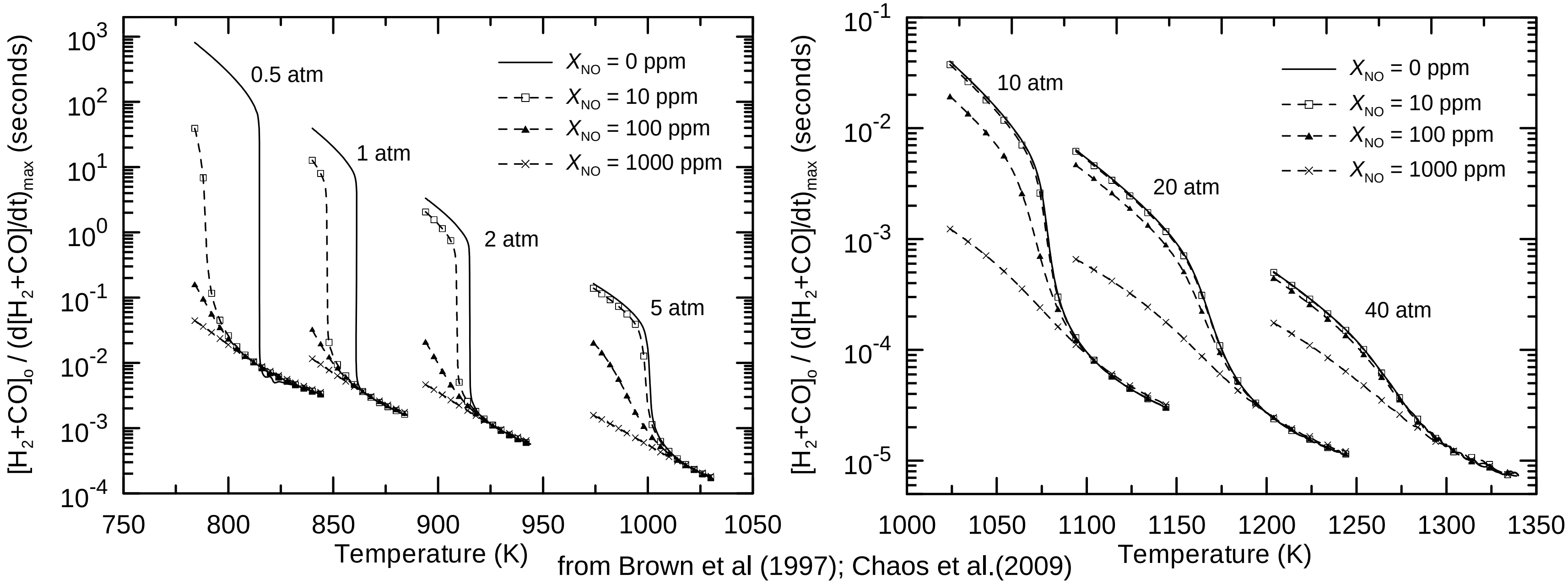


Computed fuel profiles during ignition of stoichiometric fuel/air mixtures at isochoric conditions. Fuel mole fraction (X_F) normalized initial mole fraction ($X_{F,0}$); time normalized by each ignition delay time. $\Sigma(C_2 - C_4)$ olefin mass fraction normalized by initial fuel mass fraction.

F.L. Dryer , Proc Combust Ins. (2014) In press

Overall Reaction Rate Variations with P

Conditions - $H_2/CO/O_2/N_2/Ar = 6.25/6.25/6.25/18.125/63.125$



from Brown et al (1997); Chaos et al.(2009)

- “Explosion limit” moves to significantly higher temperatures at increased operating pressures.
- Change in maximum reaction rate decreases dramatically at higher pressures.
- Small amounts of NO/NO_2 can have dramatic effects on the maximum rate of reaction and ignition phenomena near the extended second limit.
- Effect is even more dramatic at higher hydrogen content.
- Most conservative control of reaction rate is *Temperature*.

M. Chaos, M.P. Burke, Y. Ju, F.L. Dryer, Syngas chemical kinetics and reaction mechanisms, in: T.C. Lieuwen, V. Yang, R.A. Yetter (Eds.), *Synthesis Gas Combustion: Fundamentals and Applications*, Taylor & Francis, 2009, pp. 29–70.

Methyl Radical Ignition Kinetics

$CH_4+M=CH_3+H+M$

$CH_4+O_2=CH_3+HO_2$

$CH_3+O_2=CH_3O+O$

$CH_3+O_2=CH_2O+OH$

$CH_3+CH_3+M=C_2H_6+M$

$C_2H_6+CH_3=C_2H_5+CH_4$

$C_2H_5+(O_2, M) \rightarrow$ radicals

$CH_3+HO_2=CH_3O+OH$

$CH_3+O_2=CH_3O_2 \rightarrow$ radicals

- Because of the slow reactions of methyl radicals with oxygen,it is difficult to develop the radical pool in pure methane oxidation.
- Addition of small hydrocarbons or NOx can accelerate ignition processes of pure methane.

- Because NO_2 react directly and rapidly with methyl radicals, the radical pool is developed faster.
- The resulting NO regenerates NO_2 through reaction with HO_2 radicals.
- High pressure accentuates HO_2 coupling.

$CH_3+NO_2=CH_3O+NO$

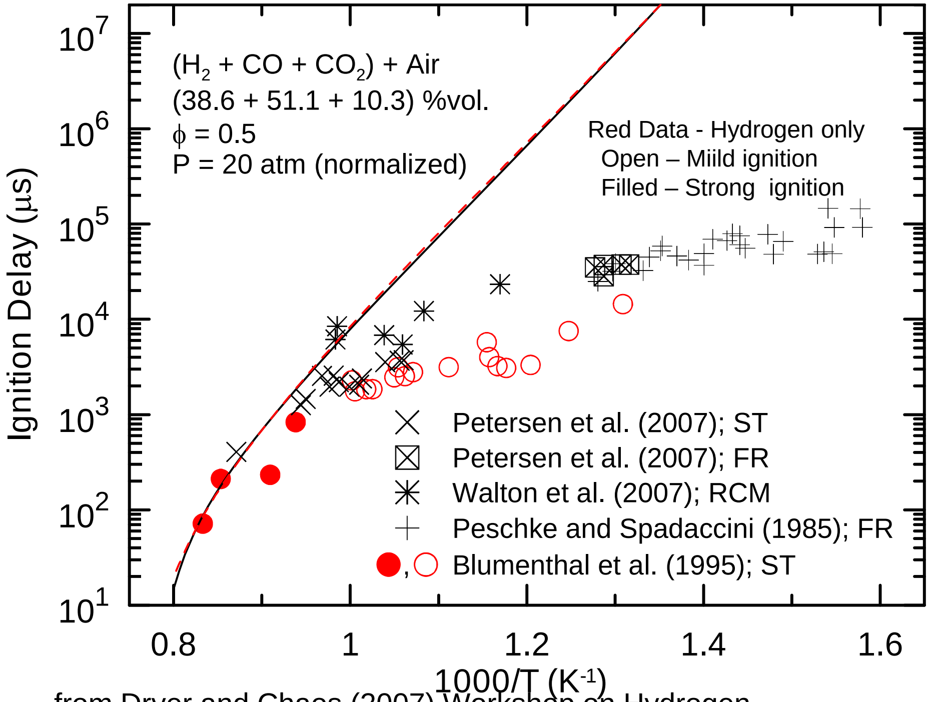
$CH_3O+M=CH_2O+H$

$CH_2O+OH=HCO+XH$

$HCO+O_2=CO+HO_2$

$NO+HO_2=NO_2+OH$

Experimental Ignition Results for Hydrogen and Syngas



from Dryer and Chaos (2007) Workshop on Hydrogen Combustion in Gas Turbines, EPRI Washington, DC March 22; Later published in: Dryer and Chaos (2008); Chaos and Dryer (2008); Chaos et al. (2009).

Shock Tube Ignition Measurements –

- At lower T where the onset of the large model/experiment discrepancies occur, the ignition process in reflected shock experiments is identified as “mild” (open symbols) observations and *are not homogenous events.*

Rapid Compression Machine Measurements -

- RCM experiments are sometimes affected by mild ignition transition effects (e.g., Walton et al. 2007) while others (Lee and Hochgreb (1998), Mittal et al.; 2006) for hydrogen and syngas ignition follow homogenous predictions (Chaos and Dryer, 2008). Recent RCF data clearly indentify that mild ignition observations *are not homogeneous events*.

Flow Reactor Measurements -

- Flow reactor ignition delays are subject to large uncertainties when measurements are undertaken in the mild ignition regime for hydrogen (Vermeersch, 1993; Beerer and McDonald, 2009; Santoro and coworkers, 2010). Recent work of Santoro and others suggests that flow tube mixture preparation methods appear to affect experimental observations.

In applied combustion systems, high hydrogen content fuels may exhibit very short ignition delays in comparison to ***homogeneous*** *kinetic predictions. Actual values are better represented by experimental correlations or models empirically adjusted to reproduce experimental data, e.g., see Chaos et al. (2008, 2009). Small perturbations of the system in the mild ignition regime can lead to the noted experimental behavior. The source(s) of such perturbations that result in local thermal center formation are numerous and likely cannot be eliminated. The above curve serves as essentially an engineering design limit for a specific mixture. Translating these results to gas turbine applications that reflect fuel injection and mixing processes over a range of energy densities, equivalence ratios, and operating pressures are complex.*