An Experimental and Chemical Kinetics Study of the Combustion of Syngas and High Hydrogen Content Fuels

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National Energy Technology Laboratory

FY10 Advanced Turbines Peer Review

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Project Overview:
Scope of Work

Studies of high pressure HHC fuel kinetics using Laminar Flow Reactor (HPLFR) (Dryer)

Measurements of burning rates and intermediate species of high pressure HHC fuel combustion by using a nearly constant-pressure bomb with TALIF and LIF (Ju)

Kinetic assessment, validation, and development of a comprehensive C1 mechanism (Ju)

HHC fuels ignition delay studies in a high-pressure, high-temperature flow reactor (Santoro)

Presentation Part 1
(Princeton University)

- **Development of validated high hydrogen syngas kinetic mechanism at pressures of gas turbine conditions**
- **Development of computationally efficient, reduced kinetic modeling algorithm**
- **Conclusion**
- **Future work**

1. Development of validated high hydrogen syngas kinetic mechanism at pressures of gas turbine conditions

Motivation

- **H_2/O_2 system**
  - Core subset mechanism for all hydrocarbon fuels
  - Major compositions of high hydrogen syngas for advanced turbines
- **Combustion at high pressure, low flame temperature, fuel-lean conditions in advanced turbines**
- **Previous H_2 flame measurements at high pressures are relatively sparse**
  - *Tse et al. 2000, Bradley et al. 2008, Burke et al. 2010, Burke et al. 2011*
  - Few flame measurements focus on *high pressures* (>10 atm) and *low flame temperatures* (1400-1800K) – substantial modeling difficulties

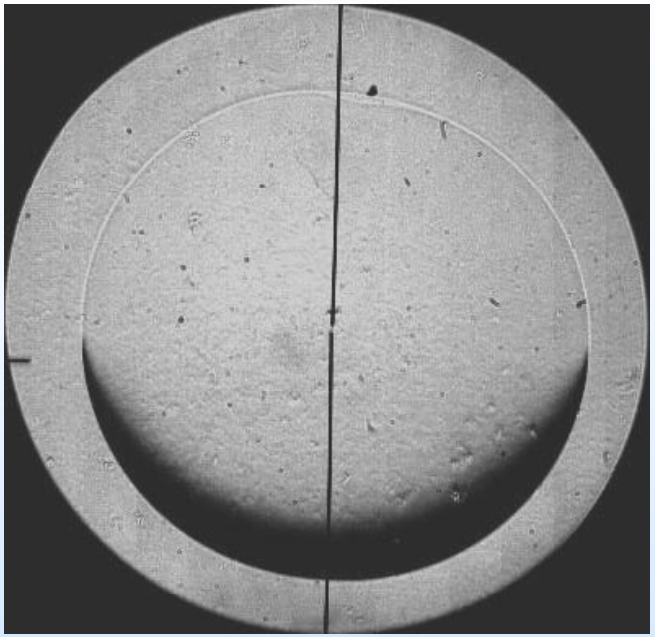
Objectives

- **Test H_2/O_2 Mechanism performance at GT conditions**
  - Measure burning rates of syngas-relevant mixtures for
    - Equivalence ratio: 0.3 to 2.5
    - With CO / CO_2 / CH_4/C_2H_4 / C_2H_6 dilutions
    - Pressure: 1 to 25 atm
    - Flame temperature: 1400 K to 1800K
  - Mechanism assessment: measurements vs. recent kinetic models

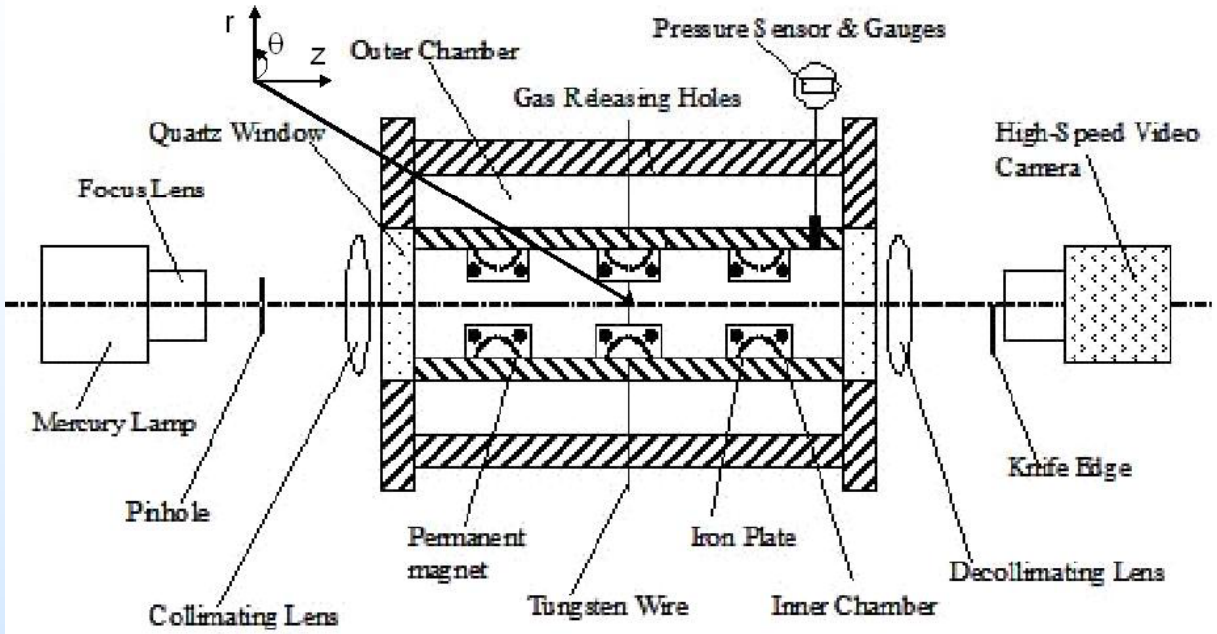
- **Analysis of kinetic pathways at high pressures**
  - With varying equivalence ratio
  - With additives and diluents

- **Update H_2/O_2 kinetic model**

Experimental Methods (I): Apparatus



(Taylor 1991, Faeth & co-workers 1992)



(Tse et al. 2000, Qin & Ju 2005)

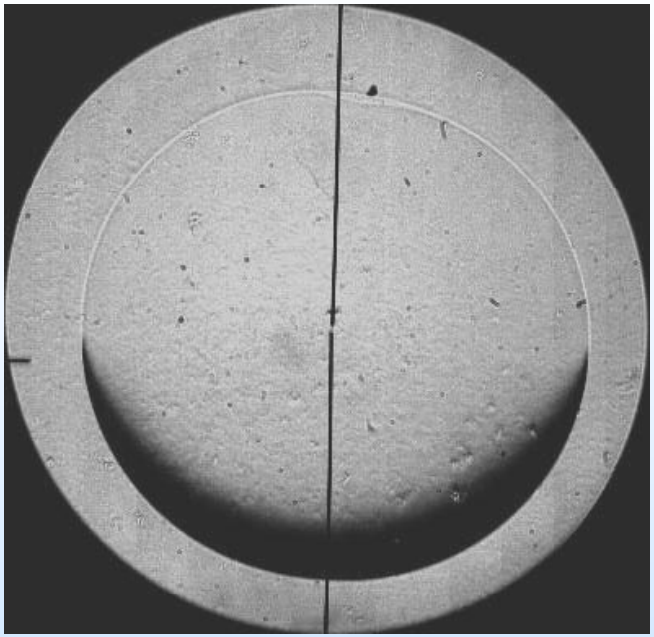
Stretch-corrected burning velocities from outwardly propagating flames at constant-pressure

Present experiment *(Qin & Ju 2005)*:

- Dual-chambered cylindrical bomb
- Initial pressures up to 30 atm
- Dimensions: 10 cm dia. by 15 cm length

X. Qin & Y. Ju, *Proc. Combust. Inst.*, 2005
Burke, Dryer, Ju, Combust. Flame, 2010.

Experimental Methods (II): Technique



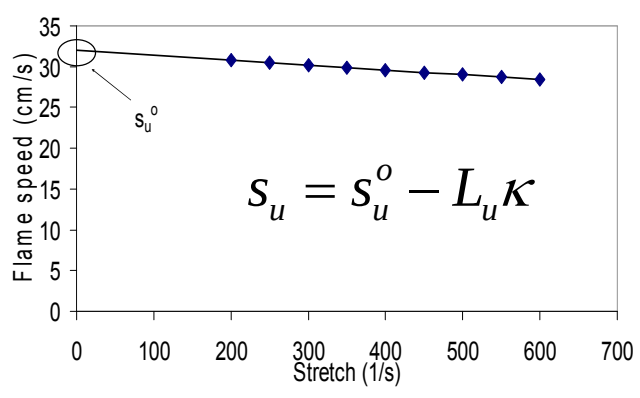
(Taylor 1991, Faeth & co-workers 1992)

Constant-Pressure Method: **Conventional method**

1. Ignition at the center
2. High-speed Schlieren imaging
3. Measure flame front history: r_f vs. t
4. Extrapolate to zero stretch rate

Assumption

$$s_u = \frac{\rho_b}{\rho_u} \cdot \left(\frac{dr_f}{dt} - \cancel{u_b}^{\,0} \right) \qquad \kappa = \frac{2}{r_f} \cdot \frac{dr_f}{dt}$$



Stretch-corrected burning velocities from outwardly propagating flames at constant-pressure

1. S.C. Taylor, *Phd. Thesis (Leeds University)*, 1991.
2. G.M. Faeth & co-workers 1992.

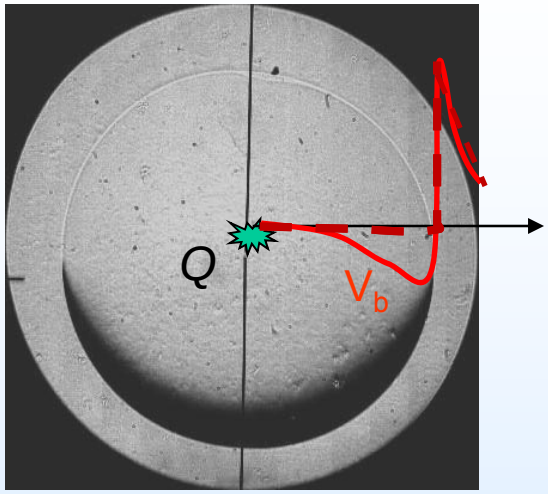
Experimental Methods (III): Flow correction method

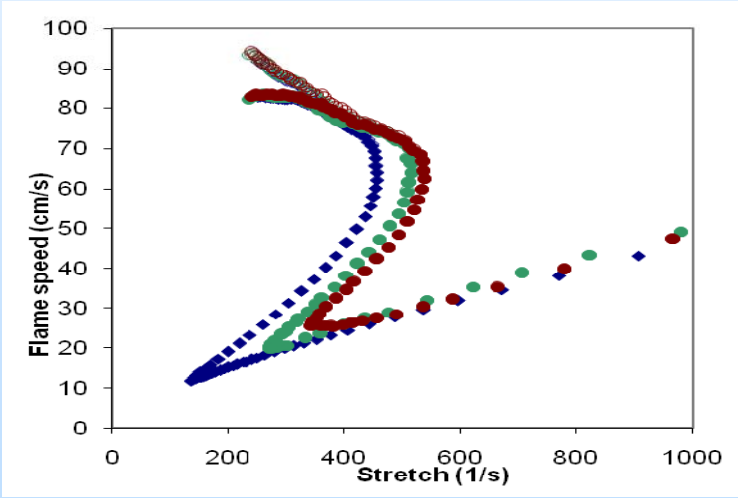
Compression, cylindrical confinement induces flow in the burned gas

Flame speed calculation must account for flow motion:

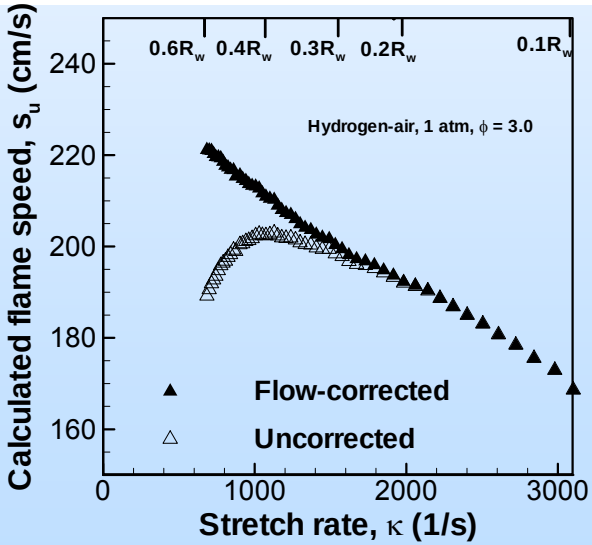
$$s_u = \frac{\rho_b}{\rho_u} \cdot \left(\frac{dr_f}{dt} - u_b \right) = \frac{\rho_b}{\rho_u} \cdot \frac{dr_f}{dt} \left(1 + \frac{\rho_u - \rho_b}{\rho_u} \varpi \right)^{-1}$$

(Burke et al. 2009)





(Chen et al. 2009)

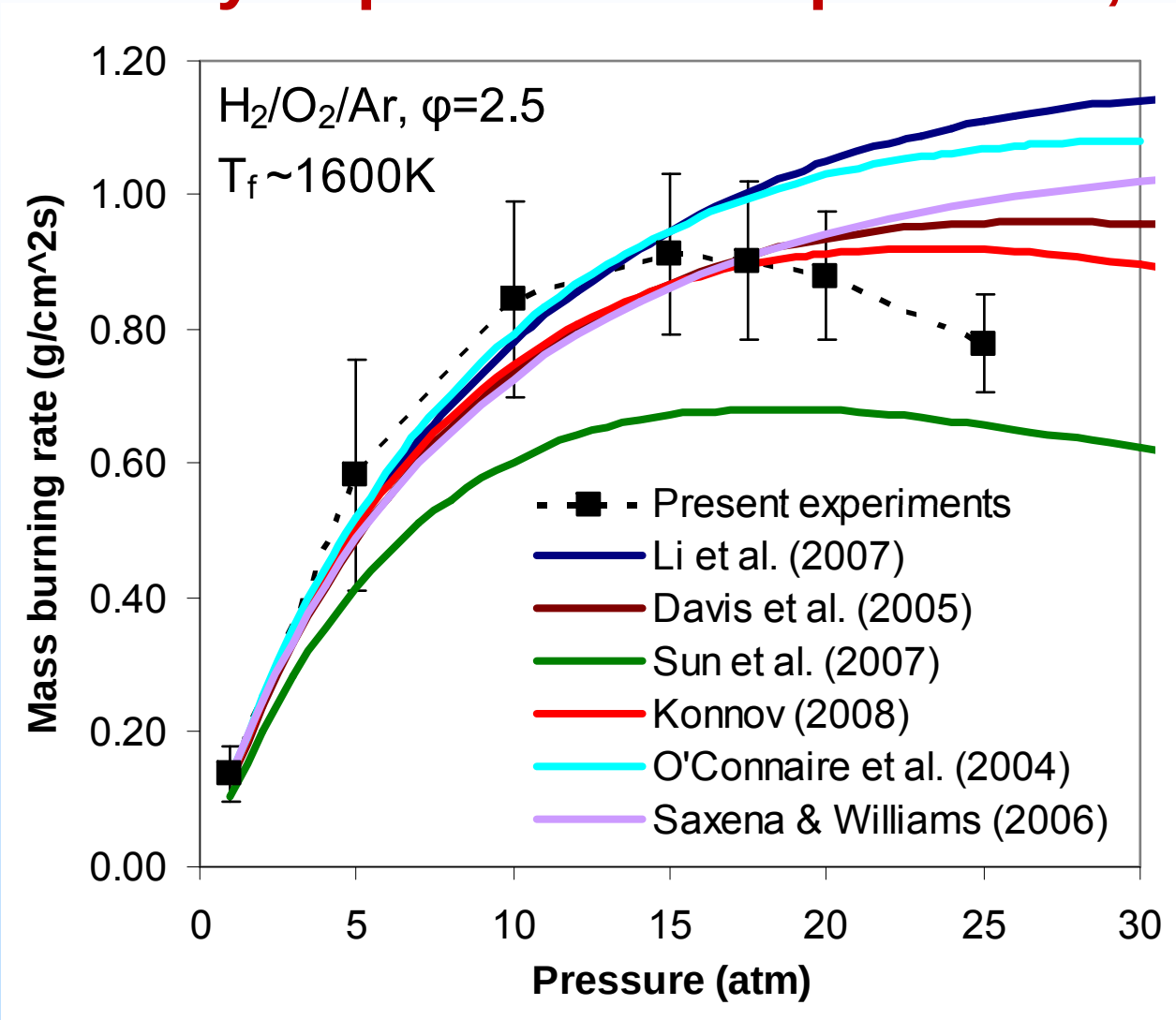


M.P. Burke, Z. Chen, Y. Ju, F.L. Dryer, *Combust. Flame* 156 (2009) 771-779.

Z. Chen, M.P. Burke, Y. Ju, *Proc. Combust. Inst.* 32 (2009) 1461-1469.

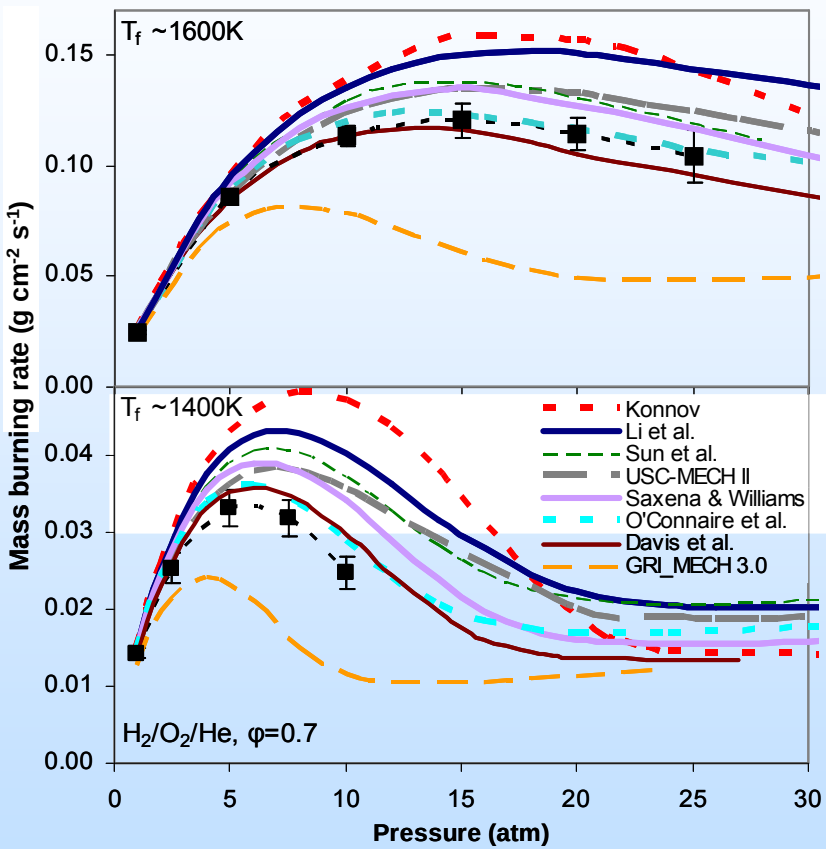
Experimental data and mechanism validation

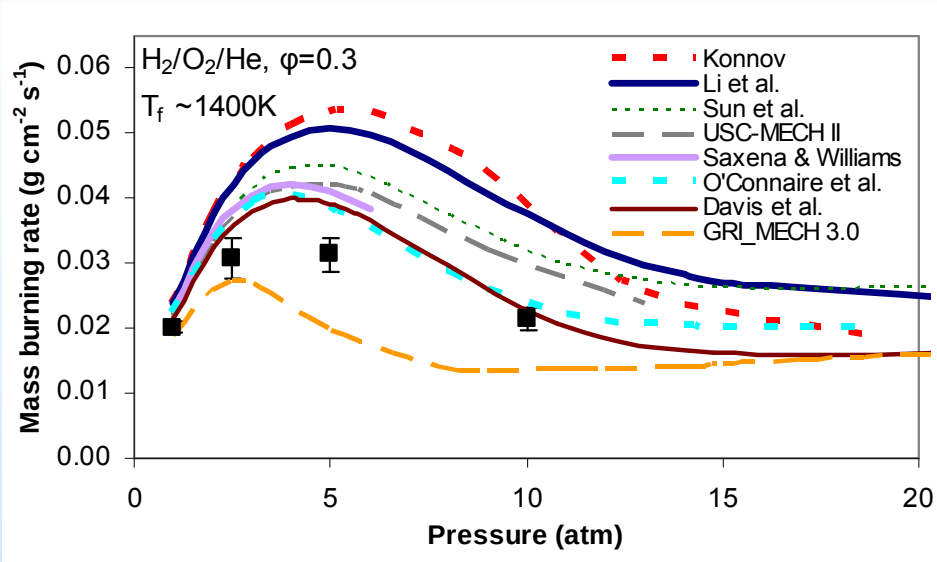
Burning velocity dependence on pressure, rich H_2/O_2



Experimental data and model validation:

Lean H_2/O_2/diluent mixtures



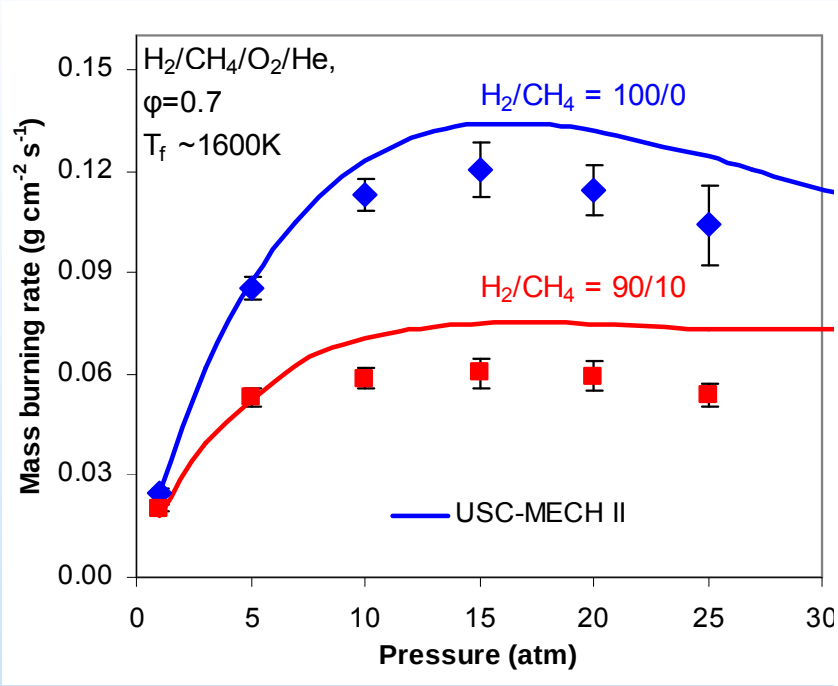


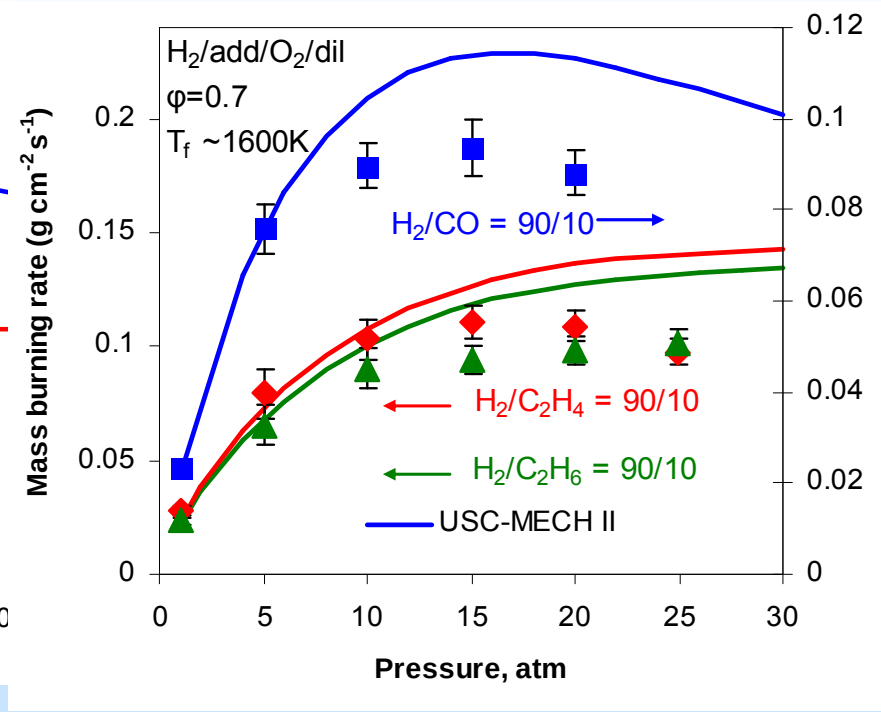
- Mass burning rate increases then decreases with pressure
- Pressure of peak burning rate is lower for lower flame temperatures
- Large variations among models – up to a factor of 4
- None of the models capture pressure dependence for very lean mixtures

M.P. Burke, F.L. Dryer, Y. Ju, "Assessment of kinetic modeling for lean $H_2/CH_4/O_2$/diluent flames at high pressures," *Proceedings of the Combustion Institute* (2010) in press.

Experimental data and mechanism validation

$H_2/O_2/$*fuel-additive*/diluent mixtures



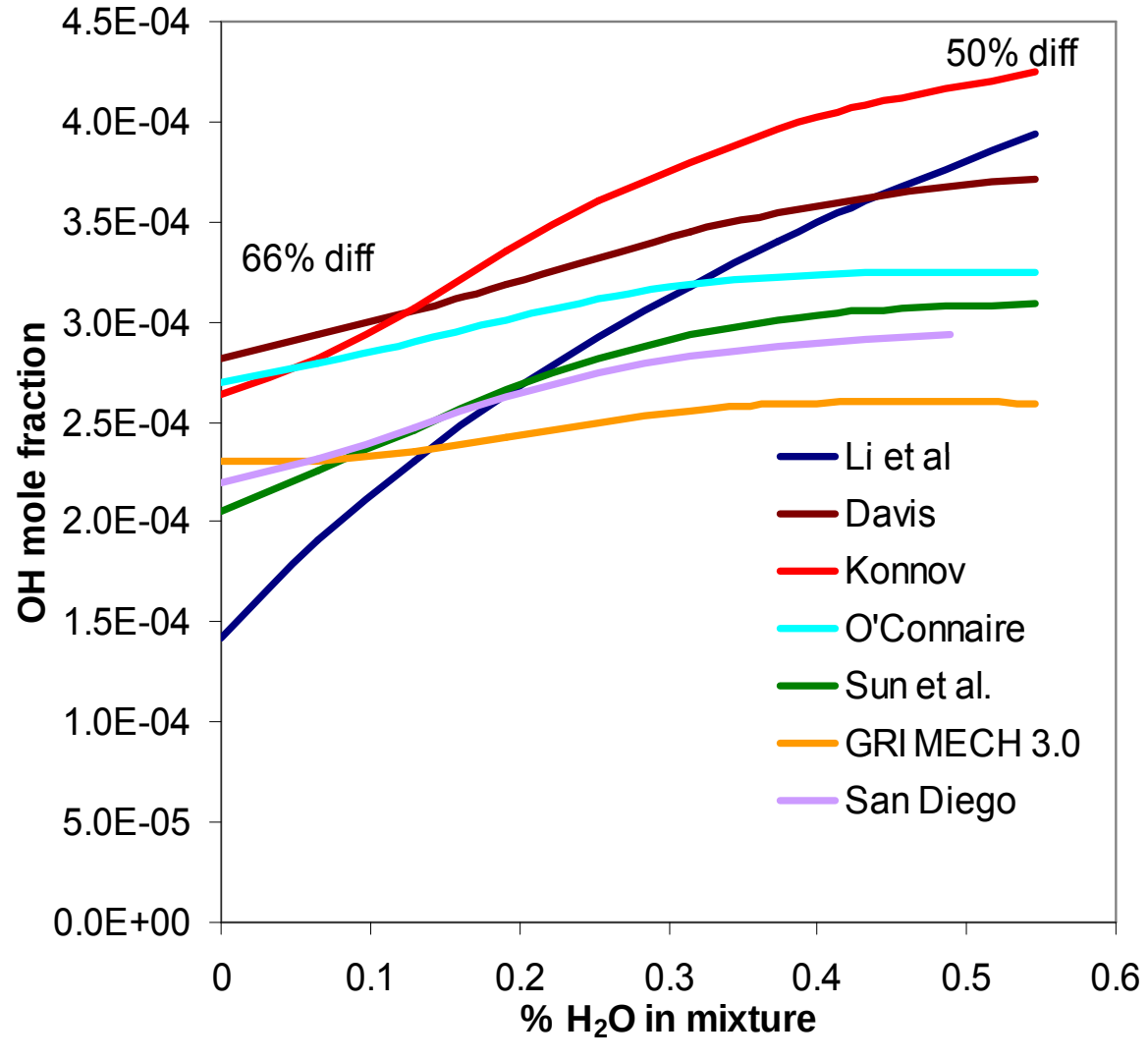


- Model over-predicts flame burning rates for HHC fuels with CO, CH_4, C_2H_4, C_2H_6

M.P. Burke, F.L. Dryer, Y. Ju, *Proceedings of the Combustion Institute* (2010) in press.

J. Santner, M.P. Burke, F.L. Dryer, Y. Ju, in preparation.

Large uncertainties in existing hydrogen models



Comparison of predicted peak OH concentrations of hydrogen flames by seven different kinetic models.

Questions Prompted by Results

- What happens to the kinetics with increasing pressure? CO/HC addition?
- How can such extensively validated models be so unconstrained?
- How can we improve kinetic modeling?

Effect of Pressure on Kinetics (I)

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

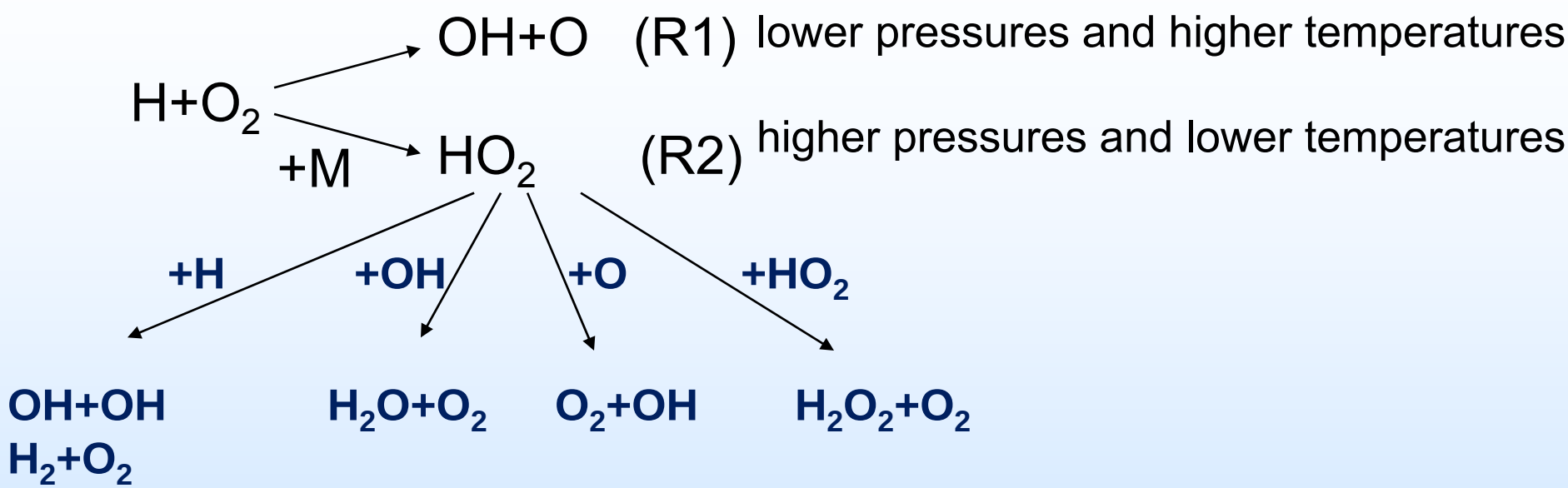
$$H + O_2 \xrightarrow{+M} HO_2 \quad (R2)$$ higher pressures and lower temperatures

- HO_2 paths are "terminating" at low P's and T's
  - Responsible for second explosion limit in homogenous kinetics

$$\frac{2k_1}{k_2[M]} < 1 \longrightarrow \text{Not explosive}$$

$$\frac{2k_1}{k_2[M]} > 1 \longrightarrow \text{Explosive}$$

Effect of Pressure on Kinetics (II)



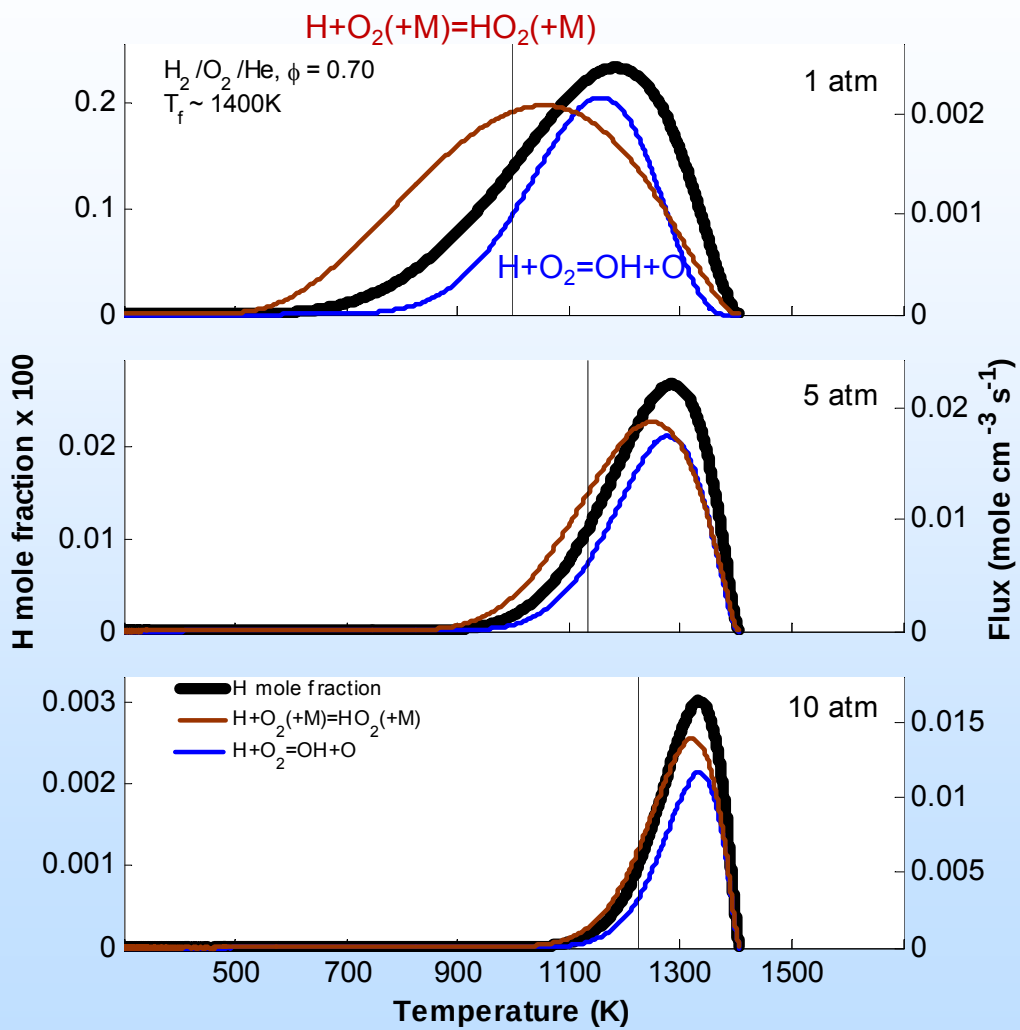
- **R1/R2 competition still controls pressure dependence**
- **New branching and termination reactions becomes important**

$H+HO_2=OH+OH$
$=H_2+O_2$

$OH+HO_2=H_2O+O_2$

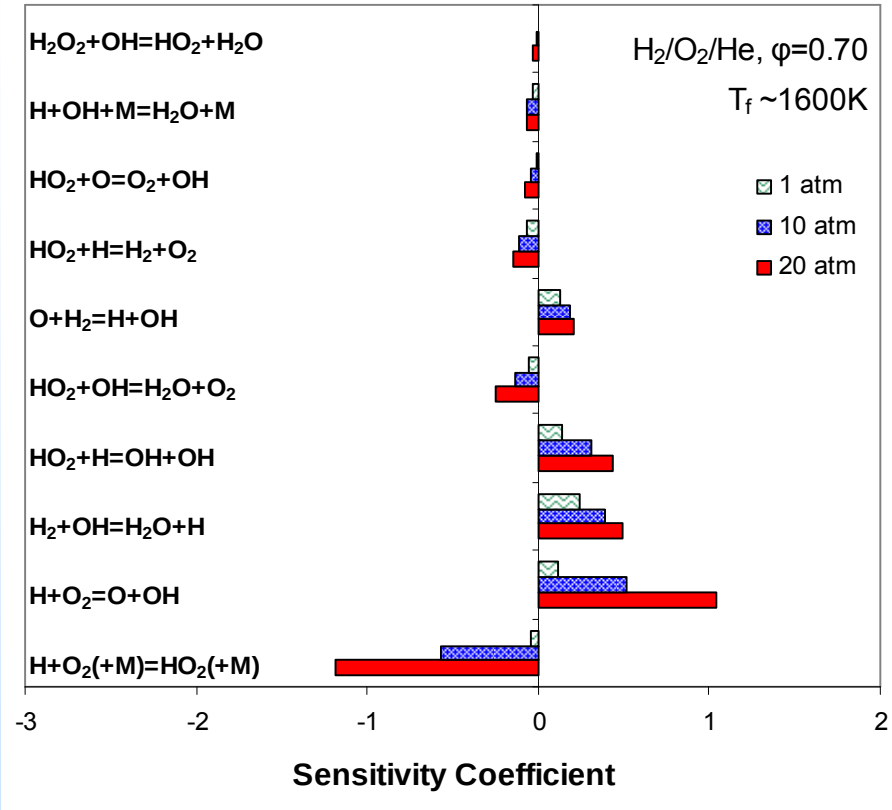
1. M.A. Mueller, T.J. Kim, R.A. Yetter, F.L. Dryer, *Int. J. Chem. Kin.*, 1999.

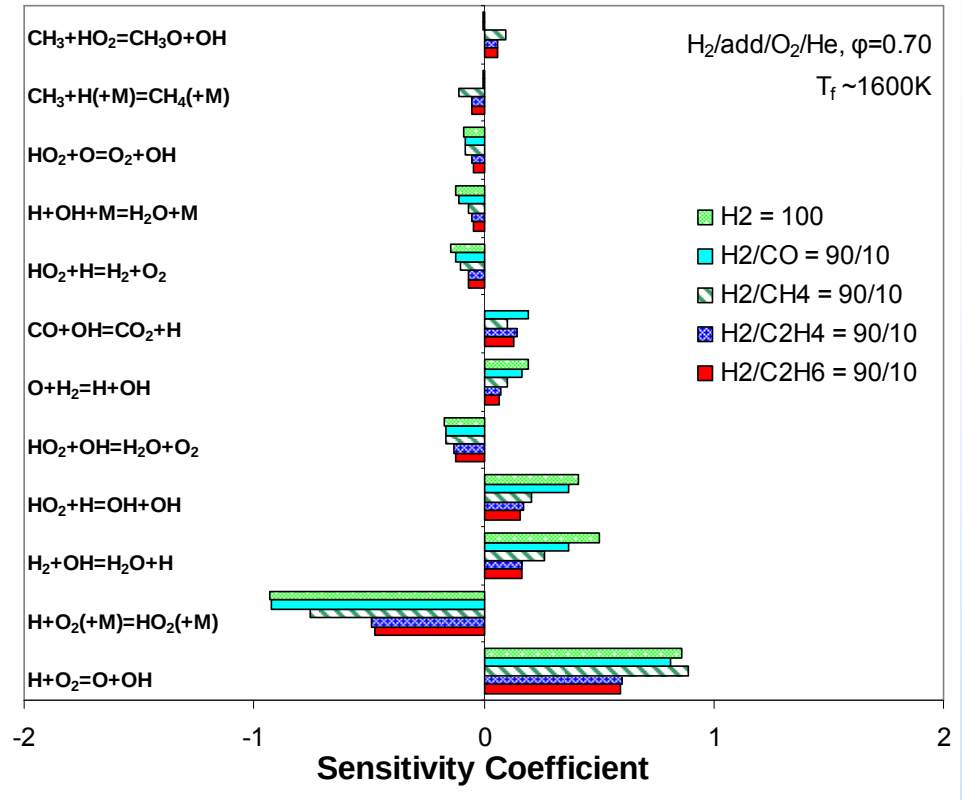
Effect of Pressure on H flux



- **Flame structure shifted to higher T's to promote branching**
- **Increased flux through $H+O_2+M$ relative to $H+O_2$**
- **Increased flux through HO_2 channels**
  - Inhibit reaction
  - Compete w/ branching reactions

A-factor Sensitivity of Mass Burning Rate





- Pure H_2 flames
  - Sensitivity increases with pressure
  - Pressure dependence governed by $H+O_2$, $H+O_2(+M)$, HO_2+radical reactions

- HHC fuel flames
  - $CO+OH=CO_2+H$ and CH_3 reactions also sensitive
  - Largely governed by H_2 kinetics

An updated H_2/O_2 kinetic-transport model

- Updated model uses the 19-reaction mechanism of Li et al.
- Primary emphasis on high-pressure reaction-diffusion processes:
  - HO_2 production
    - e.g. $H+O_2(+M)=HO_2(+M)$
  - HO_2 consumption
    - e.g. HO_2+H/O/OH/HO_2 reactions
  - H_2O_2 consumption pathways
    - e.g. $H_2O_2(+M)=OH+OH(+M)$
  - Transport
    - e.g. H atom diffusion

For more information, see our poster "Updated H_2/O_2 Model to Address High-Pressure Flame Burning Rate Discrepancies"

M.P. Burke, Y. Ju, F.L. Dryer, S.J. Klippenstein, "An updated model and discussion of challenges for modeling the H_2/O_2 reaction mechanism in high-pressure flames," in preparation for *IJCK* (2010).

Updated model performance – H_2 targets

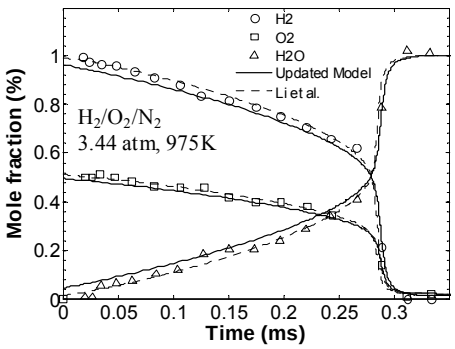


Figure 10.

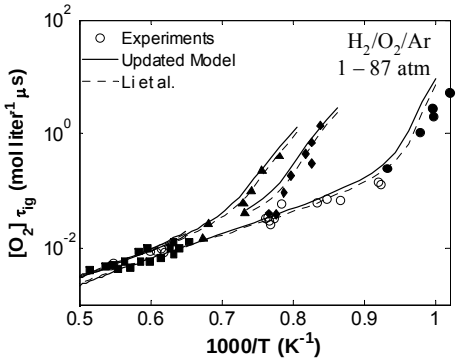


Figure 12.

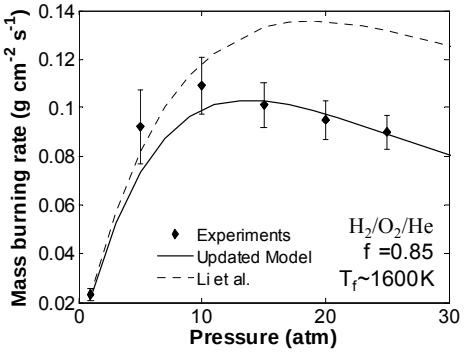


Figure 14.

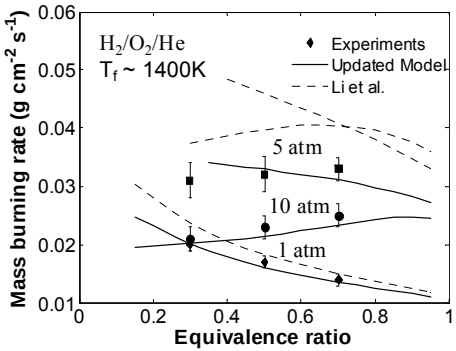


Figure 16.

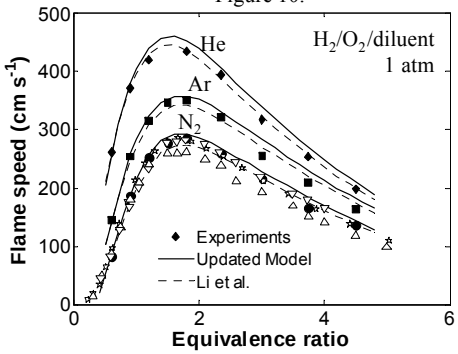


Figure 11.

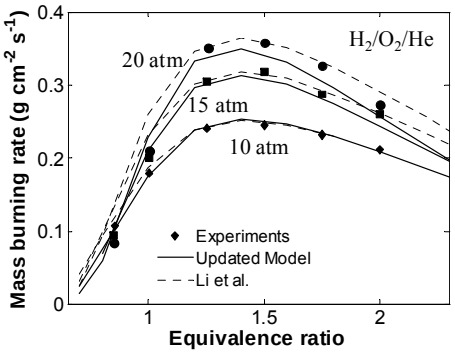


Figure 13.

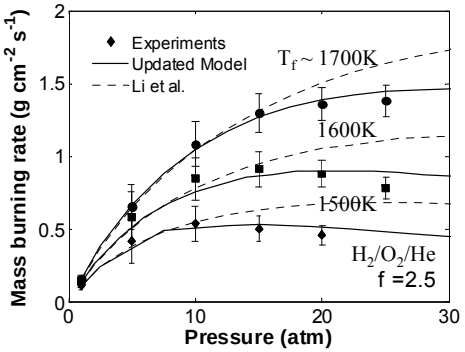


Figure 15.

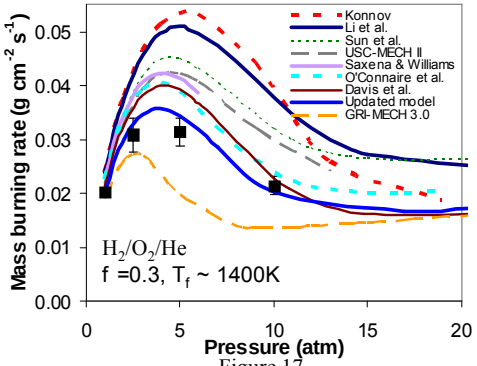
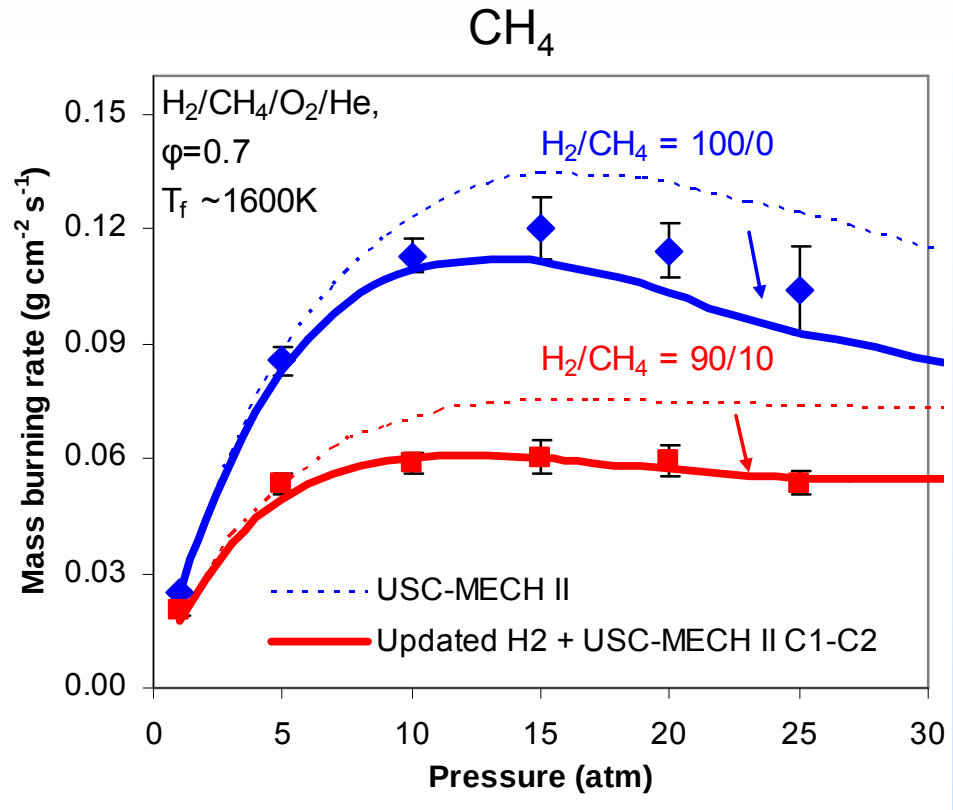


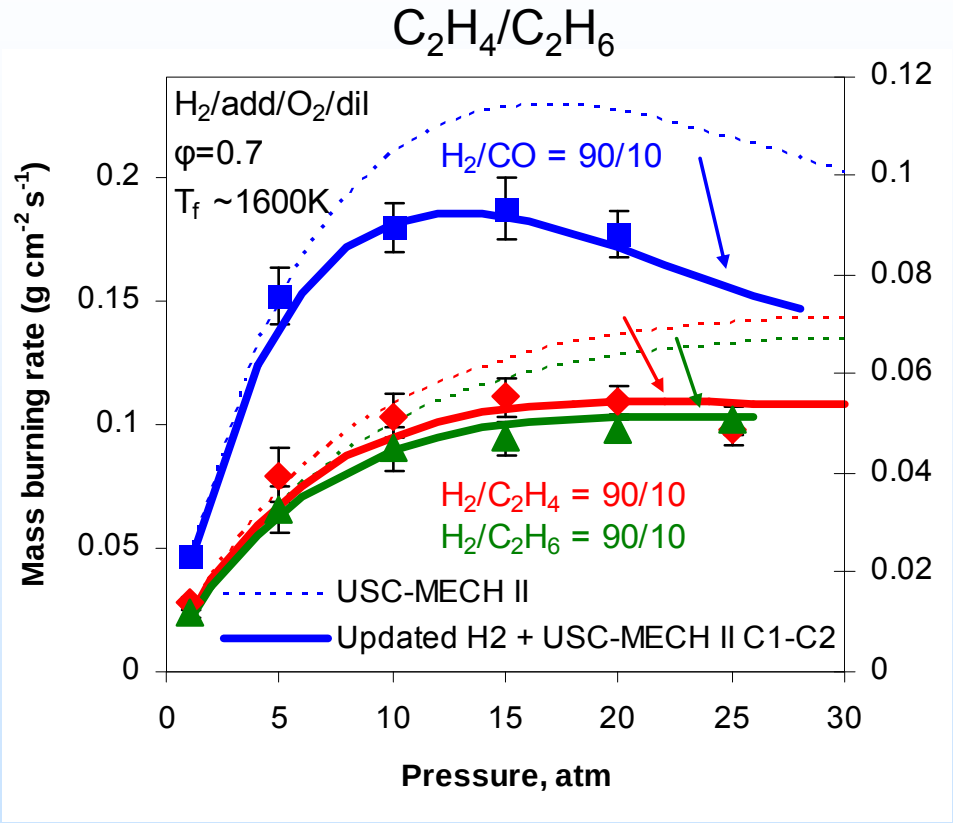
Figure 17.

- Reproduces previous validation targets of Mueller et al. and Li et al. including flow reactor speciation, ignition delays, and flame speeds.
- Shows significant improvements against high-pressure, low-flame-temperature data.
- Predicts wide range of flame speed targets within 20%.

M.P. Burke, Y. Ju, F.L. Dryer, S.J. Klippenstein, "An updated model and discussion of challenges for modeling the H_2/O_2 reaction mechanism in high-pressure flames," in preparation for *IJCK* (2010).

Improvements for H_2/fuel-additive flames

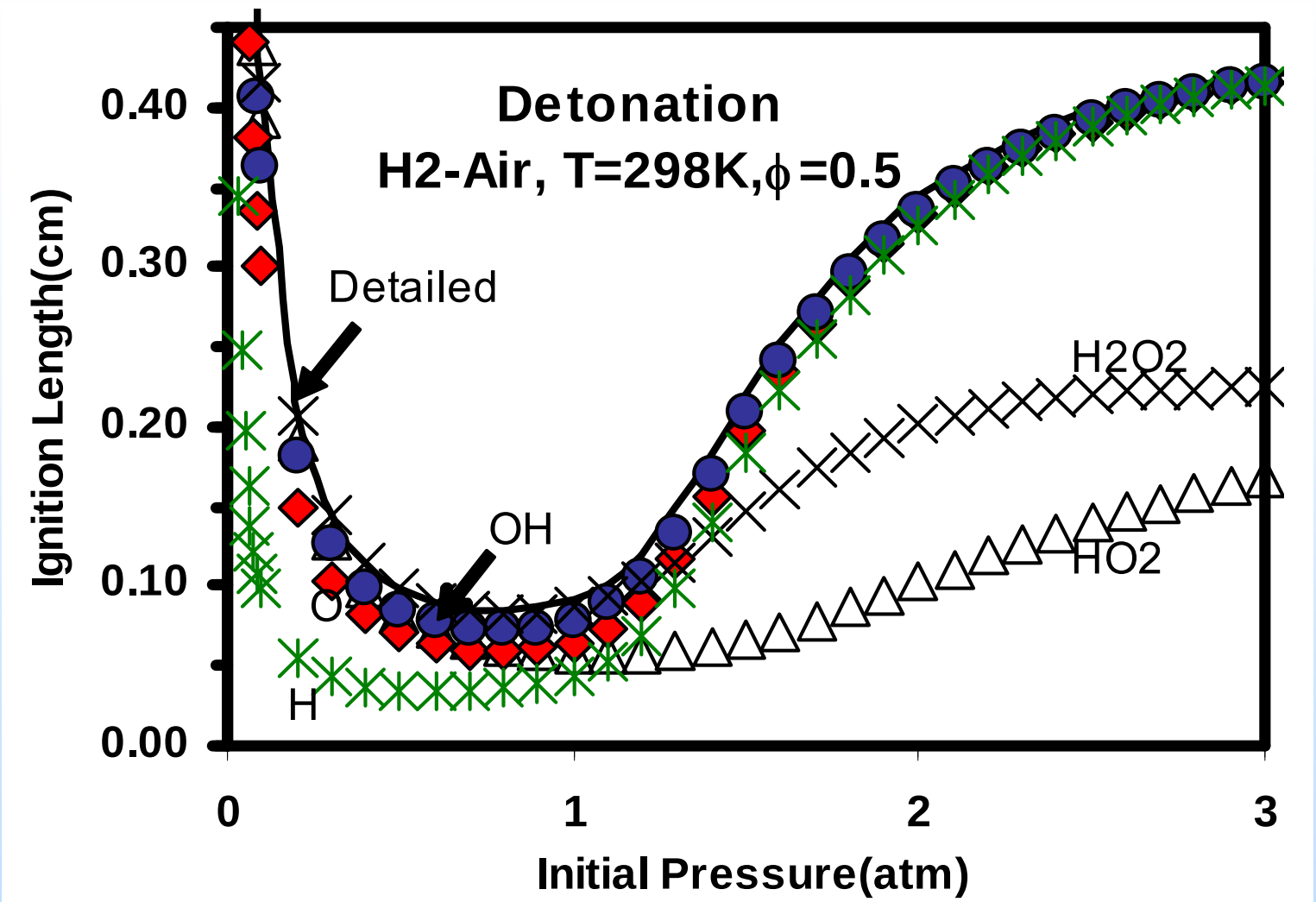




- Updated H_2 model improves HHC fuel predictions with CO, CH_4, C_2H_4, and C_2H_6

2. Development of reduced-order kinetic mechanism

Full hydrogen model vs. Quasi-steady state assumption

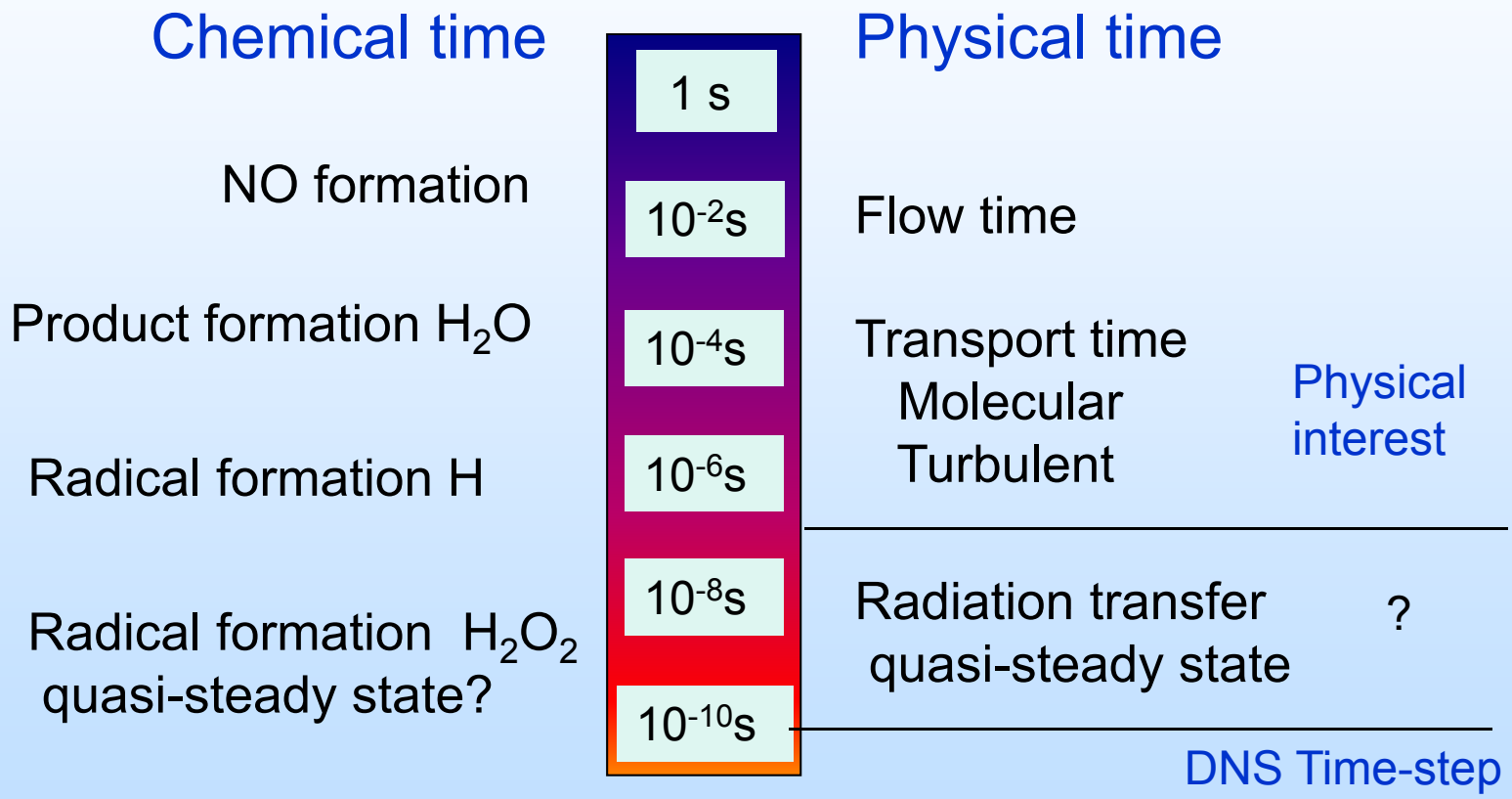


No species can be reduced! How to reduce chemistry size?

Time scales are very different!

A dynamic multi-time scale (MTS) kinetic reduction model

Time scales in reactive flow



Opportunities: Multi Time Scale Method (MTS)

The Basic Idea of Multi-Time Scale Method: timescale changes!

$$Y_k = K_k e^{-\frac{t}{\tau_k}}$$

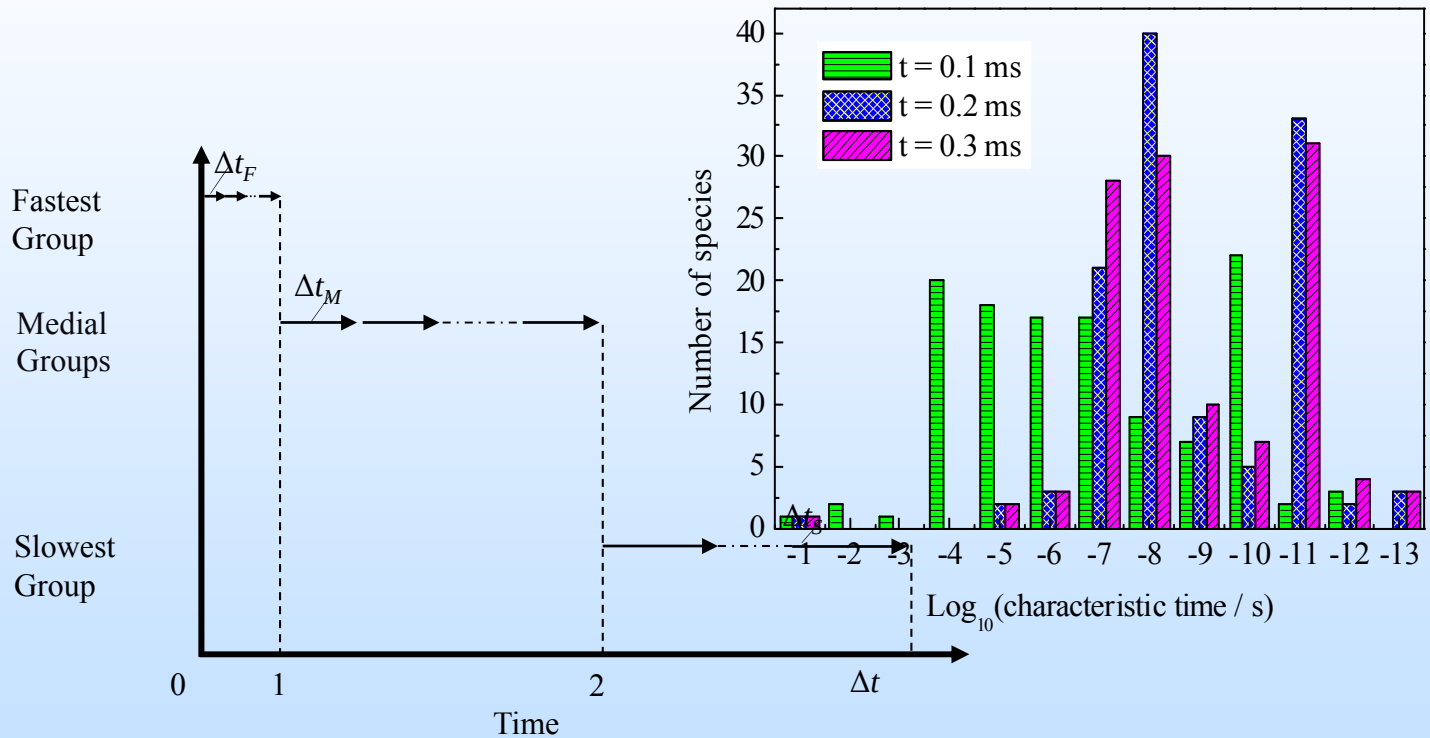
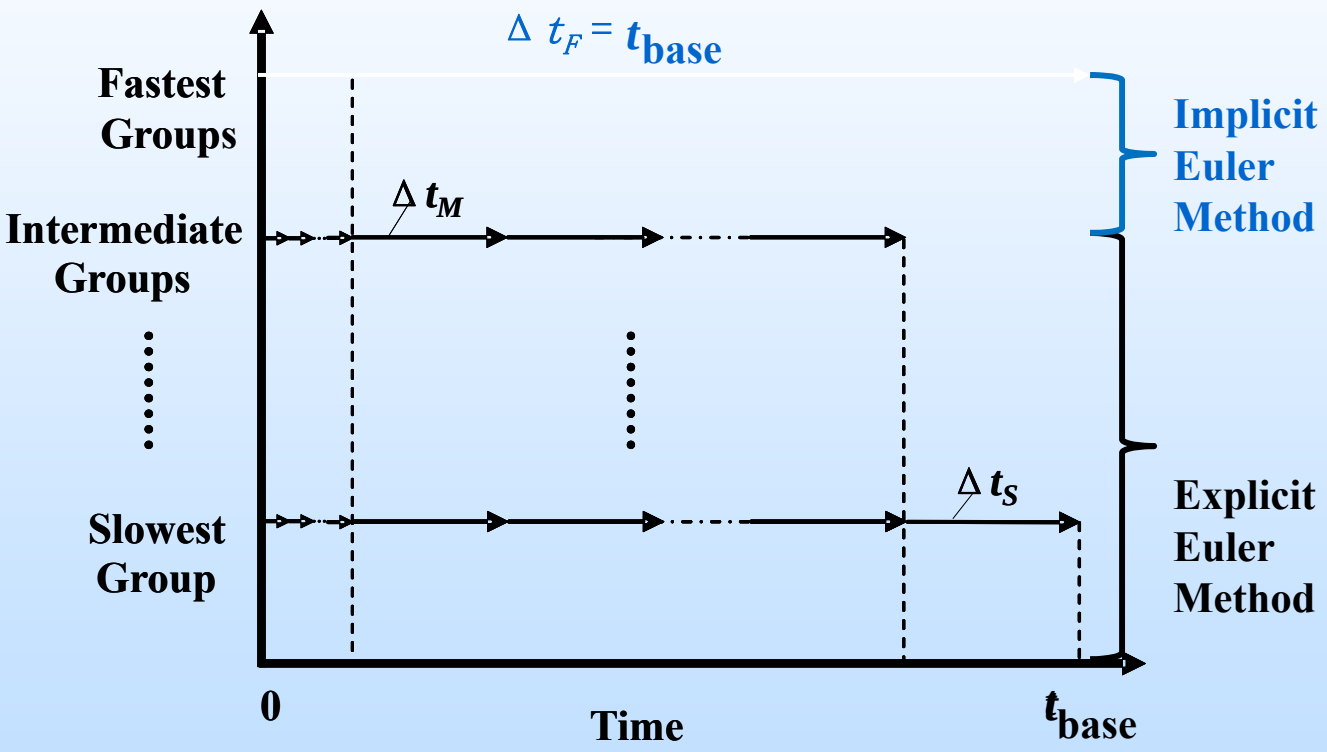


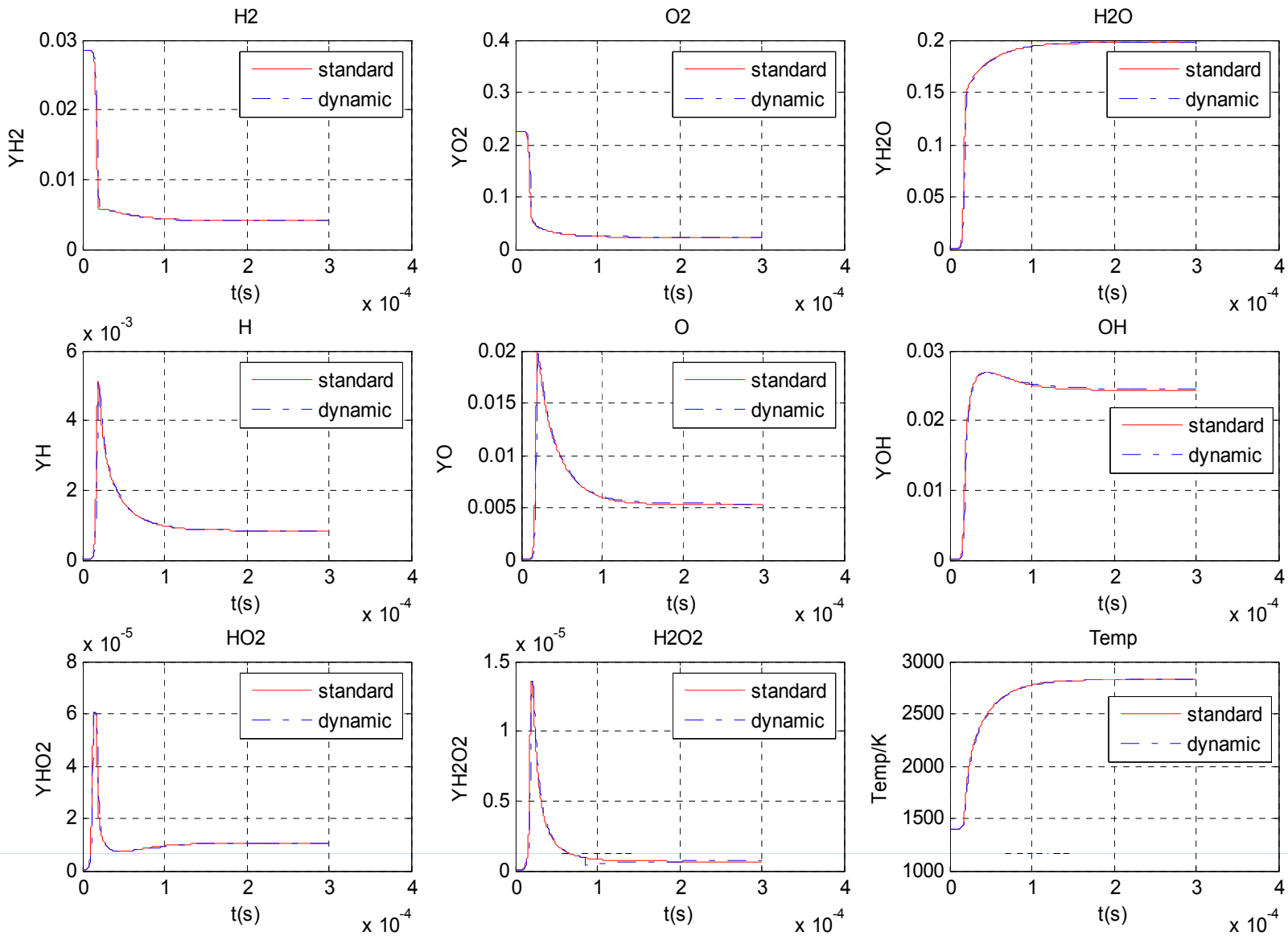
Diagram of multi time scale scheme

Δt_F is the time step of the fastest group, Δt_M is the time step of the medial group, and Δt_S is the time step of the slowest group

Hybrid Multi Time Scale Method (HMTS)

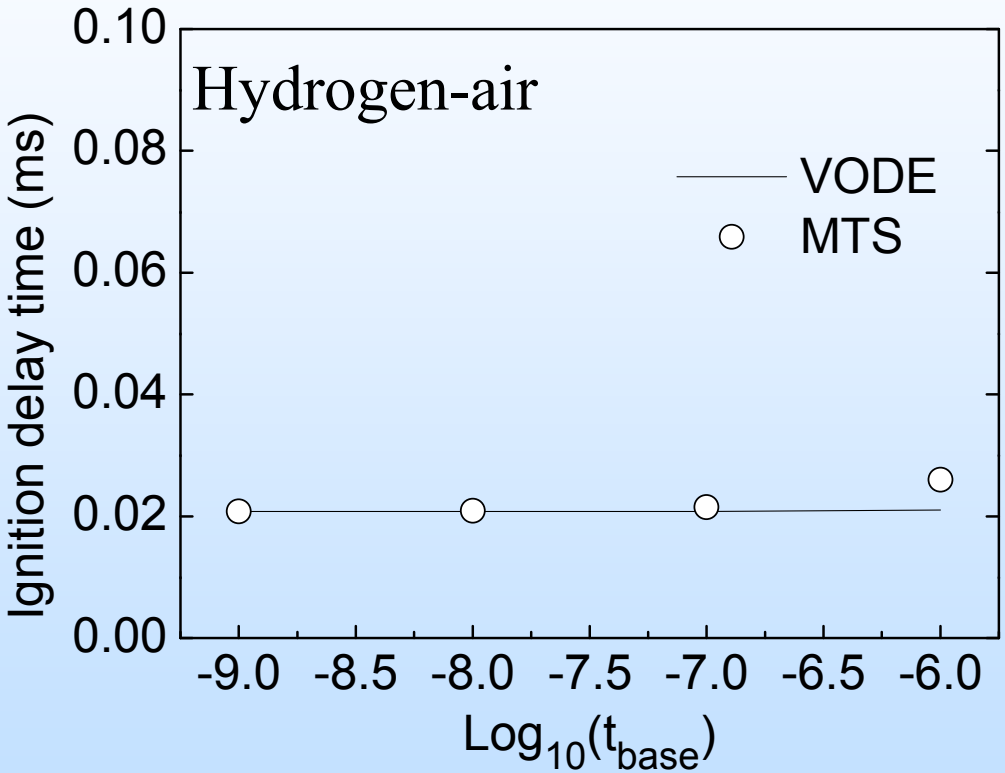


Multi-time Scale method vs. VODE, H_2/air ignition history



Homogeneous ignition of hydrogen with air

MTS vs. VODE



Gou et al. Combust. Flame, 2010

Comparison between MTS and ODE solver

No.	Model	Base Time Step(s)	Initial Pressure (atm)	Initial Temperature (K)	RTOL	ATOL	CPU Time(s)		CPU Time Saving
							ODE	MTS	
a1	H_2	1.0E-6	1	1200	1.0E-4	1.0E-13	0.28	0.13	53.6%
a2	H_2	1.0E-7	1	1200	1.0E-4	1.0E-13	2.58	1.31	49.2%
a3	H_2	1.0E-8	1	1200	1.0E-4	1.0E-13	24.9	7.56	69.6%
a4	H_2	1.0E-9	1	1200	1.0E-4	1.0E-13	260	18.4	92.9%
b1	CH_4	1.0E-6	1	1400	1.0E-4	1.0E-13	123	25	79.7%
b2	CH_4	1.0E-7	1	1400	1.0E-4	1.0E-13	1269	181	85.7%
b3	CH_4	1.0E-8	1	1400	1.0E-4	1.0E-13	14639	1029	93.0%
c1	$C_{10}H_{22}$	1.0E-6	1	1400	1.0E-4	1.0E-13	86	14	83.7%
c2	$C_{10}H_{22}$	1.0E-7	1	1400	1.0E-4	1.0E-13	773	125	83.8%
c3	$C_{10}H_{22}$	1.0E-8	1	1400	1.0E-4	1.0E-13	7609	1049	86.2%

Presentations & publications

- Jounal Publications
  - M.P. Burke, M. Chaos, Y. Ju, F.L. Dryer, S.J. Klippenstein, "An updated model and discussion of challenges for modeling the H_2/O_2 reaction mechanism in high pressure flames," in preparation for the *International Journal of Chemical Kinetics* in 2010.
  - M.P. Burke, F.L. Dryer, Y. Ju, "Assessment of kinetic modeling for lean $H_2/CH_4/O_2$/diluent flames at high pressures," *Proceedings of the Combustion Institute* (2011) in press, doi:10.1016/j.proci.2010.05.021.
  - X. Gou, W. Sun, Z. Chen, and Y. Ju, "A dynamic multi-timescale method for combustion modeling with detailed and reduced chemical kinetic mechanisms, Combustion and Flame 157 (2010) 1111–1121.

- Presentations
  - M.P. Burke, M. Chaos, Y. Ju, F.L. Dryer, "An updated model and discussion of modeling challenges in high-pressure H_2/O_2 flames," Spring Technical Meeting of the Combustion Institute, Boulder, Colorado, March 2010.
  - M.P. Burke, Y. Ju, F.L. Dryer, "Assessment of kinetic modeling for lean $H_2/CH_4/O_2$/diluent flames at high pressures," International Symposium on Combustion, Tsinghua University, Beijing, China August 2010.
  - M.P. Burke, M. Chaos, Y. Ju, F.L. Dryer, S.J. Klippenstein, "Updated H_2/O_2 model to address high-pressure flame burning rate discrepancies," International Symposium on Combustion, Tsinghua University, Beijing, China August 2010 (poster).
  - M.P. Burke, M. Chaos, Y. Ju, F.L. Dryer, S.J. Klippenstein, "A revised H_2/O_2 kinetic model for high-pressure flames," 49th AIAA Aerospace Sciences Meeting and Exhibit, Orlando, Florida, January 2011.
  - J. Santner, M.P. Burke, F.L. Dryer, Y. Ju, "Effect of fuel addition of CO, CH_4, C_2H_4, and C_2H_6 to H_2/O_2/He to flame burning rates at high pressures," 49th AIAA Aerospace Sciences Meeting and Exhibit, Orlando, Florida, January 2011.

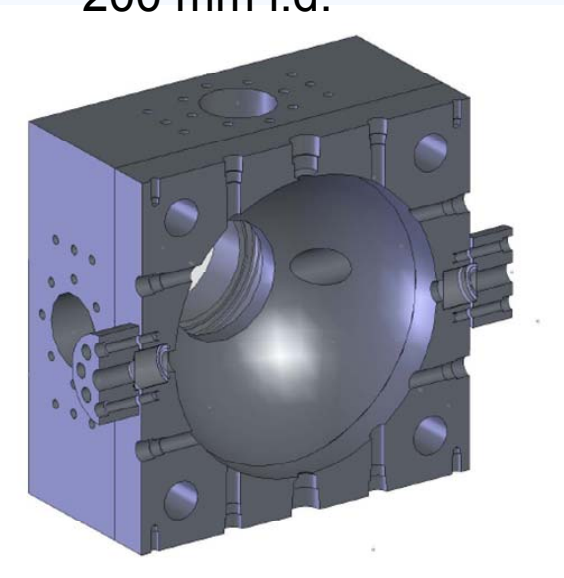
Conclusions

- **High-pressure flame burning rate data of high hydrogen mixtures are obtained. It is found that HHC fuel flame properties are largely determined by H_2 kinetics.**
- **Large uncertainties in current models is observed. None of the current models capture the negative pressure dependence of the measured burning rates at high pressures.**
- **Kinetic pathways at high pressure are analyzed and key HO_2 involved reactions are identified.**
- **An updated H_2/O_2 kinetic-transport model is developed and improved agreements with high-pressure flame burning rate data for H_2 and HHC fuels (w/ CO, CH_4, C_2H_4, C_2H_6) are observed.**
- **A computationally efficient dynamic multi-timescale method is developed.**

Future research (1)

Third-body effect of H_2O/CO_2 dilution at high pressure

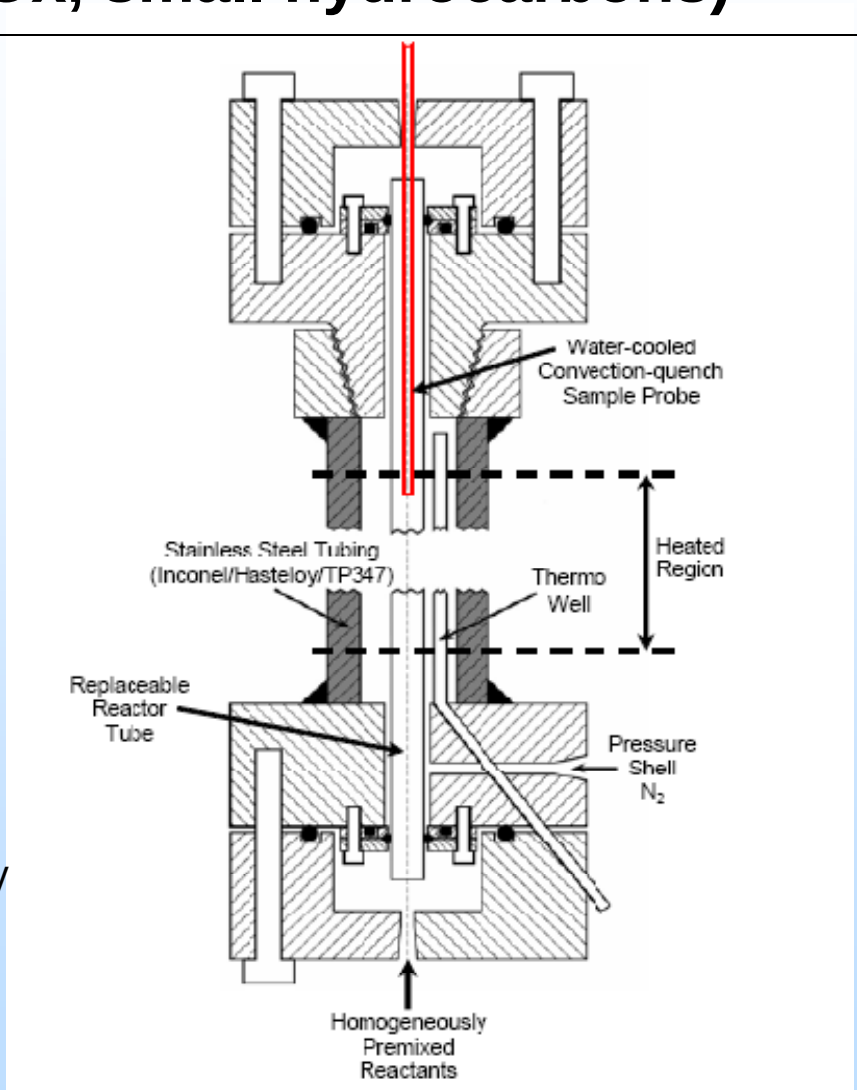
200 mm i.d.



Future research (2)

HPLFR experiments – Data on Surface effects, Diluents and Other Reactive Species (NOx, small hydrocarbons)

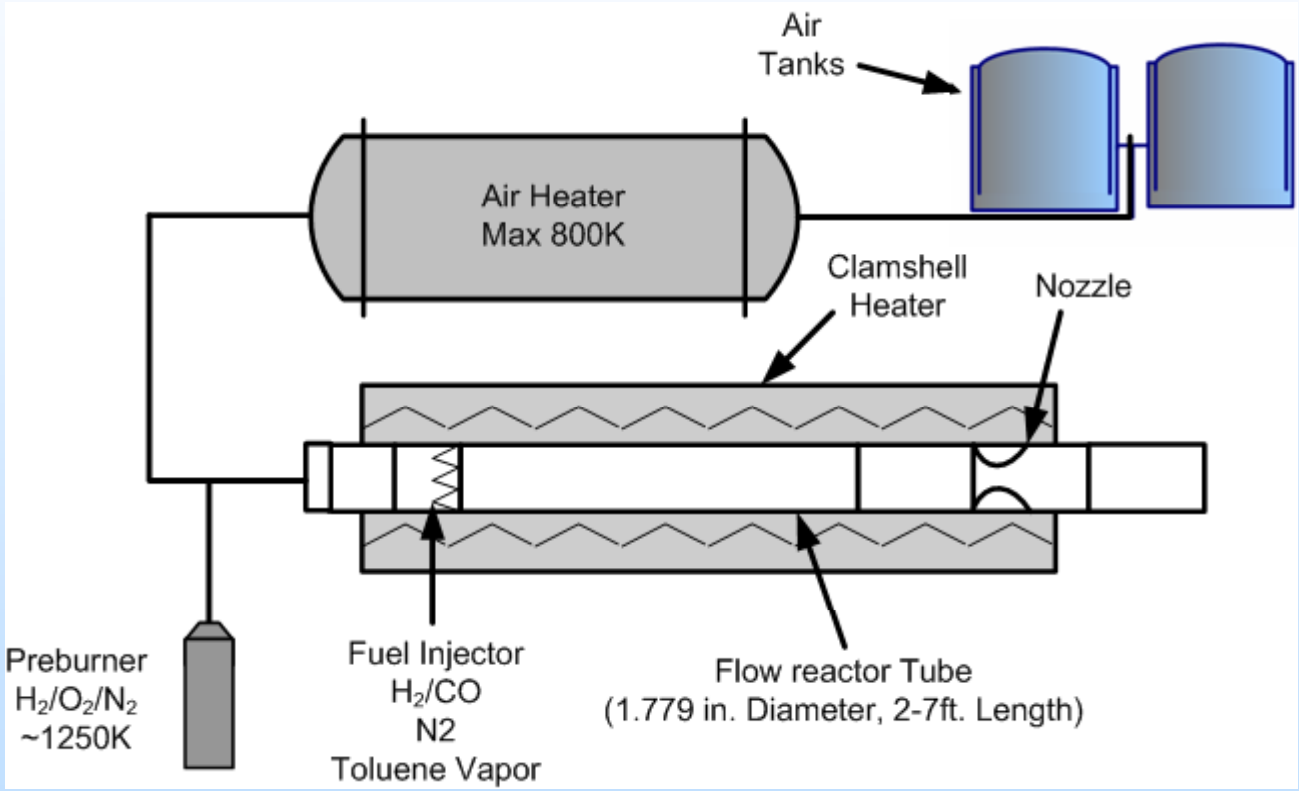
- Advantages over large scale variable pressure flow reactor (VPFR):
  - Premixed reactant studies
  - Wider range of pressures possible
  - Large variations in diluent composition possible
  - Reactor wall surface materials can be easily changed
- Current Status: (Construction supported elsewhere)
  - System has been operated at pressure, using stainless steel test section.
    - Temperature and sampling system complete.
    - Analytical micro gc, FTIR, and NDIR systems installed and tested by Nov 30.
    - Experiments underway to verify P, T and residence time operating ranges.
    - Silica test sections constructed and ready for installation after initial experiments using stainless reactor section.
  - Experiments on hydrogen in various diluent/oxidizer mixtures, Dec. 2010.
  - Contaminant addition experiments thereafter.



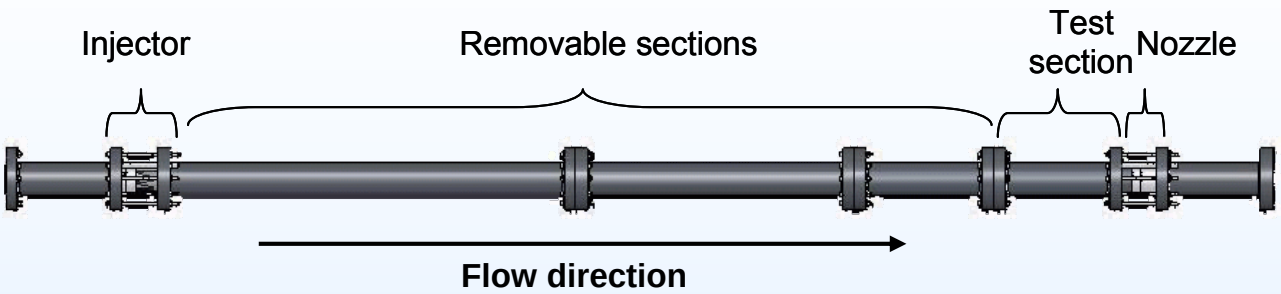
Schematic of the High Pressure Laminar Flow Reactor

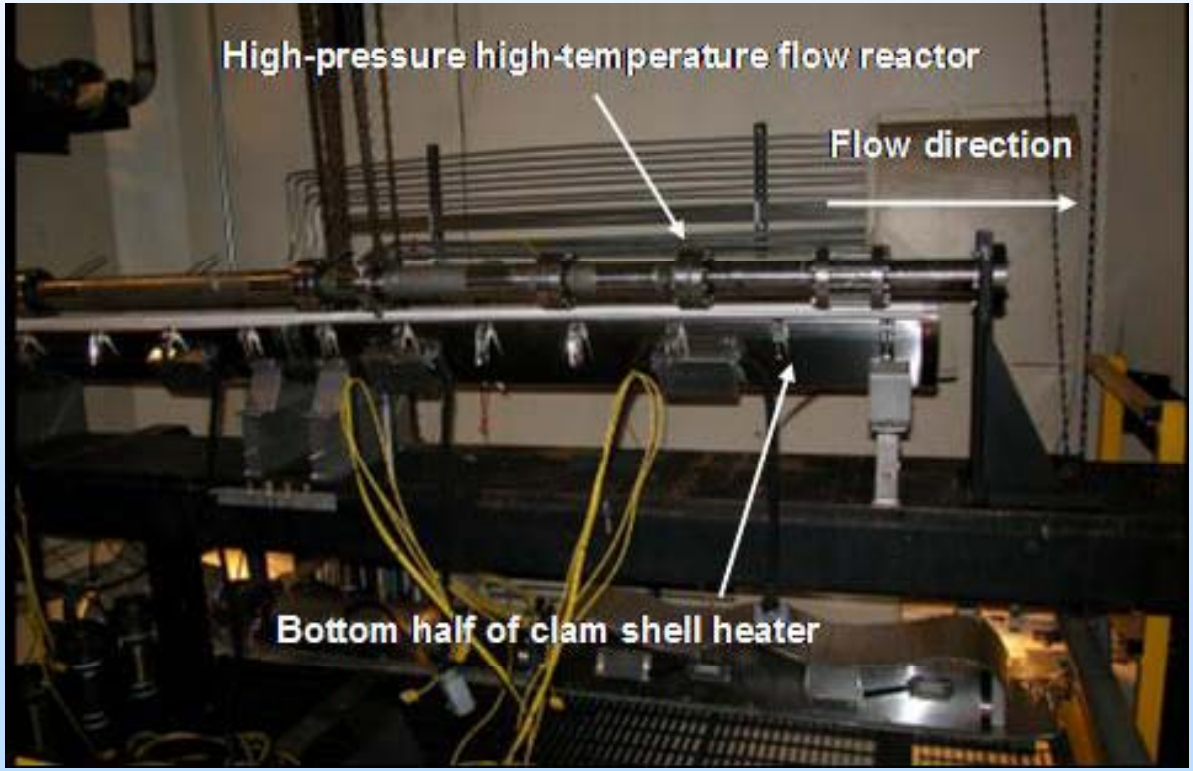
Questions?

High Pressure High Temperature Autoignition Flow Reactor



High-Pressure High Temperature Flow Reactor



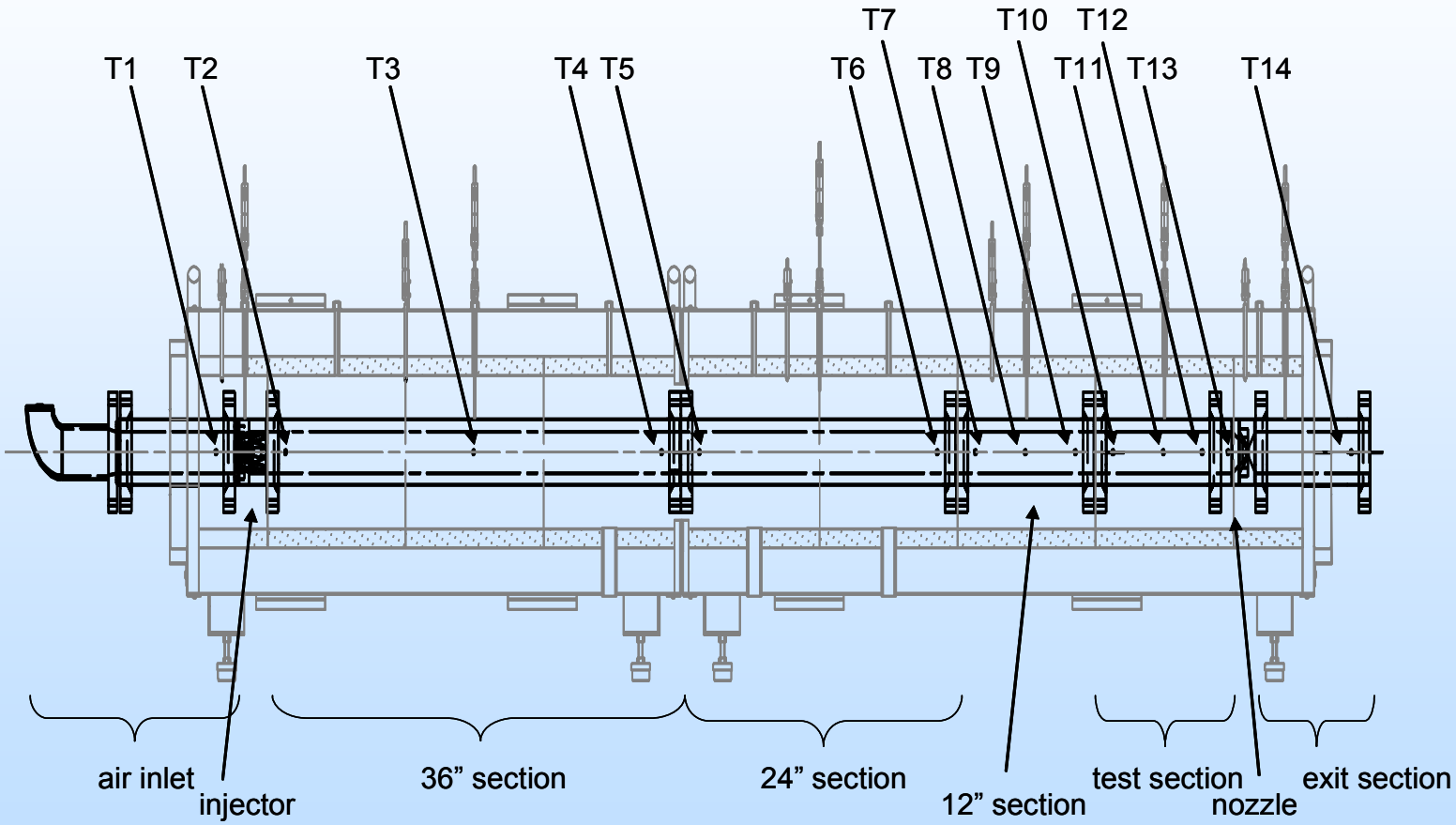


Flow Reactor Details

- The variable-length test section (maximum length of 2.13 m (7 ft)) has a circular cross section (diameter of 43 mm (1.7 in.)).
- The test section is instrumented with pressure transducers and an axial array of thermocouples. Such measurements are necessary to document the conditions at which autoignition occurs.
- With respect to the air flow conditions, a maximum flowrate of 2.5 kg/s (5.5 lbm/s) is supplied from two blowdown tanks to an electric resistance-type air heater that can heat approximately 0.45 kg/s (1 lbm/s) of air to a maximum temperature of ≈950 K (1710 R).
- Maximum pressure of 30 atm.

Thermocouple Array

Wall thermocouple positions



Array of thermocouples located 0.2 inches from the wall that provides for detection of the autoignition event in the flow reactor tube

Motivation Previous Results Ignition Delay Events

Three types of ignition events were observed for the syngas and hydrogen studies conducted:

- The most prevalent event was ignition near the injector face as the air temperature is increased from its starting value. More specifically such ignition events occur in the region between the injector face and the first thermocouple, which is 27.25 cm (10.73 in.) downstream of the injector face.
- In the second type observed, autoignition does occur in the flow reactor tube downstream of the injector. However, the location of the event varies in terms of the position in the flow reactor tube for similar conditions.
- The third type observed involved cases where no ignition was observed with run times of several seconds or longer.

Clearly, the data obtained does not provide a single value of the ignition delay time as should be expected.

Previous Tabulated Data

	ϕ	% H_2 in Fuel	P (atm.)	T (K) at ign. Loc	velocity (m/s)	t (ms)	t_{adj} (ms) to 20 atm
2008 Work (75% H_2/25% CO) Re=126000	0.98	74.3	9.6	748.2	8.9	258.0	123.2
	0.98	74.0	9.8	734.4	8.7	31.2	15.3
	0.99	73.9	9.7	730.2	8.7	31.2	15.1
	0.97	73.7	10.2	764.9	8.4	236.4	121.1
	0.98	73.2	10.0	730.1	8.4	142.3	70.9
2009 Work (100% H_2) Re=63750	0.51	100	23.3	792.5	4.3	396.0	461.1
	0.52	100	23.0	759.6	4.3	139.4	160.4
	0.51	100	22.7	762.5	4.3	323.1	366.3
	0.47	100	24.7	767.3	4.2	48.0	59.1
	0.51	100	23.9	771.2	4.4	217.6	259.6

Flow reactor length = 2.16 m

Recent Results

	ϕ	% H_20 in Fuel	P (atm.)	T(K) at ign. loc	velocity (m/s)	t (ms)
2010 Studies (100% H_2) Re=241300	0.462	8.3	18.9	823	24	80.2
	0.461	8.3	18.8	820	24	65.6
	0.463	8.3	18.8	820	24	4.2
	0.466	8.3	18.7	802	24	42.7
2010 Studies (H_2 + 0.5% toluene) Re=241300	0.463	8.3	18.9	817	24	4.2
	0.463	8.3	19.1	816	24	64.9
	0.464	8.3	18.8	815	24	4.2

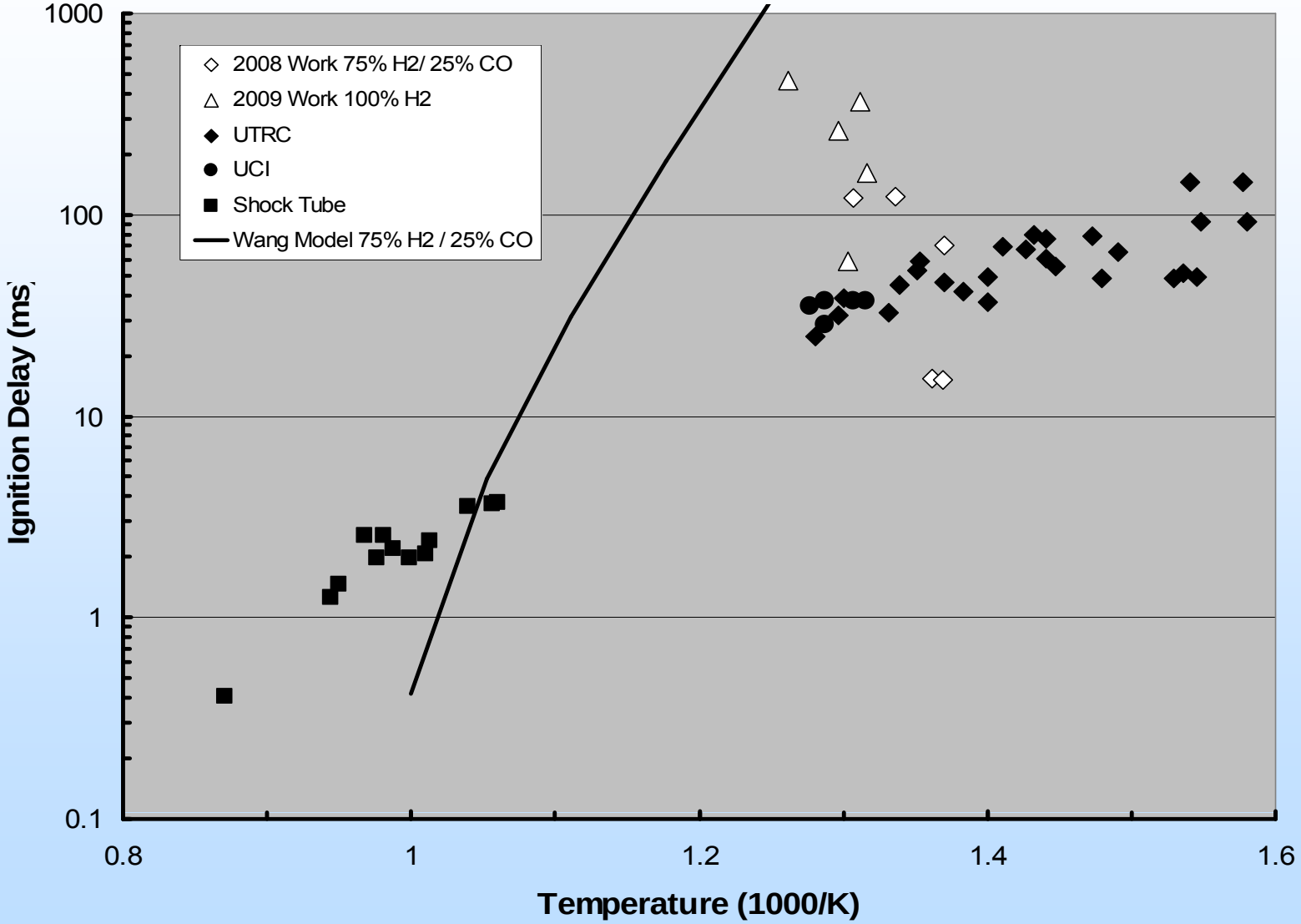
Flow reactor length = 2.16 m Residence time 90 ms

Summary

- Autoignition time observed to vary under similar conditions as seen before.
- Most recent data obtained at higher temperatures and Reynolds numbers
- Analysis to date has been preliminary and more detailed analysis is on going

Backup slides

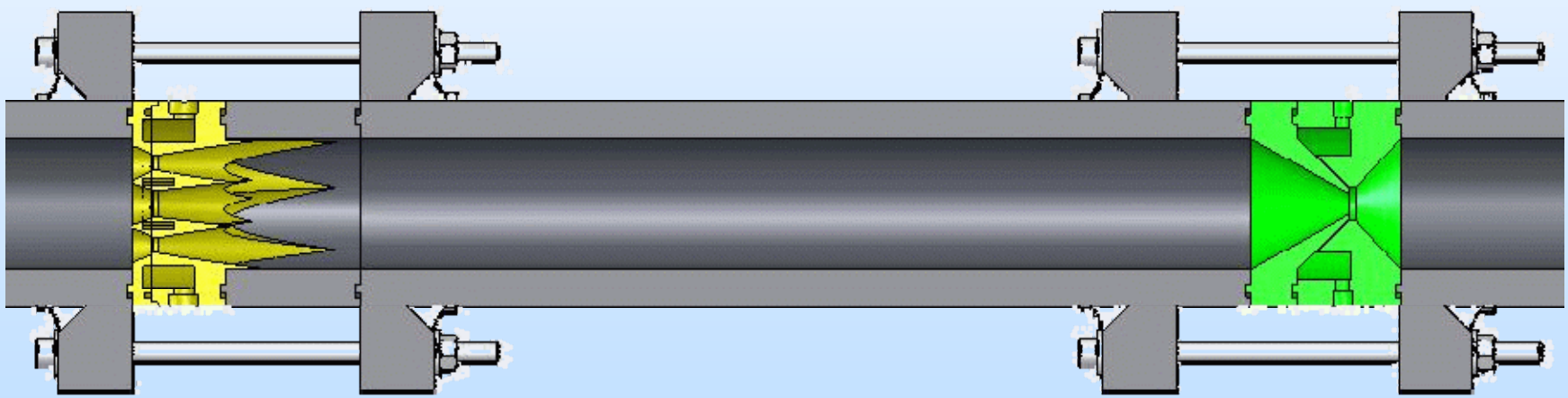
Plot of the Results for the Autoignition Time for Cases Where Ignition Occurred in the Reactor Tube



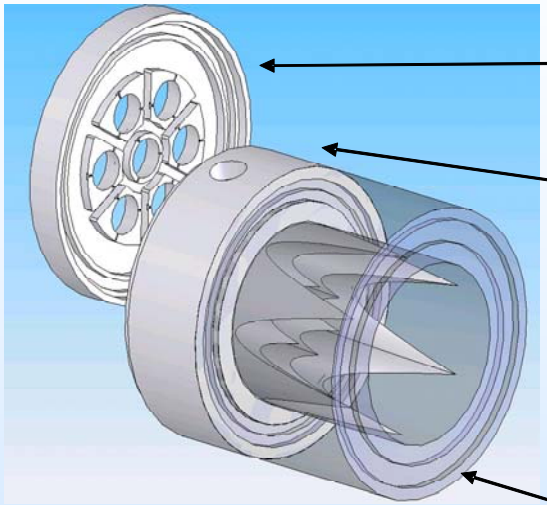
Flow Reactor Design

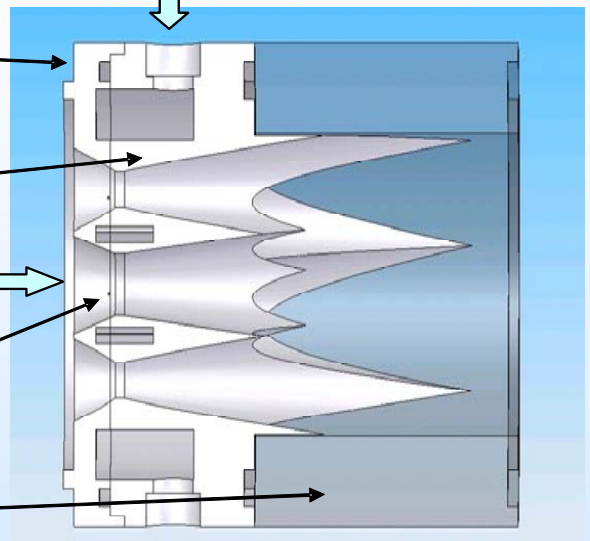
- Instrumented test section before nozzle
- Sonic nozzle and water quenching to isolate test section from afterburner
- Injector design
  - Venturi design for rapid mixing with minimal recirculation zones
  - 7 venturis with 3 fuel injection holes just upstream of throat

- Re# (Max) = 5×10^5 to 3×10^6

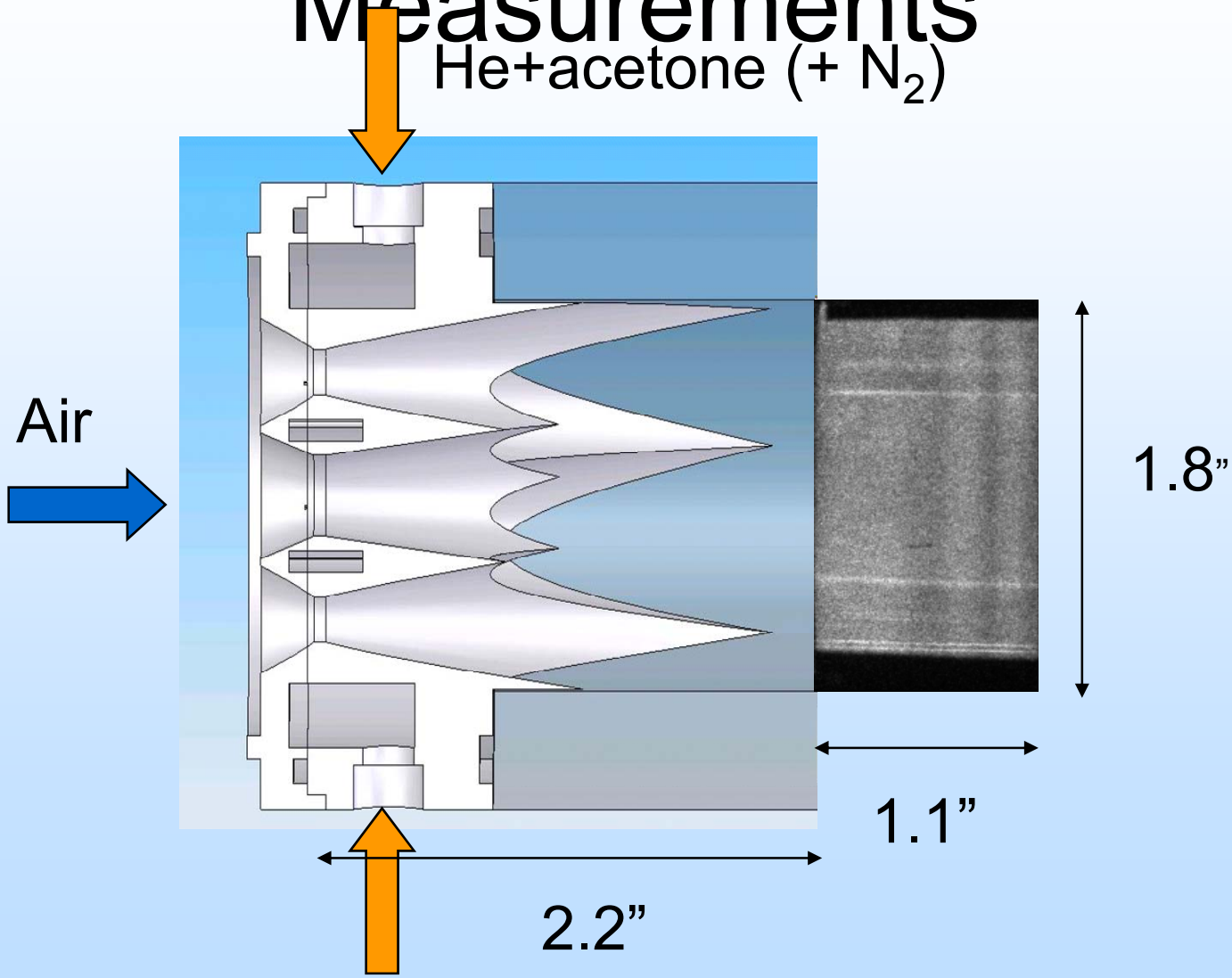


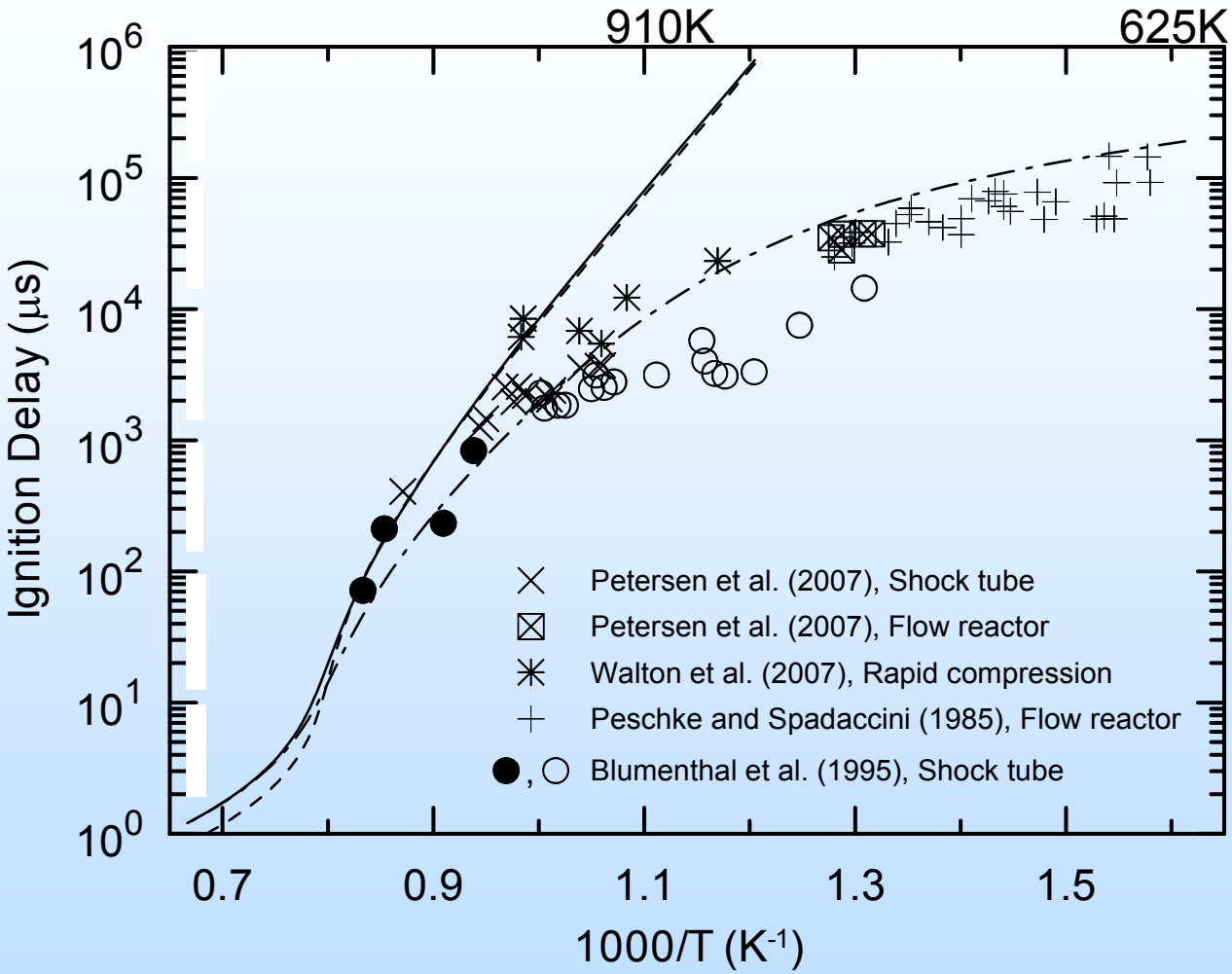
Injector Design Concept and Resulting Hardware





Field of View for Acetone PLIF Measurements





Significant difference between model prediction and measurements of ignition delay time for temperatures between 900K – 625K (1150ºF - 665ºF)