Combustion Studies of Alcohols, Esters and Hydrogen Rich Fuels

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Overview

Fuels Combustion Research Laboratory's contribution to CEFRC efforts

- Generation of motivating fundamental experimental observations that elucidate the interactions of bio-derived molecular components and structures with components found in petroleum derived fuels.
- Provision of experimental validation data for development and refinement of detailed kinetic models for esters and alcohols.
- Experimental determination of elementary kinetic rates important to the decomposition and oxidation of hydrocarbons and hydrocarbon oxygenates.

Accomplishments

- Chemical Kinetics of iso-Propanol and t-Butanol Pyrolysis and Oxidation
- Auto Ignition of n-heptane/Butanol Blends in Ignition Quality Tester
- Methyl Formate Decomposition, and Oxidation in Low Pressure Flames

} Bio-derived fuels

- An Updated Kinetic/Transport Model for H_2/O_2

} Sub-model improvements

Chemical Kinetics of *iso*-Propanol and *t*-Butanol Pyrolysis and Oxidation

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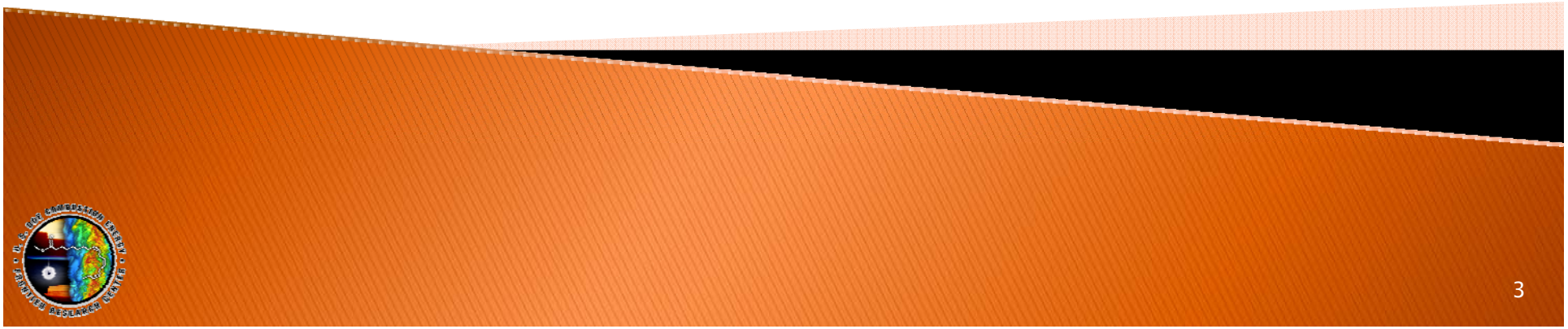
Collaboration with H. J. Curran (NUIG)
[2]Department of Mechanical and Aerospace Engineering, Princeton University



"Next-generation" biofuels – Alcohols

Flow reactor study on *iso*-propanol and *tert*-butanol

Motivation

- Lower soot / polyaromatic hydrocarbon emissions.
- Few studies on next generation, higher molecular weight oxygenated fuels $\longrightarrow$ Experimental data needed for extensive model validation.
- Experimental determination of the dehydration rate constants for n/i-propanol and *tert*-butanol.
- Detailed speciation data for alcohol oxidation obtained at T<950 K.
- Detailed mechanistic study is needed to understand the combustion of these alcohols and interactions with two stage kinetics of large carbon number hydrocarbons.

Experimental conditions

Iso-propanol

Experiment	T (K)	P (atm)	Molar conc'n (ppm)
Pyrolysis History	800 -1000	12.5	5000
Pyrolysis Reactivity (τ = 1.8 s)	550 -1025	12.5	5000
Oxidation Reactivity (τ = 1.8 s, φ=1)	520 - 1010	12.5	2500
Pyrolysis with radical trapper (1,3,5-TMB)	900 - 1000	12.5	1200 equimolar

Tert-butanol

Experiment	T (K)	P (atm)	Molar conc'n (ppm)
Pyrolysis History	720-1000	12.5	2500
Pyrolysis Reactivity (τ = 1.8 s)	500 - 975	12.5	2500
Oxidation Reactivity (τ = 1.8 s, φ=1)	676- 918	12.5	2500
Pyrolysis with radical trapper (1,3,5-TMB)	1020, 1080	3.0	1540 equimolar

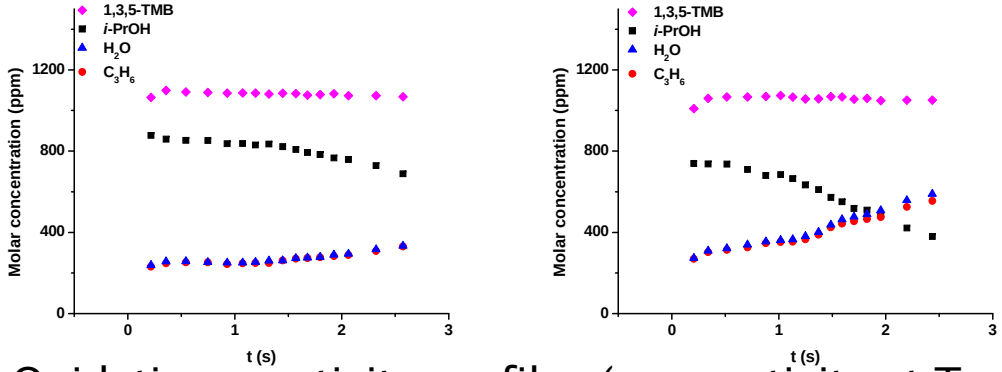
Preliminary results on pyrolysis/oxidation

- Level to which water and olefin yield in equal quantities gives evidence of radical trapper methodology. Rate of dehydration reaction extracted experimentally

  iso–propanol: $i\text{-}C_3H_7OH \leftrightarrow C_3H_6 + H_2O$

  tert–butanol: $t\text{-}C_4H_9OH \leftrightarrow C_4H_8 + H_2O$

- Radical trapper addition to extract water elimination rate constant

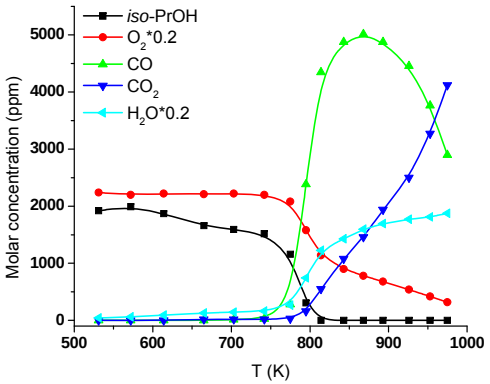


***Iso*–propanol** pyrolysis with radical trapper:

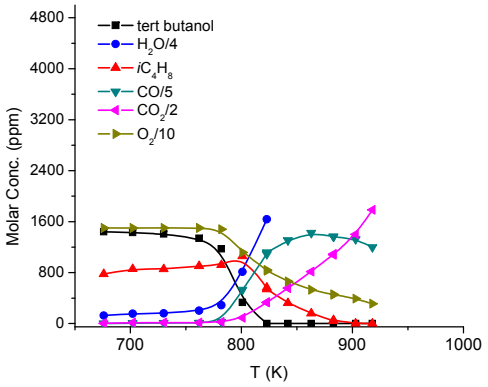
1200 ppm $i\text{-}C_3H_7OH$
1200 ppm 1,3,5-TMB
P = 12.5 atm

- Oxidation reactivity profiles (no reactivity at T < 775K)

Oxidative conditions:
P = 12.5 atm



iso–propanol



t–butanol

Autoignition of Fuel/Butanol Blends in an Ignition Quality Tester

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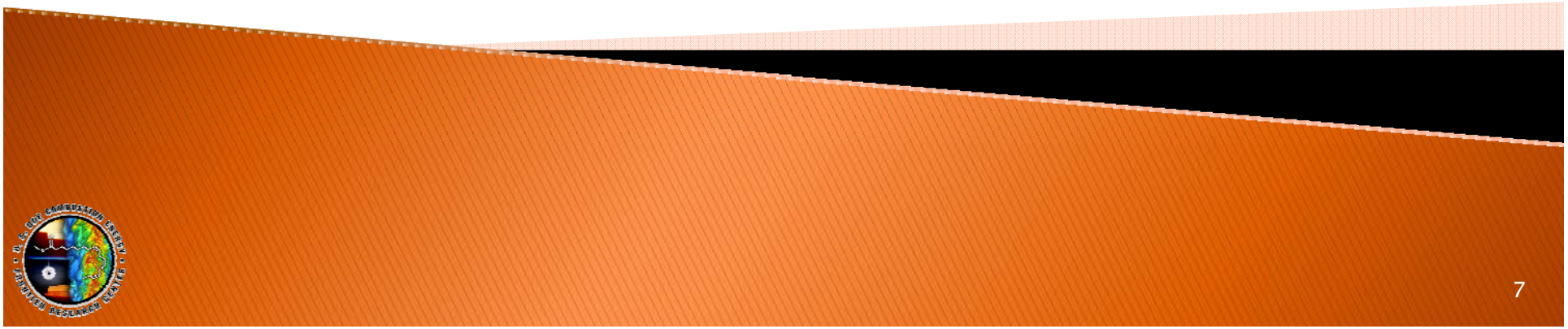


Autoignition of Butanol?

Motivation

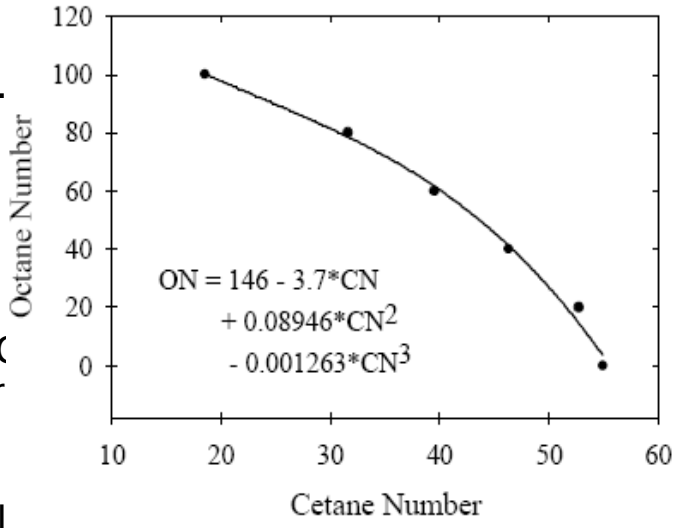
- Isomers of butanol have been identified as promising candidates of 2nd generation bio fuels.
- Little fundamental work available on how these alcohols interact with hydrocarbons found in conventional petroleum derived fuels- likely end use scenario for these bio generated materials.

Objectives

- Scan ignition behavior trends in isomeric structures.
  - Engine-relevant pressure, temperature and fuel loading.
  - Identify "interesting" behaviors to focus more fundamental studies.
- Examine kinetic coupling of components in fuel blends.

Experiments: A study of comparative *ignition quality*

- Trends in reactivity extendable to conventional HCSI, DI engine applications as well as high-efficiency PCCI futur designs.
- Comparisons among butanols at similar volumetric blending in n-heptane and a real low-cetane diesel fuel.

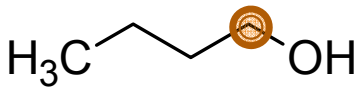


Reactivity Trends – Neat Butanols

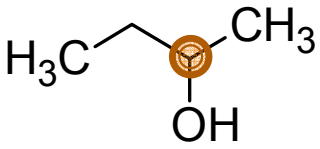
Pure Component	Avg. Measured DCN	MON
t-butanol	<7.18	94
i-butanol	8.51	94
2-butanol	8.54	91
n-butanol	12.02	78
n-heptane	53.8†	0†

Increasing Reactivity

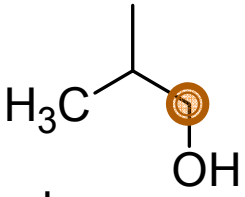
1-butanol



(+/-)2-butanol

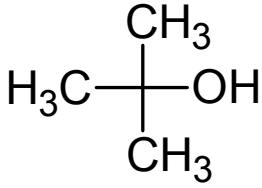


i-butanol



α-hydrogen C-H bond sites indicated

t-butanol (TBA)



Reactivity Trends – Blends

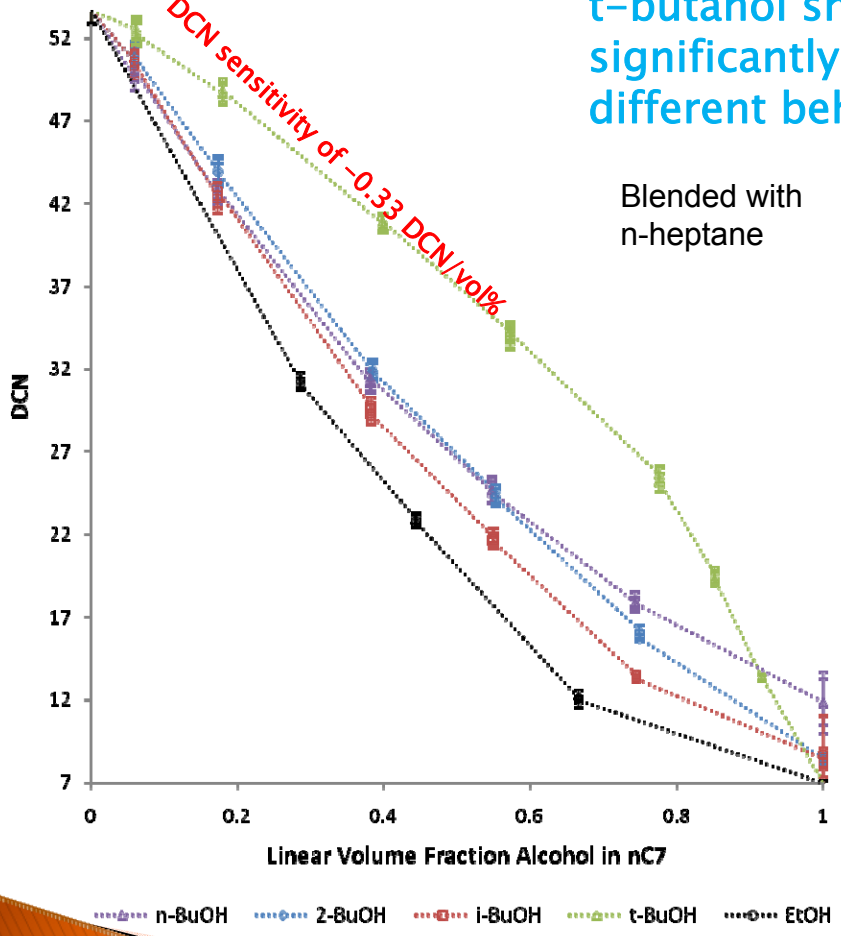
Increasing alcohol content

Increasing alcohol content

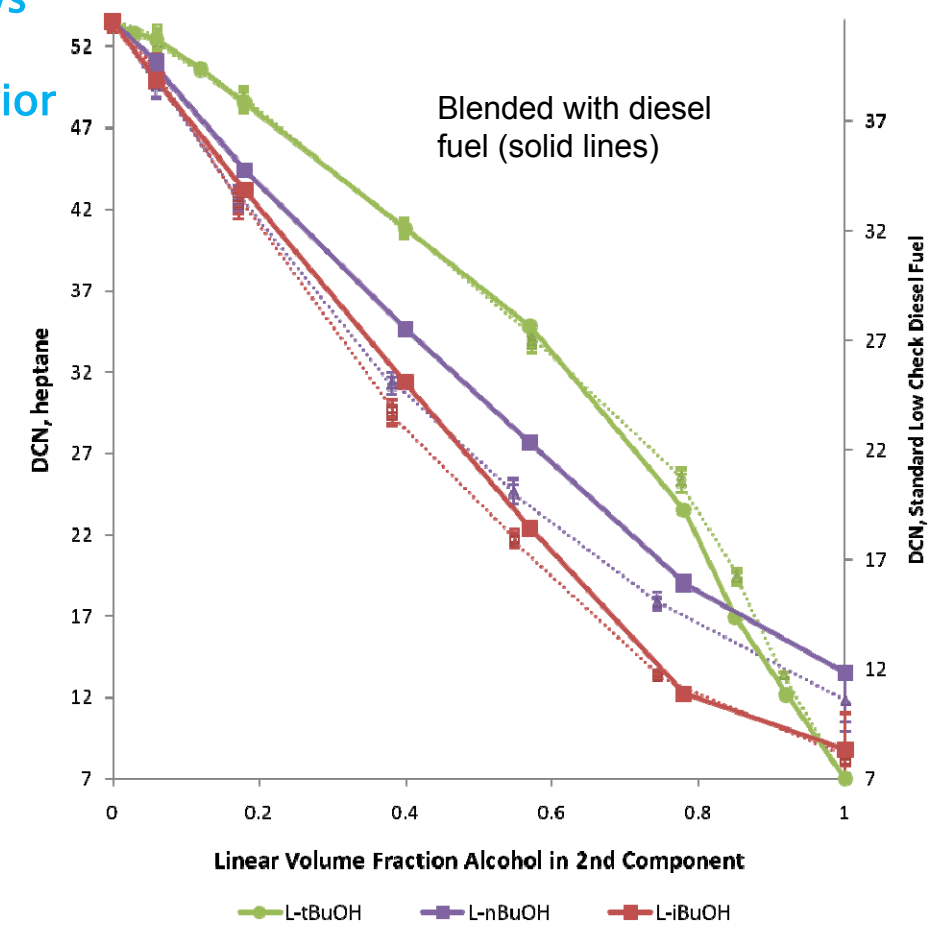
t-butanol shows significantly different behavior

DCN sensitivity of ~0.33 DCN/vol%

Blended with n-heptane



Blended with diesel fuel (solid lines)



Proposed Mechanism for TBA Behaviour

Radical pool generation relatively slow in pure TBA

- Unimolecular processes slow at IQT conditions, mostly abstraction reactions governing ignition.
- Low temperature O_2 addition reactions evidently less important (Cullis & Warwicker) than for large carbon number hydrocarbons.
- β hydrogen atoms less prone to abstraction than α atoms

  BDEs of ~101 vs. 93–95 kcal/mol.
- Subsequent radical decomposition leads to straight-chain reactions and stable products.

$$X + TBA \rightarrow XH + \cdot CH_2(C)(CH_3)_2OH \qquad \text{(abstraction)}$$

$$\cdot CH_2(C)(CH_3)_2OH \rightarrow \text{i-butene} + OH \qquad (\beta\text{-scission})$$

for X=OH, product is H_2O

Key difference between TBA & other BuOHs is selectivity of OH generation process: other BuOHs will mostly produce less reactive HO_2 radical.

Methyl Formate Decomposition, and Oxidation in Low Pressure Flames

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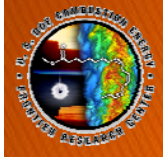


Methyl Formate Oxidation ?

Motivation – (1) Diesel Combustion

- Methyl formate (MF) is major intermediate in Dimethoxy methane (DMM) oxidation and dimethyl ether (DME) oxidation in presence of NO_x.
- Understanding chemical mechanism of MF oxidation => refine understanding of DMM/DME oxidation.

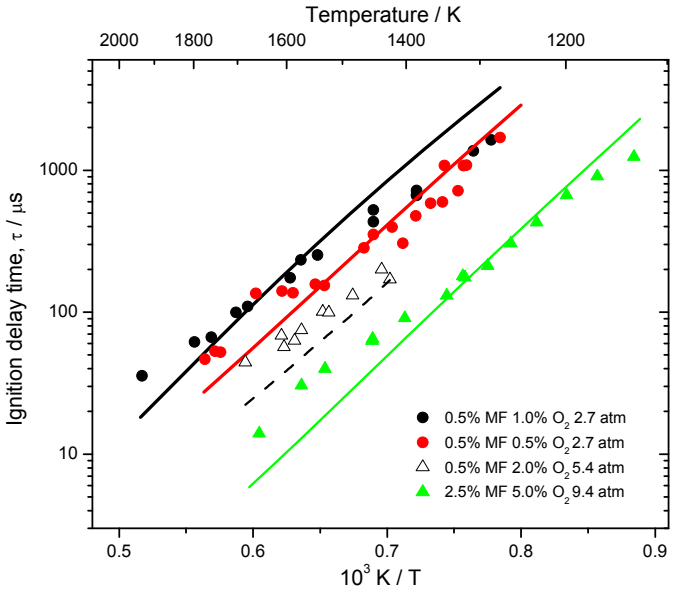
Motivation – (2) Biodiesel Combustion

- Biodiesel consists primarily of long alkyl chain methyl esters.
- Role of ester functionality on biodiesel oxidation remains to be fully understood quantitatively.
- Study of smaller carbon number esters can lead to better understanding of functional behavior in large carbon number species.

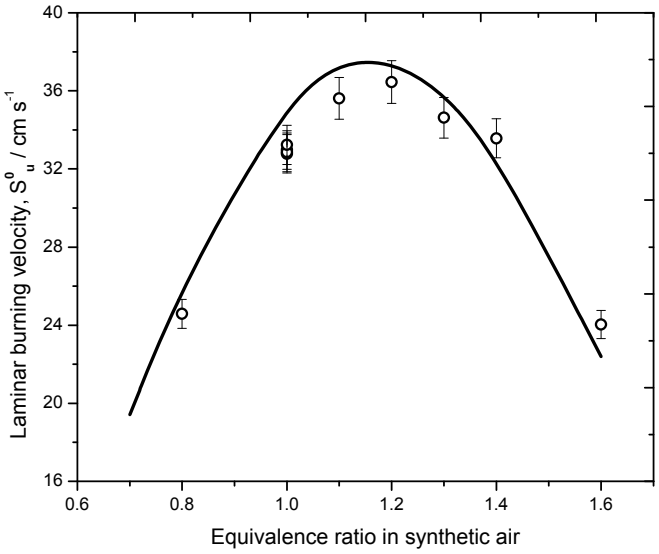
Methyl formate is simplest methyl ester.

Methyl Formate Kinetic Model

- Dooley et al. Int. J. Chem. Kin. 2010.
- Validation – High temperature shock tube ignition delays.
  – Laminar burning velocities.



MF shock tube ignition delay times. Experiment (symbols) and simulation (lines).



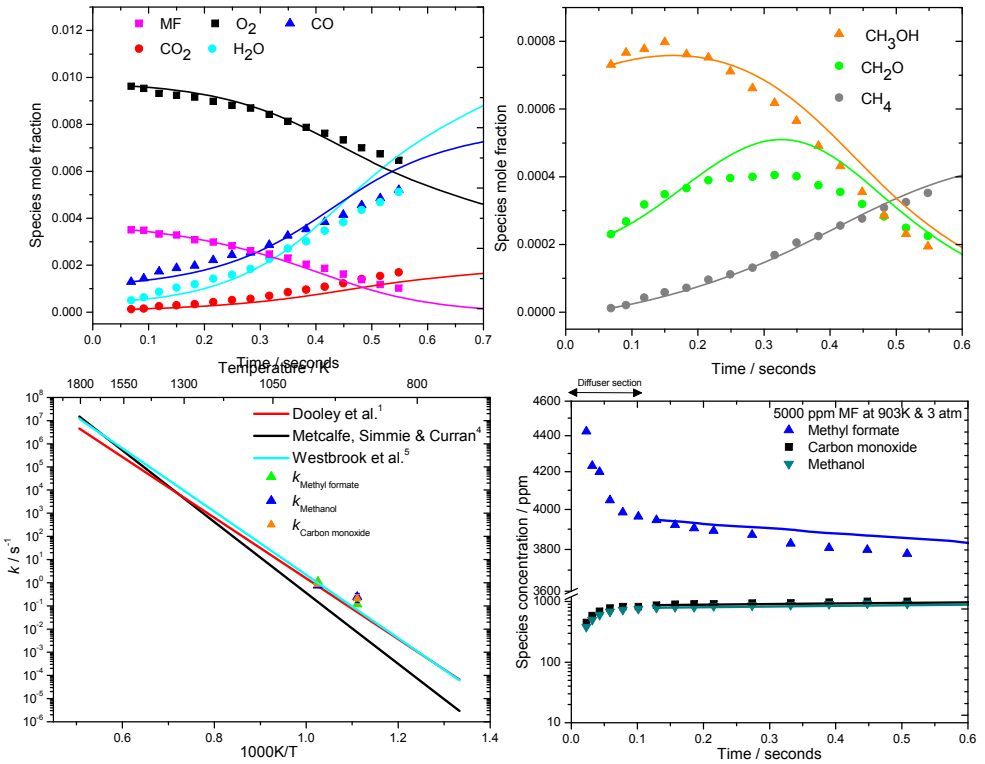
Laminar burning velocities of $MF/O_2/N_2$ freely propagating flames at 1 atm. Experiment (symbols) and simulation (line).

Methyl Formate Model Validation

- Flow reactor speciation data measure methanol, formaldehyde and methane from MF oxidation.

- Pyrolysis measurements show large amounts of methanol and carbon monoxide, indicative of molecular decomposition of methyl formate.

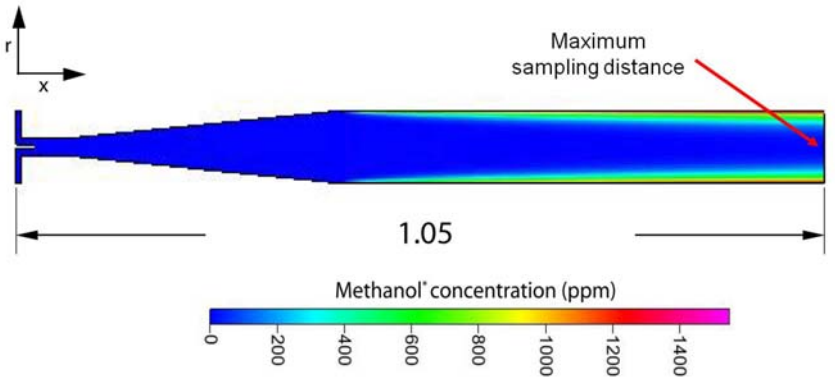
- Kinetics of MF decomposition highly contentious, reported activation energies span 48-77 kcal mol^{-1}(!)



Speciation data from flow reactor oxidation of 0.005/0.01/0.985 MF/O_2/Ar, ϕ=1.0, at 3.0 atm and 975K (top) and 900 K (bottom). Experiment (symbols) and simulation (lines). Rate constant data for MF decomposition.

Methyl Formate Decomposition

Potential effect of wall catalytic reactions evaluated by conducting LES of the entire VPFR geometry.

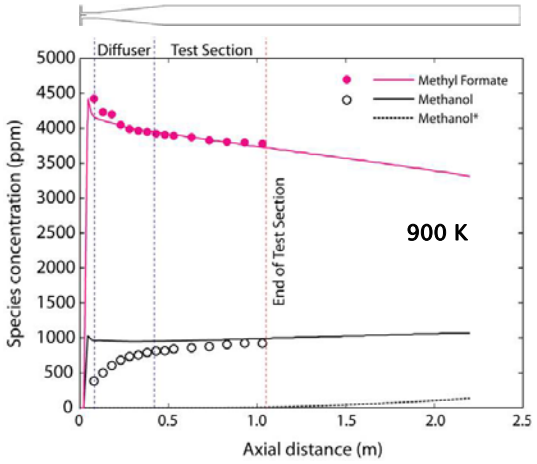


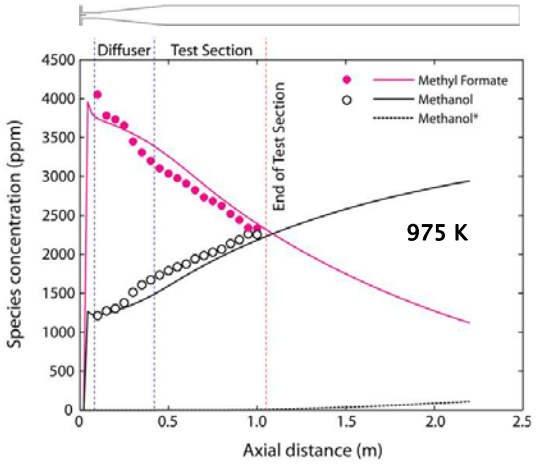
$$CH_3OCHO_{(surface)} \leftrightarrow CH_3OH^*_{(surface)} + CO^*_{(surface)}$$

Products of wall catalytic processes confined in the viscous sub-layer region.

Heterogeneous surface perturbations cannot significantly affect the measurement of the gas phase reaction (of negligible quantity at the center line less than 4%)

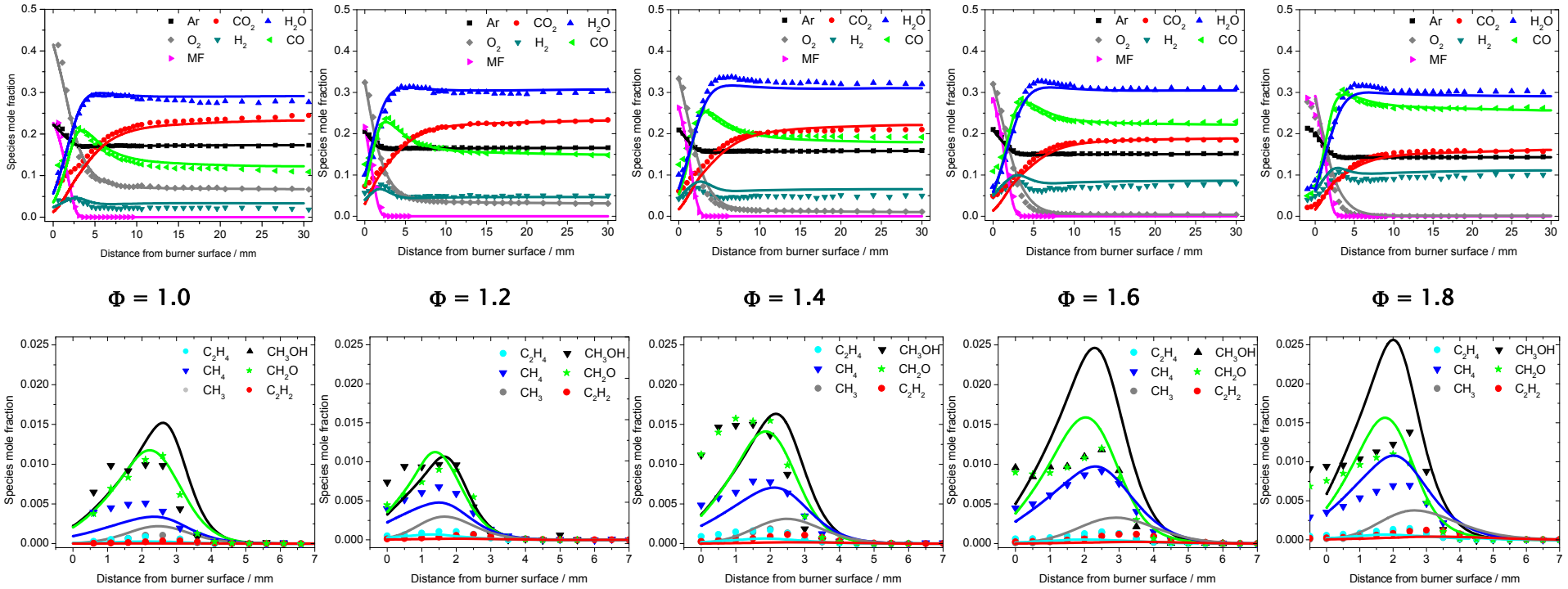
Calculated concentration of CH3OH* in the reactor environment at 975 K, 3 atm, 14.344 g/s flow rate of 5000 ppm of MF in N_2.





Axial profile of MF and gas phase (methanol) vs potential heterogeneous catalytic (methanol*) products for 5000 ppm MF in N_2 at 3 atm at the center line (lines and symbols represent calculations and experiments, CO omitted for clarity)

All Conditions



Experimental data (symbols) and simulation (lines) of MF oxidation in MF/O_2/Ar , Φ = 1.0–1.8, 22–30 Torr flames

- Model captures experimental measurements well.
- Manuscript in review with further details and analyses.

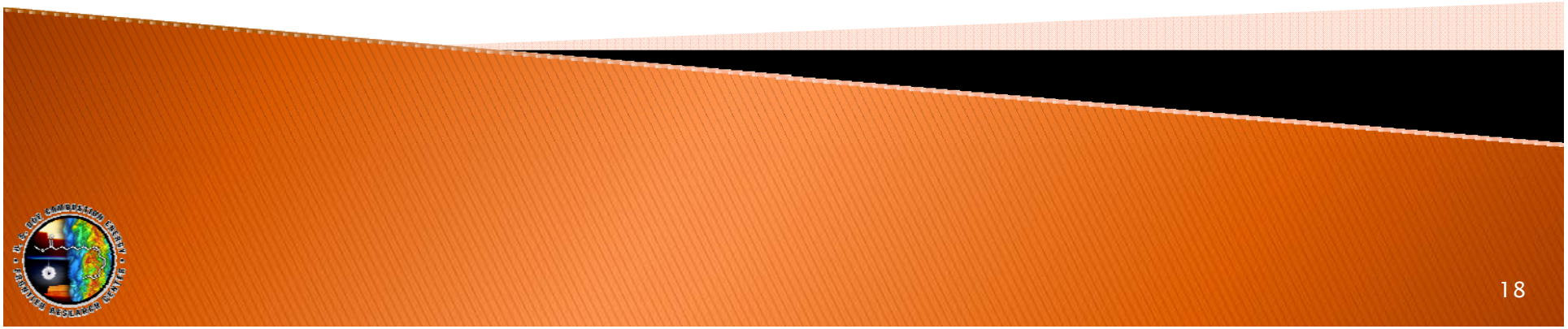
Updated H_2/O_2 Kinetic Transport Model to Address High Pressure Flame Modeling difficulties

M. P. Burke[1], M. Chaos[2], Y. Ju[1], F. L. Dryer[1],
S. Klippenstein[3]

[1]Department of Mechanical and Aerospace Engineering, Princeton University

[2] F. M. Global

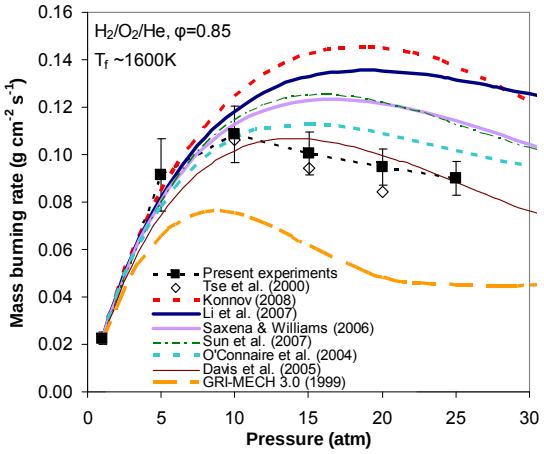
[3]Argonne National Laboratory

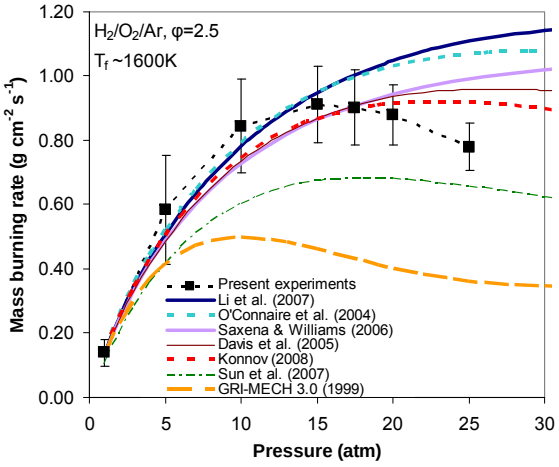


Motivation

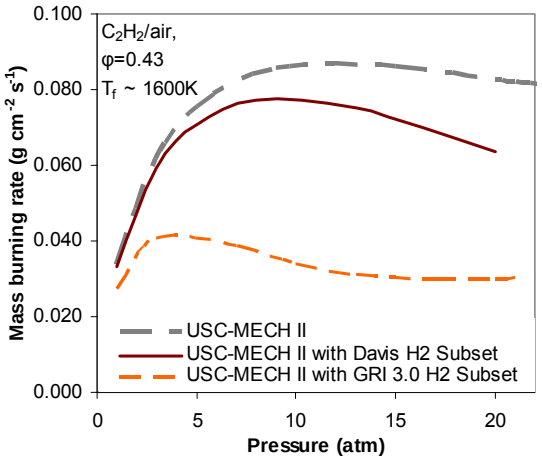
- H_2/O_2 kinetic sub-model – Fundamental topic w/ applications:
  - Hierarchical development of all HC kinetic models.
  - Accurate kinetic/transport models needed for syngas and high hydrogen content fuels to be used in IGCC applications.
    - High pressure, low flame temperature, fuel-lean and/or diluted combustion conditions used in most applications (to control NO_x emissions).

Substantial H_2/O_2 modeling difficulties in high-pressure dilute flames





H_2/O_2 modeling difficulties affect high-pressure HC flame predictions

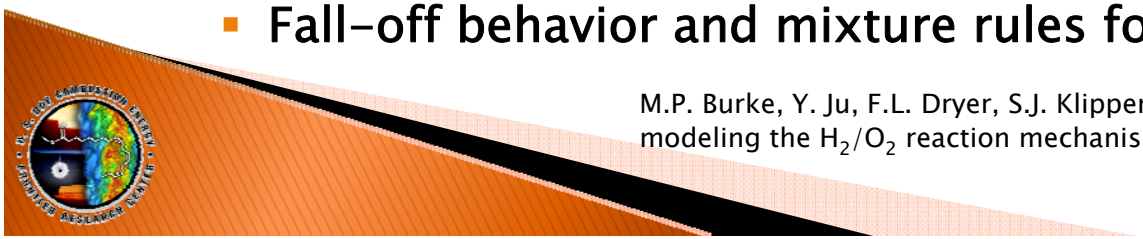


M.P. Burke, M. Chaos, F.L. Dryer, Y. Ju, *Combustion and Flame* 157 (2010) 618-631.

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

Updated H_2/O_2 Kinetic-Transport Model

- Updated model uses the 19-reaction mechanism of Li et al.
  - To incorporate recent studies on elementary reactions.
  - To improve model performance at high-pressure flame conditions.
- Treatment of the following processes/reactions were revised:
  - **Temperature and pressure dependence of HO_2 formation / consumption reactions:**
    - **$H+O_2(+M)=HO_2(+M)$**
    - **HO_2 + H/O/OH/HO_2**
  - Other reactions updated:
    - e.g. $H_2O_2(+M)=OH+OH(+M)$, $OH+H_2O_2=H_2O+HO_2$, $H+OH+M=H_2O+M$.
  - Transport updated:
    - e.g. H, H_2.
- Major sources of remaining uncertainties:
  - Temperature (and pressure) dependence of HO_2+H/OH/O/HO_2.
  - **Fall-off behavior and mixture rules for $H+O_2(+M)=HO_2(+M)$.**



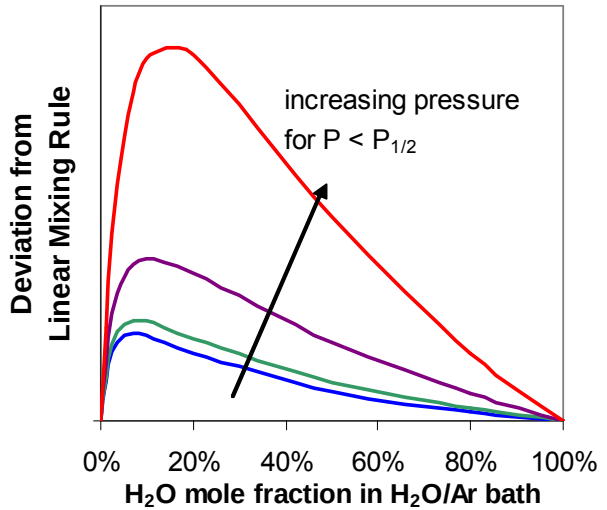
M.P. Burke, Y. Ju, F.L. Dryer, S.J. Klippenstein, "An updated model and discussion of challenges for modeling the H_2/O_2 reaction mechanism in high-pressure flames," in preparation for *IJCK* (2010).

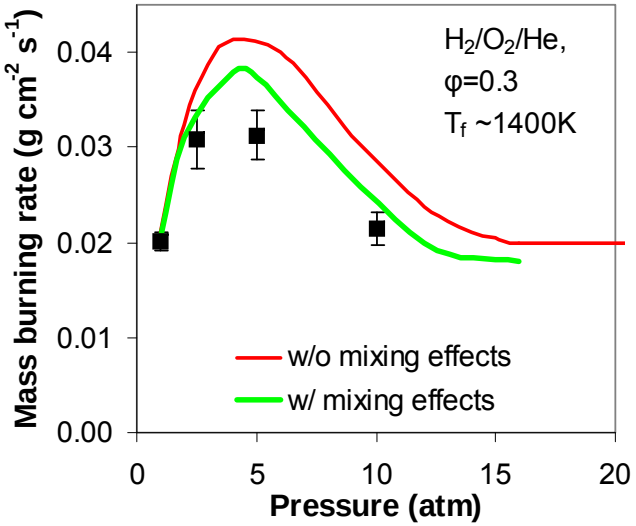
Nonlinear Bath-Gas Mixture Interaction

- Practical combustion=>multi-species bath gas.
- At best, models assume linear mixture rule:

$$k = \sum_i k_i(T,P) \cdot X_i$$

  At worst, common modeling approaches yield *n* times high-pressure limit =>but
- Different components of a multi-component bath gas "interact" in unimolecular reactions
- Nonlinearities stronger when:
  - <ΔE> difference is larger
  - Each component has nearly equal contributions to rate constant
  - Reaction is in intermediate fall-off
- Preliminary calculations and those of *Troe (1980)* show ~10% nonlinearities in low-p limit
- ~10% mixing effects yield 15% differences in burning rate predictions
- Behavior highly dependent on <ΔE> values





1. J. Troe, *Ber. Bunsenges. Phys. Chem.* 84 (1980) 829-834.
- 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

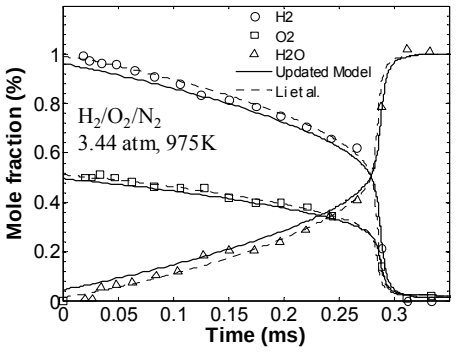


Figure 10.

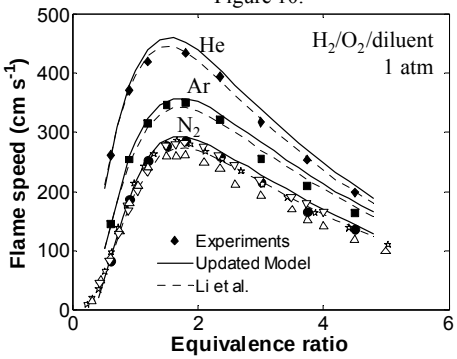


Figure 11.

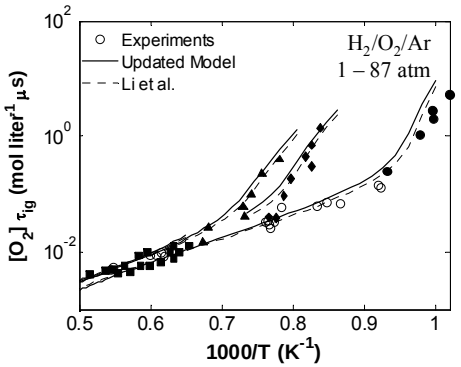


Figure 12.

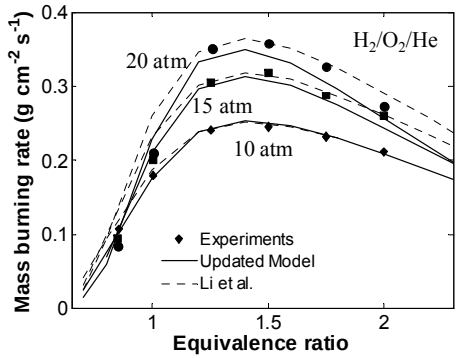


Figure 13.

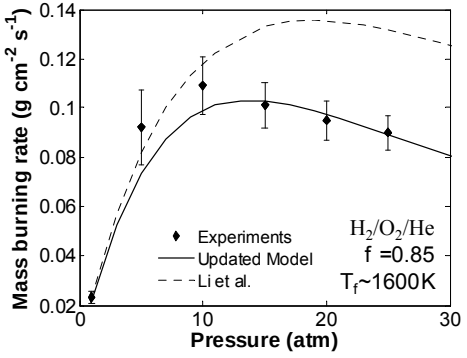


Figure 14.

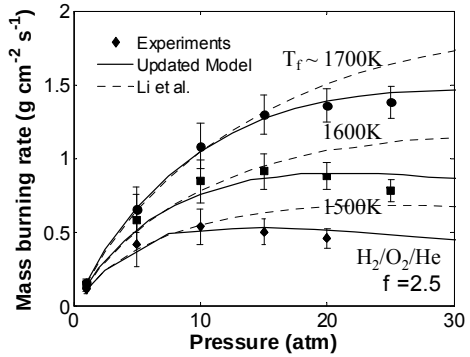


Figure 15.

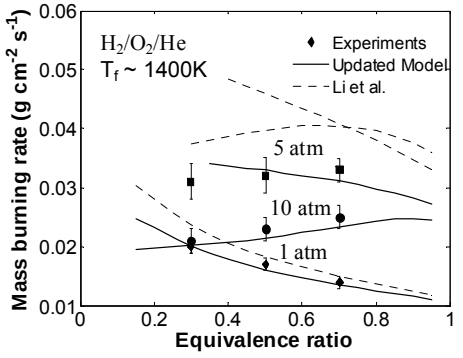


Figure 16.

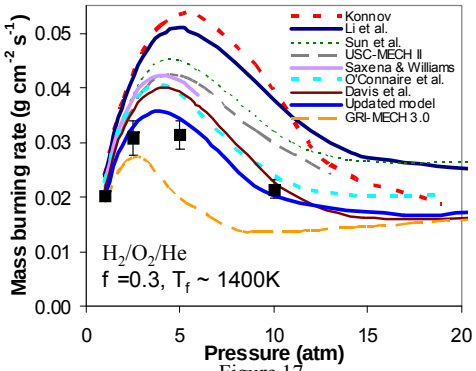


Figure 17.

- 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).

Future Plans

- Continuing efforts to contribute elementary rate constant measurements and kinetic system validation data using flow reactor techniques.

- Contributions to the small molecule chemistry that is important to high pressure oxidation kinetics of these materials.

- Development of chemical kinetics model for bio-derived fuels.

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