Combustion Studies of Alcohols, Esters and Hydrogen Rich Fuels

Frederick L. Dryer

Department of Mechanical and Aerospace Engineering
Princeton University

First Annual Conference of Combustion Energy Frontier Research Center (CEFRC)
September 23-24, 2010, Princeton, New Jersey

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

Z. Serinyel[1], J. S. Heyne[2], F.L. Dryer[2]

[1]Department of Chemistry, National University of Ireland, Galway:
Collaboration with H.C. 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

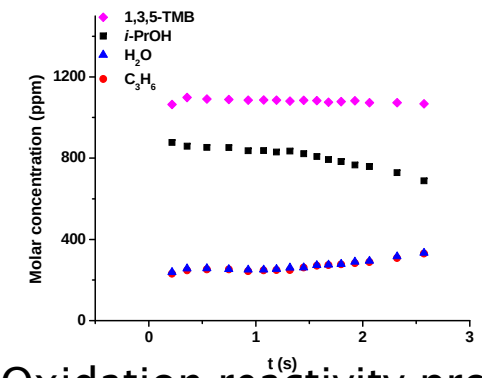
Experiment	T (K)	P (atm)	Molar conc'n (ppm)
Pyrolysis History	720–1000	12.5	2500
Pyrolysis Reactivity (τ = 1.8 s)	500 – 975	12.5	2500
Oxidation Reactivity (τ = 1.8 s, φ=1)	676– 918	12.5	2500
Pyrolysis with radical trapper (1,3,5–TMB)	1020, 1080	3.0	1540 equimolar

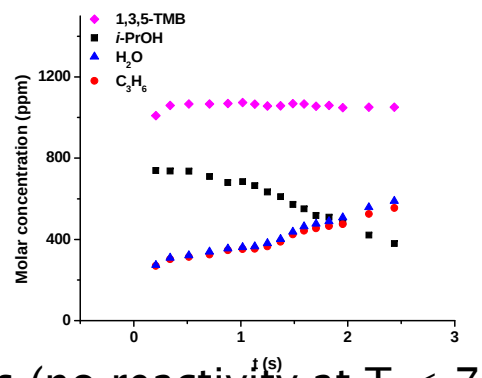
Preliminary results on pyrolysis/oxidation

- 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





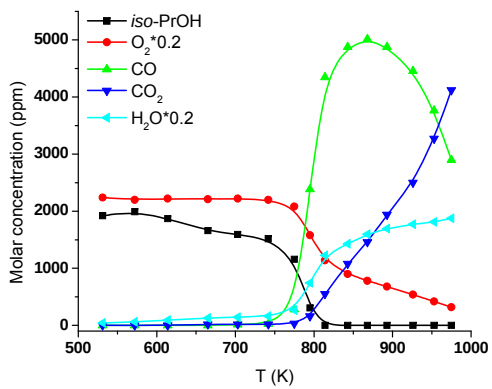
***Iso*–propanol** pyrolysis with radical trapper:

1200 ppm $i\text{–}C_3H_7OH$
1200 ppm 1,3,5–TMB
T = 900 and 950 K
P = 12.5 atm

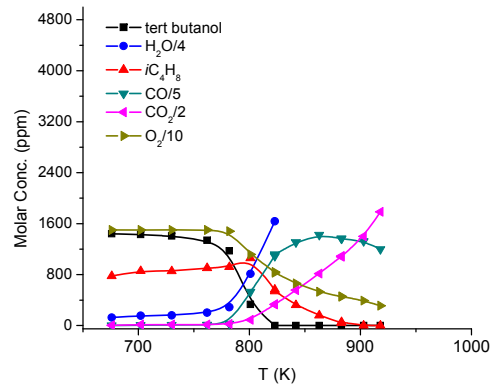
- Oxidation reactivity profiles (no reactivity at T < 775K

Oxidative conditions:

Residence time = 1.8 s
P = 12.5 atm
ϕ = 1.0



iso–propanol



t–butanol

Autoignition of Fuel/Butanol Blends in an Ignition Quality Tester

F. M. Haas and F.L. Dryer

Department of Mechanical and Aerospace Engineering
Princeton University

Autoignition of Butanol?

Motivation

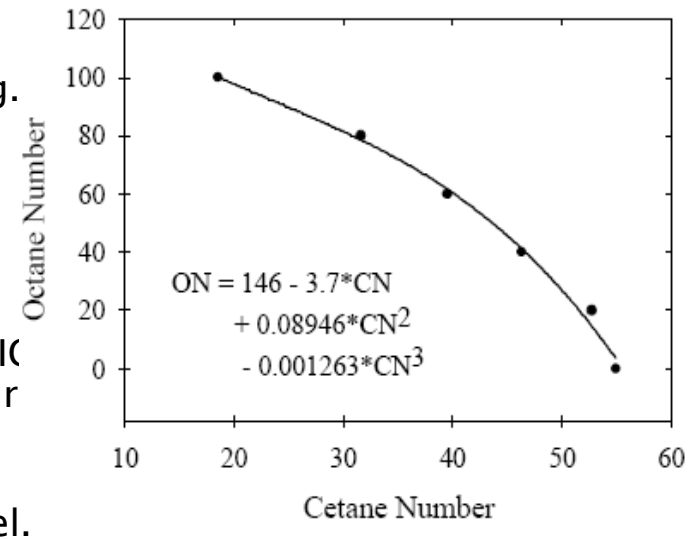
- Isomers of butanol have been identified as promising candidates of 2nd generation bio fuels.
- Little fundamental work available on how these alcohols interact with hydrocarbons found in conventional petroleum derived fuels– likely end use scenario for these bio generated materials.

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, DIC 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.

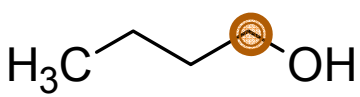


Reactivity Trends – Neat Butanols

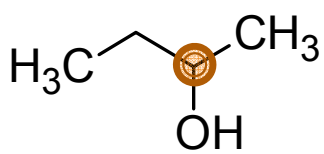
Pure Component	Avg. Measured DCN	MON
t-butanol	<7.18	94
i-butanol	8.51	94
2-butanol	8.54	91
n-butanol	12.02	78
n-heptane	53.8†	0†

Increasing Reactivity

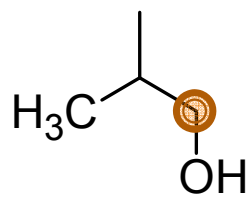
1-butanol



(+/-)2-butanol

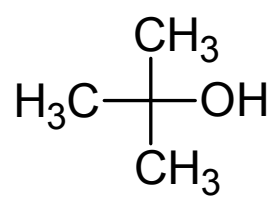


i-butanol



α-hydrogen C-H bond sites indicated

t-butanol (TBA)

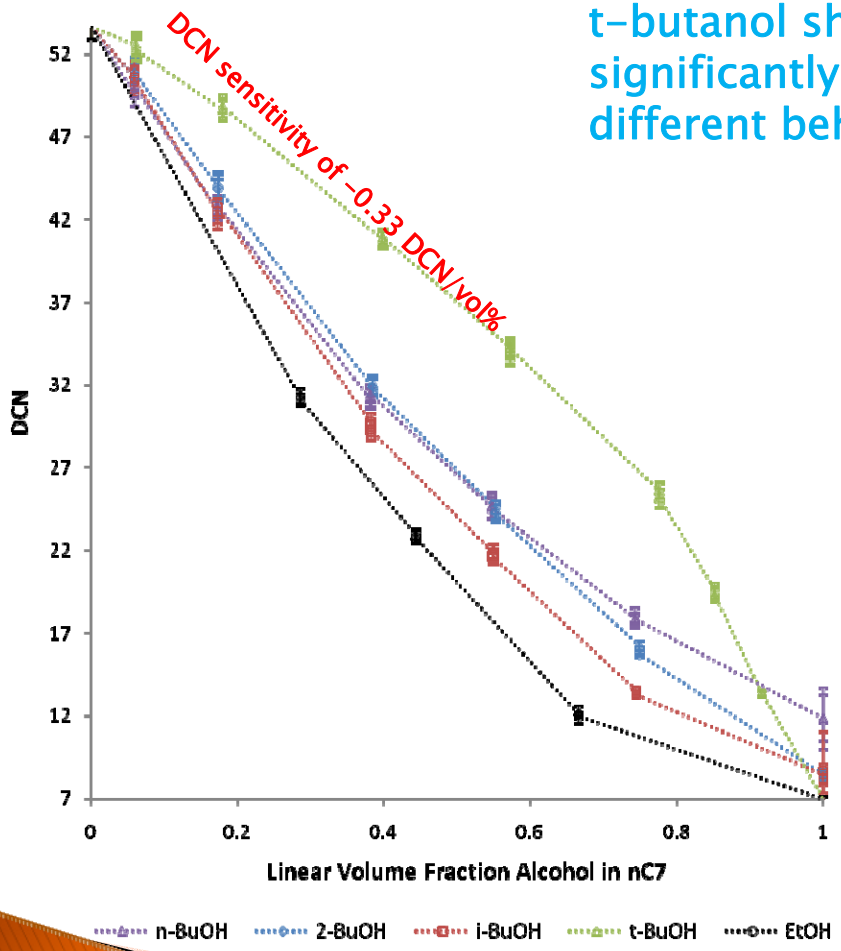


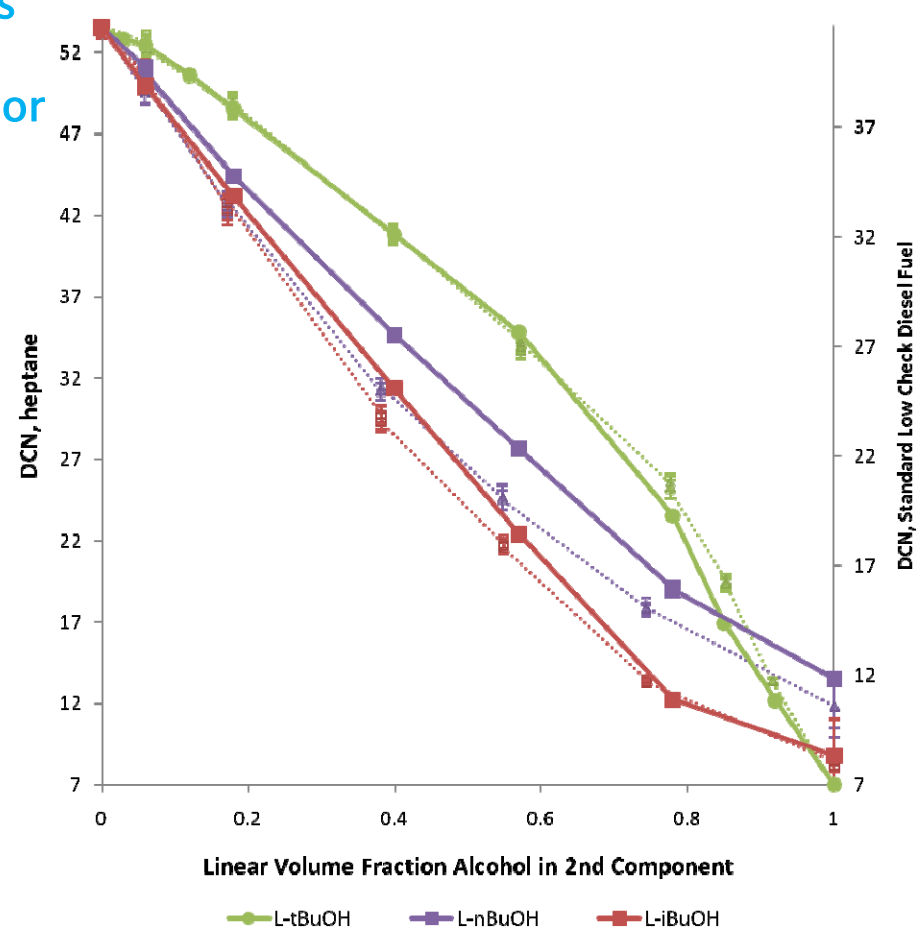
Reactivity Trends – Blends

Increasing alcohol content

Increasing alcohol content

t-butanol shows significantly different behavior





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.

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

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

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

S. Dooley[1], T.I. Farouk[1], F.L. Dryer[1], B. Yang[2], T. Kasper[2], N. Hansen[2], T.A. Cool[3]

[1]Department of Mechanical and Aerospace Engineering, Princeton University
[2]Combustion Research Facility, Sandia National Laboratories
[3]School of Applied and Engineering Physics, Cornell University

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.

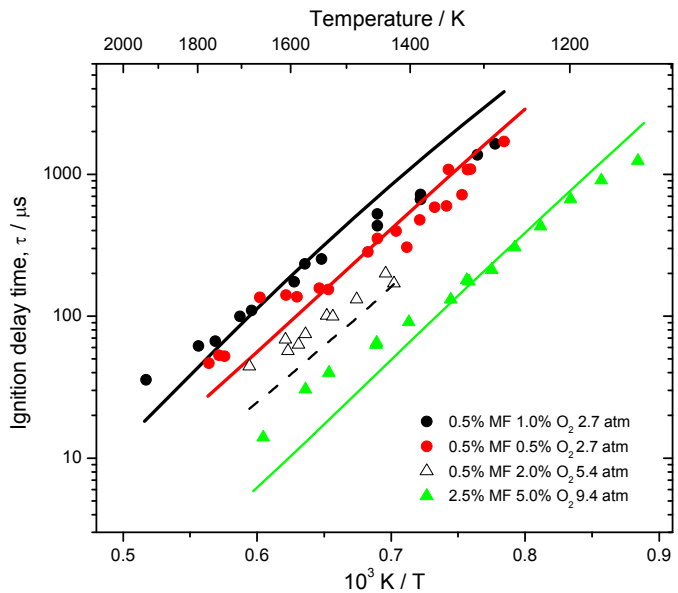
Motivation – (2) Biodiesel Combustion

- 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.

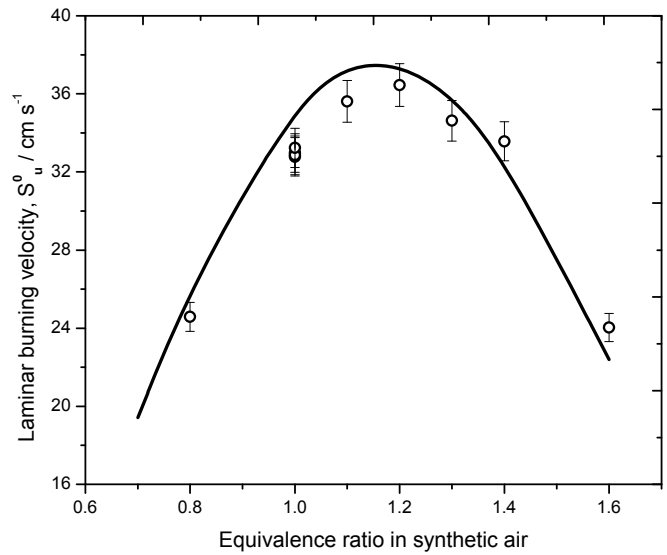
Methyl formate is simplest methyl ester.

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).



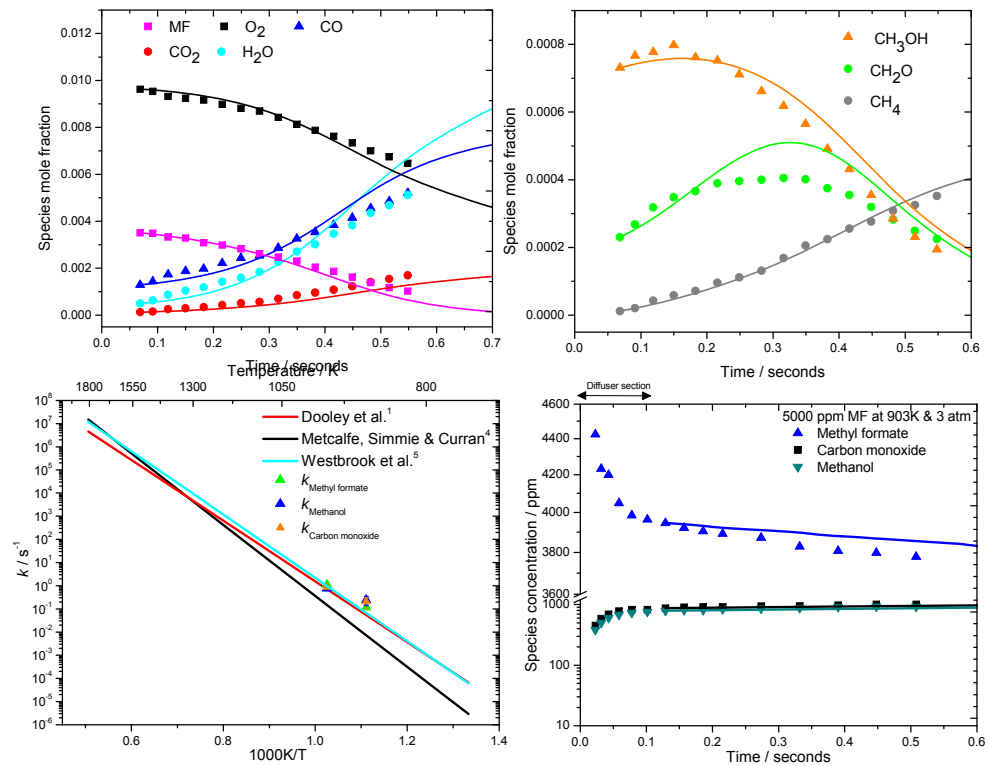
Laminar burning velocities of $MF/O_2/N_2$ freely propagating flames at 1 atm. Experiment (symbols) and simulation (line).

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.

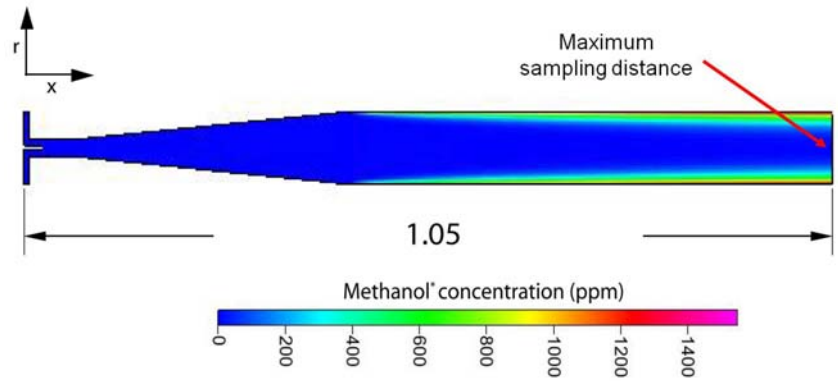
- Kinetics of MF decomposition highly contentious, reported activation energies span 48-77 kcal mol^{-1}(!)



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.

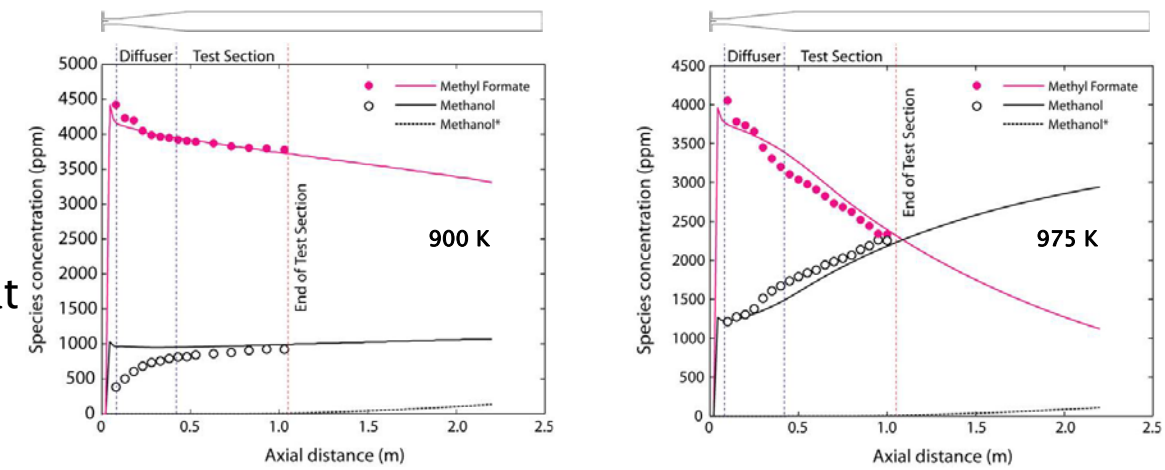


$$CH_3OCHO_{(surface)} \leftrightarrow CH_3OH^*_{(surface)} + CO^*_{(surface)}$$

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

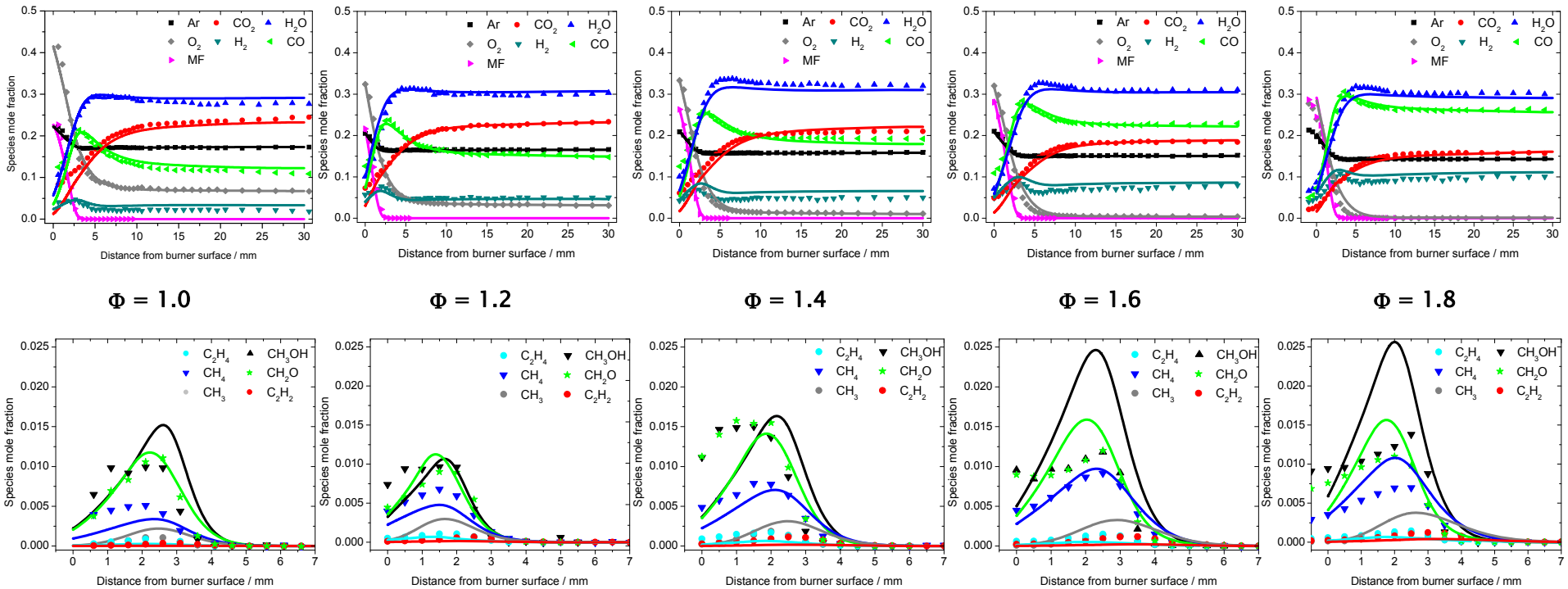
Heterogeneous surface perturbations cannot significantly affect the measurement of the gas phase reaction (of negligible quantity at the center line less than 4%)

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

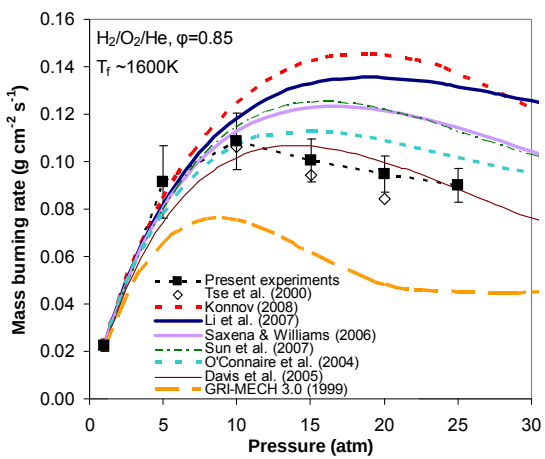
[2] F. M. Global

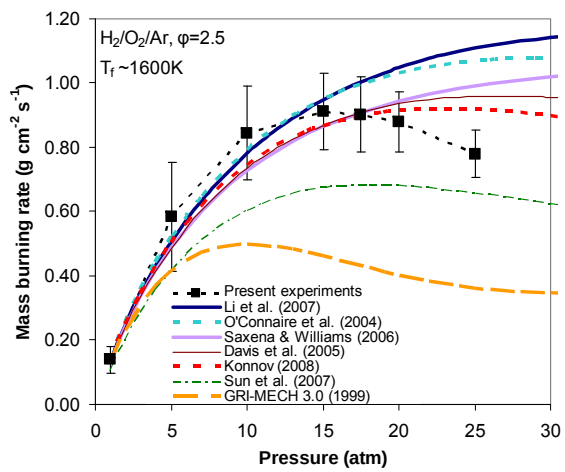
[3]Argonne National Laboratory

Motivation

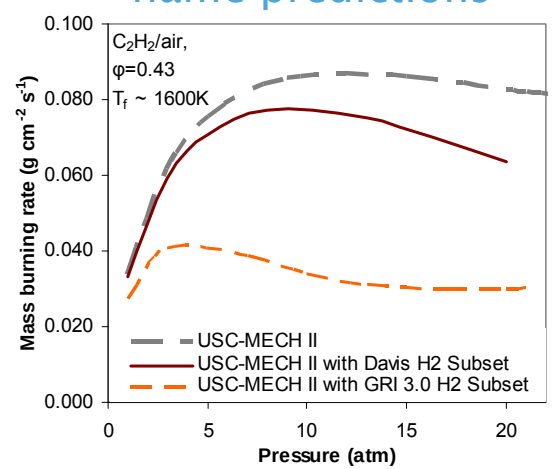
- H_2/O_2 kinetic sub-model – Fundamental topic w/ applications:
  - Hierarchical development of all HC kinetic models.
  - Accurate kinetic/transport models needed for syngas and high hydrogen content fuels to be used in IGCC applications.
    - High pressure, low flame temperature, fuel-lean and/or 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 $H+O_2(+M)=HO_2(+M)$.**

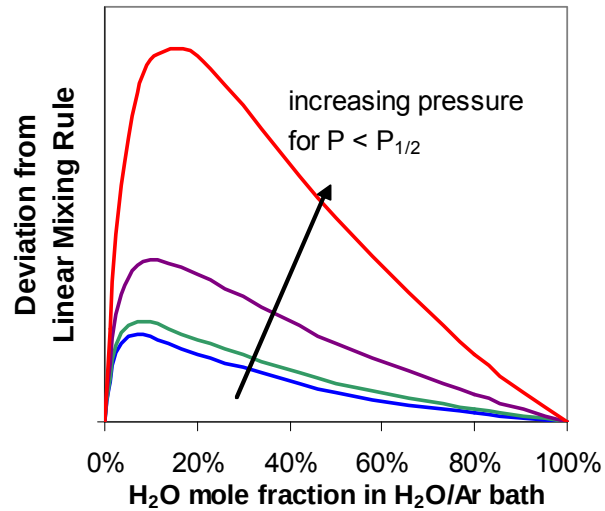
M.P. Burke, Y. Ju, F.L. Dryer, S.J. Klippenstein, "An updated model and discussion of challenges for modeling the H_2/O_2 reaction mechanism in high-pressure flames," in preparation for *IJCK* (2010).

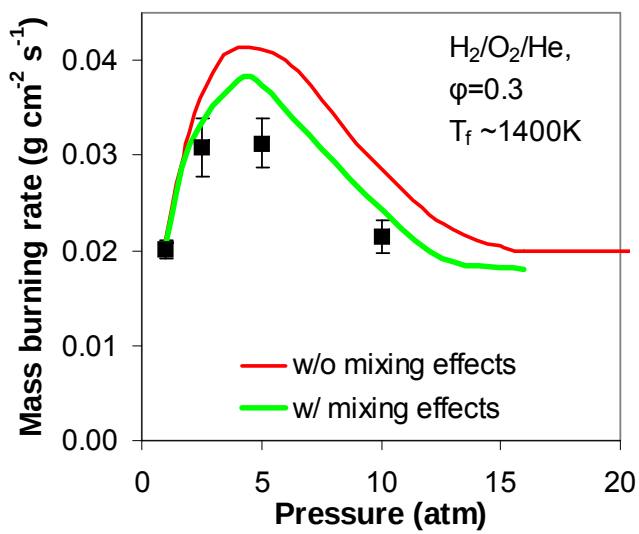
Nonlinear Bath-Gas Mixture Interaction

- 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

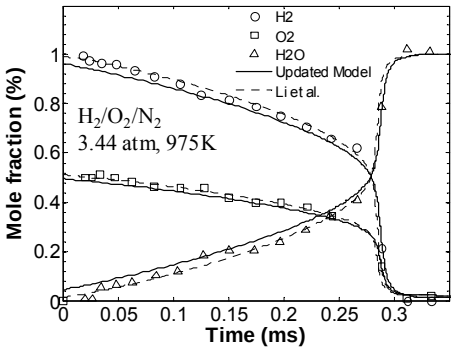


Figure 10.

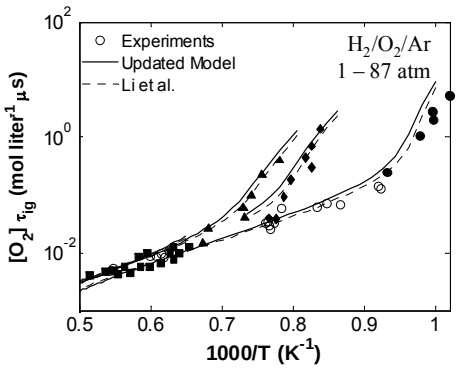


Figure 12.

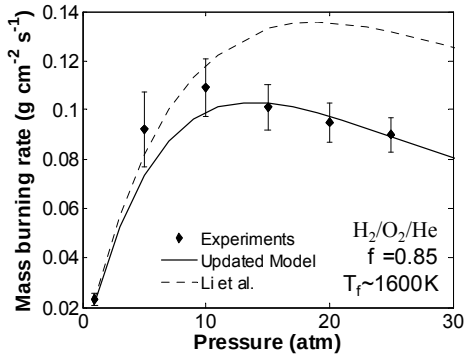


Figure 14.

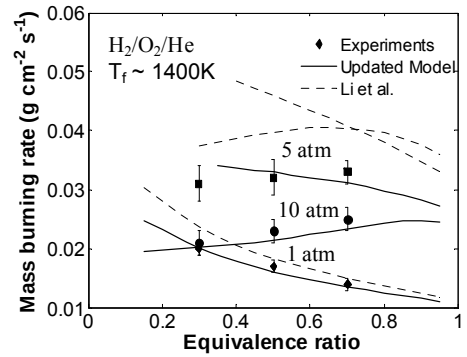


Figure 16.

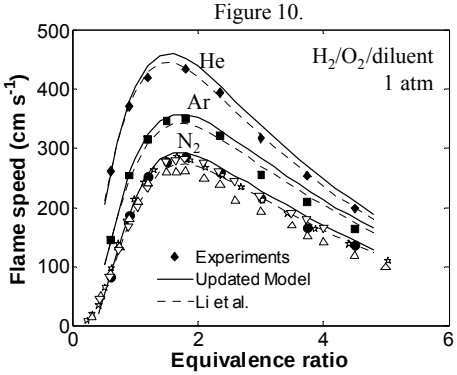
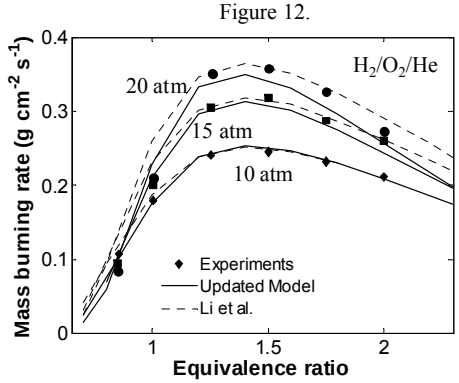


Figure 11.



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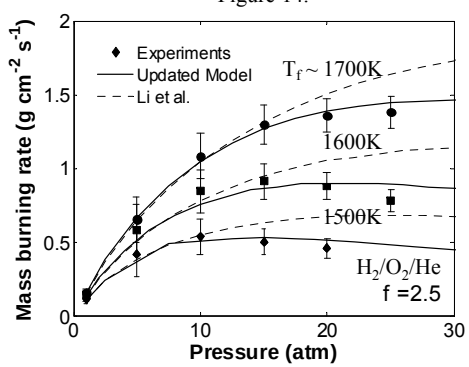

Figure 15.

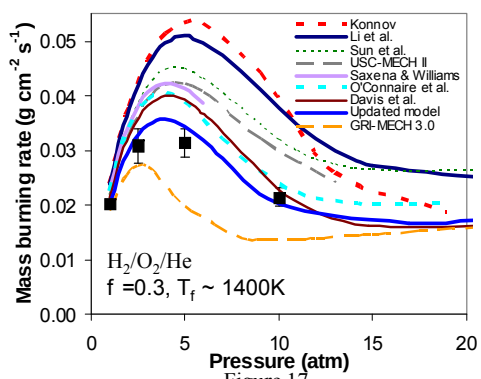

Figure 17.

- 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).

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.

Acknowledgments

- **Research Staff**: Drs. Stephen Dooley and Tanvir Farouk
- **Graduate Students**: Francis M. Haas, Joshua S. Heyne, Michael P. Burke, Zeynep Serinyel
- **Undergraduates**: Amanda Ramcharan
- **Technical Staff**: Timothy Bennett, John Grieb, Joseph Sivo
- **Collaborations**
  - Dr. Steven Klippenstein (Argonne National Laboratory)
  - Drs. Nils Hansen and Bin Yang (Sandia National Laboratories)
  - Dr. Terrance Cool (Cornell University)
  - Dr. Henry Curran (National University of Ireland, Galway)