

Constructing Accurate Combustion Chemistry Models: Butanols

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CEFRC Annual Meeting, Sept. 2010

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Dr. Stephen Klippenstein

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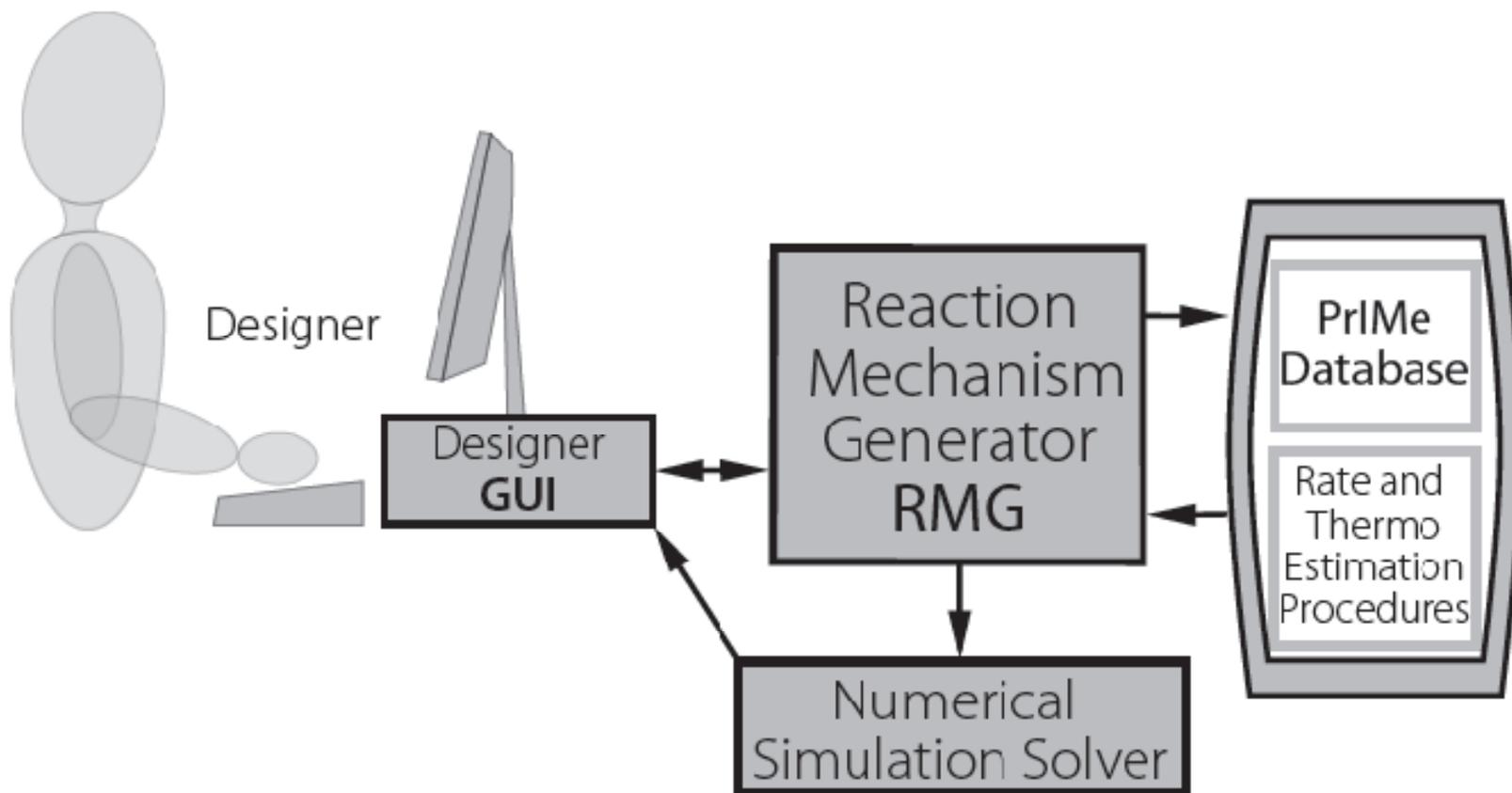
Dr. S-A Seyed-Reihani

Dr. Richard West

& MANY CEFRC MEMBERS

One of Our Project's Long-term Goals:

**Fuel, Engine, and Combustor Designers
Can Quickly *Predict* Performance of any Fuel**



RMG's

Mechanism

Construction:

1) Apply reaction operators to species in “core” to generate new rxns & species.

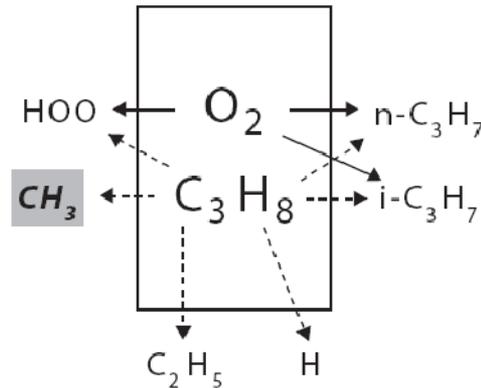
2) Estimate rate coefficients for new reactions, and thermo for new species.

3) Integrate kinetic equations; if rate of formation of an “edge” species is ever larger than tolerance, add to “core”.

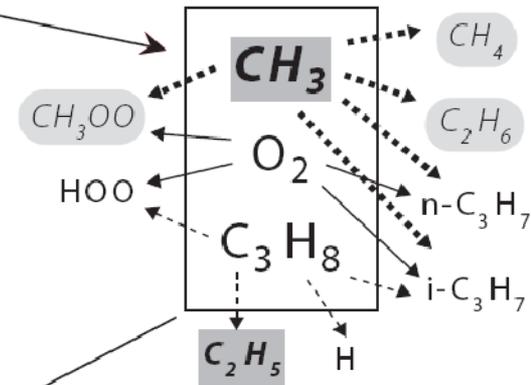
4) Iterate.

5) Repeat at each reaction condition, using model so far as “initial model”

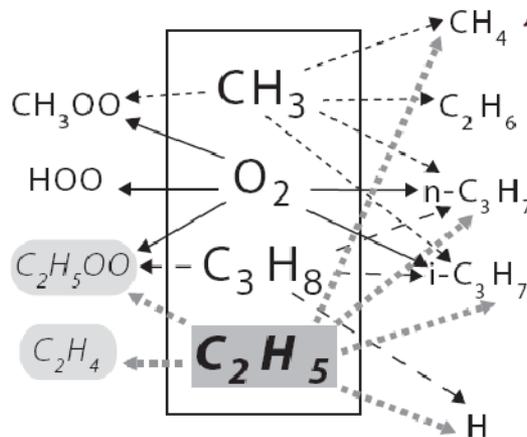
INITIAL MODEL



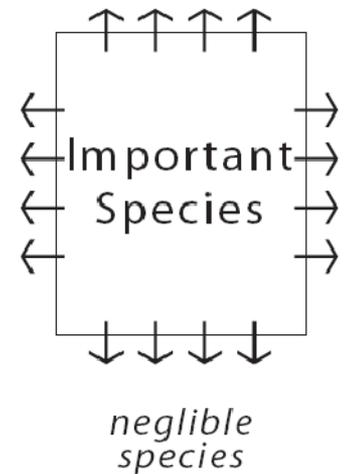
After FIRST Iteration



After SECOND Iteration

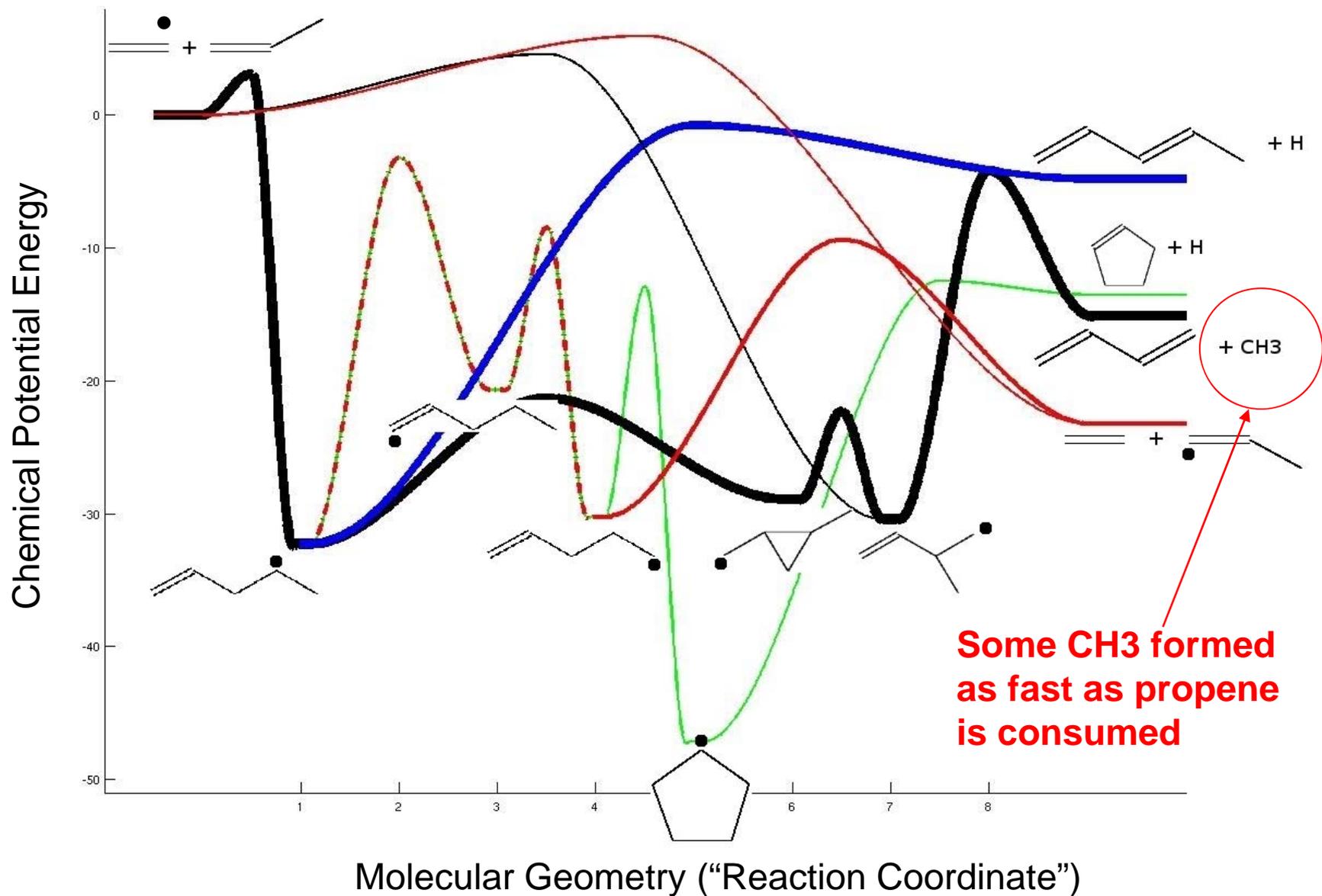


AT TERMINATION



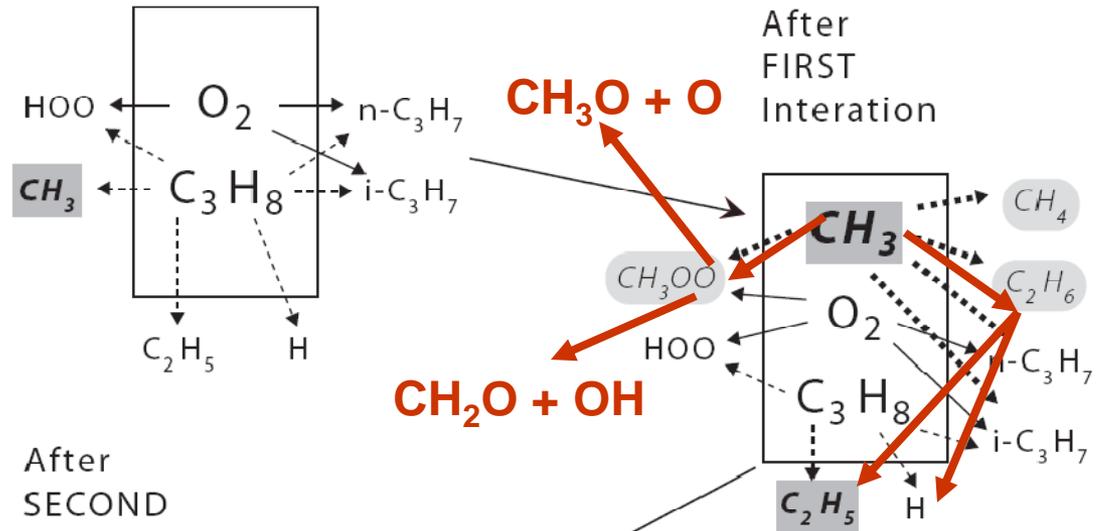
many iterations

Chemical Activation: Leap over several barriers faster than thermalization



Must modify
Mechanism
Construction
Algorithm to
identify
**chemically-
activated paths
that jump over
several transition
states** before
thermalization.

INITIAL MODEL



See papers by
D. Matheu *et al.*, J.W. Allen *et al.*

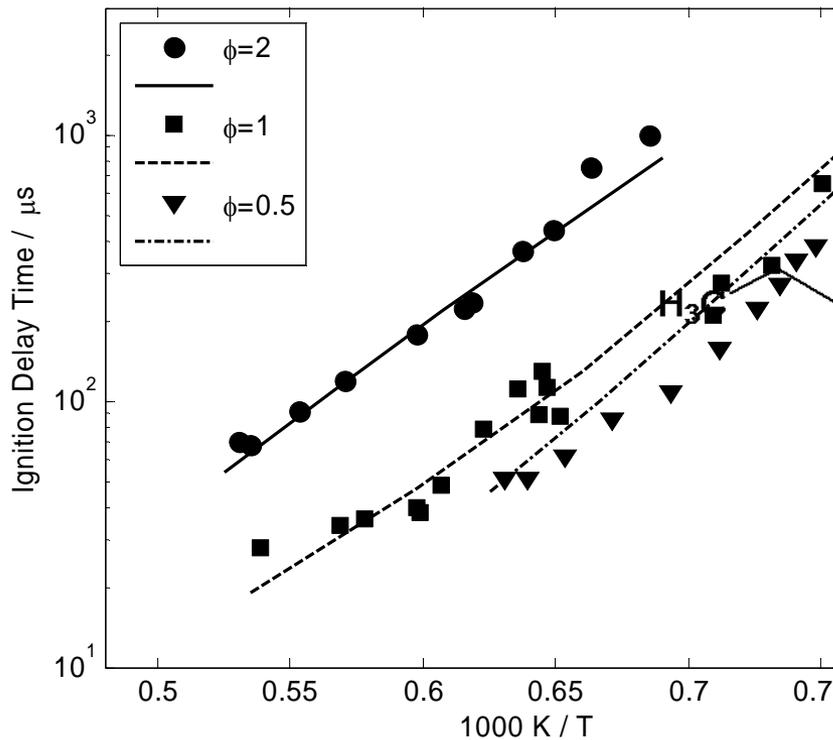
Butanols Model vs. Data

- Many new datasets measured by CEFRC and several more measured by our colleagues outside CEFRC.
 - Data is coming in faster than we can simulate it!
- Some datasets with no figures in this talk:
 - Premixed flames (N.H., H.W., K.K.-H. & F.Qi)
 - Extinction strain rates, flame speeds (C.K.L., F.E.)
 - Butanol, butanal ignition (R.H.+D.D., Galway group)
 - OH+butanols (R.H.+D.D.)
 - 2-d doped methane flame (McEnally & Pfefferle)
 - t-butanol in PFR (Dryer)
 - butanols + heptane non-intuitive mixing rule (Dryer)

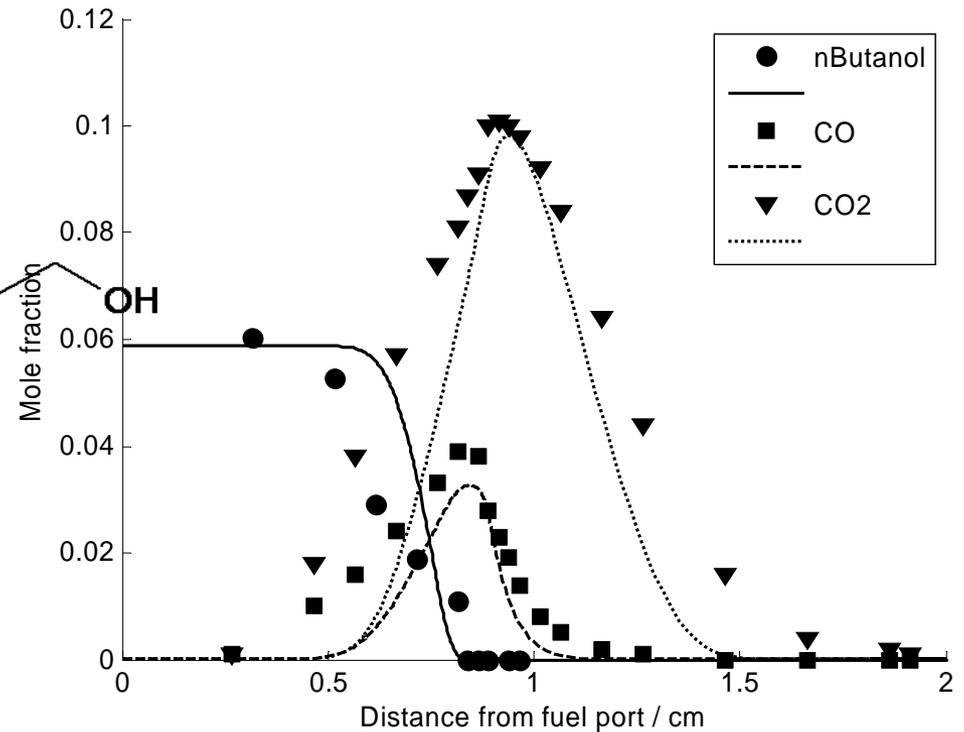
(about half of these have been compared with latest model so far)

RMG-constructed model for Butanol combustion vs. many different experiments

ignition delay (Black et al.)

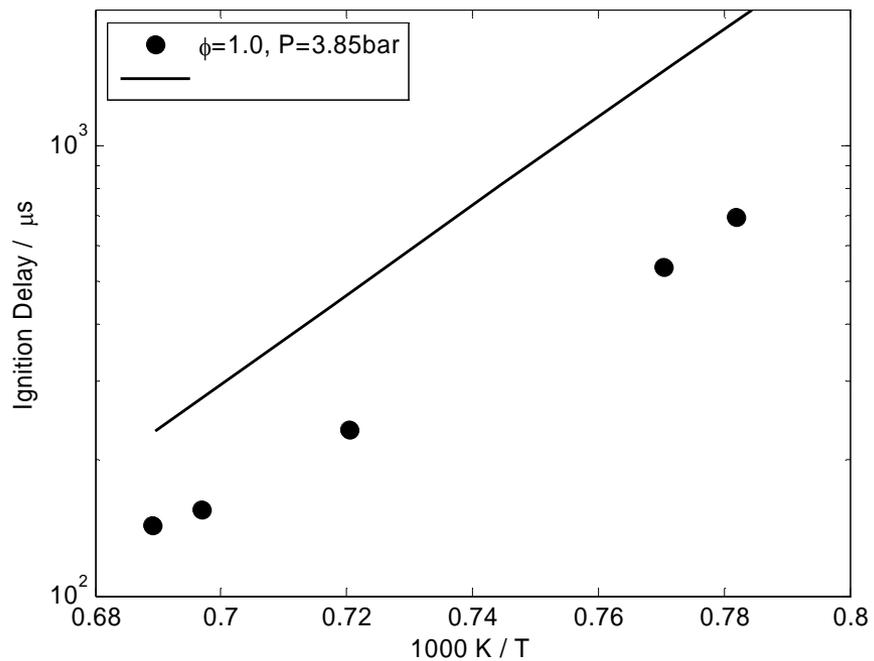


opposed-flow diffusion flame (Sarathy)

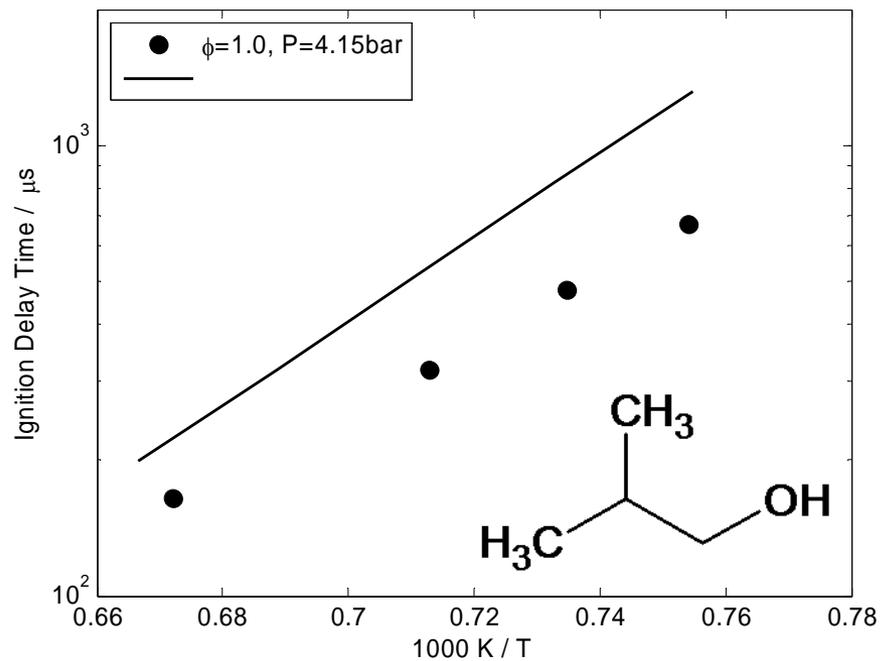


Harper et al. *Combust. Flame* (2010).
263 species, 3381 rxns

0.25% n-BuOH

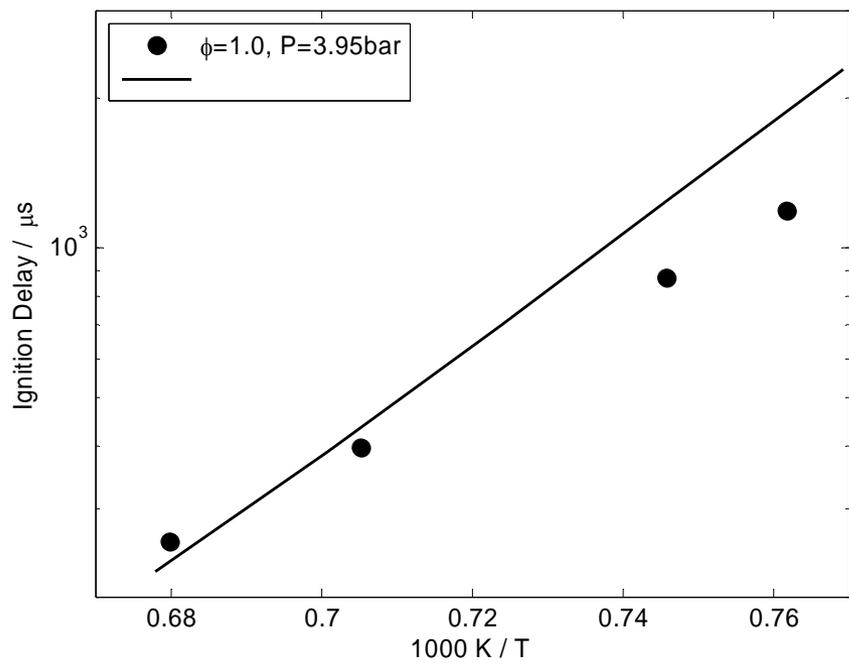


0.25% iso-BuOH

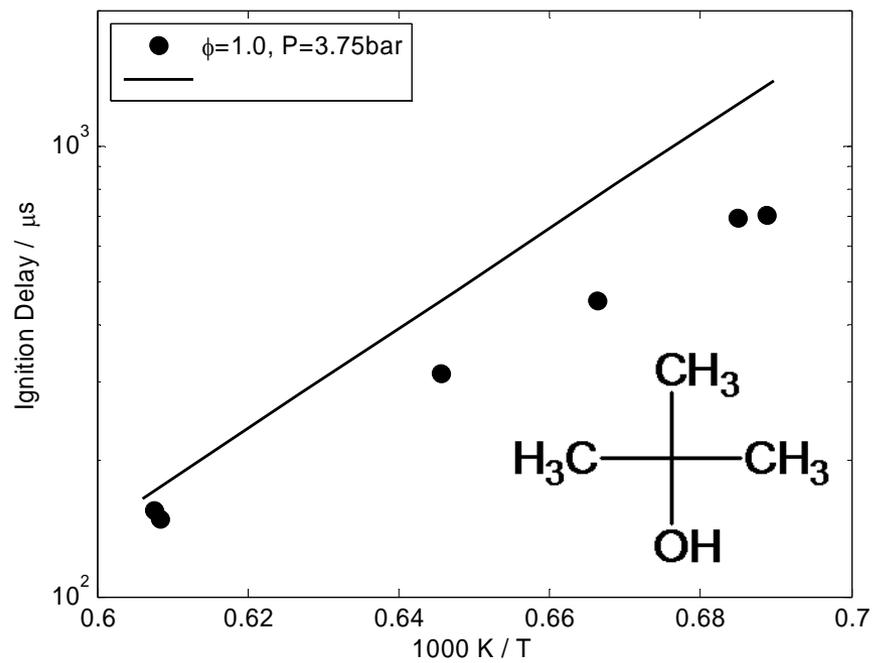


Data of Moss et al.

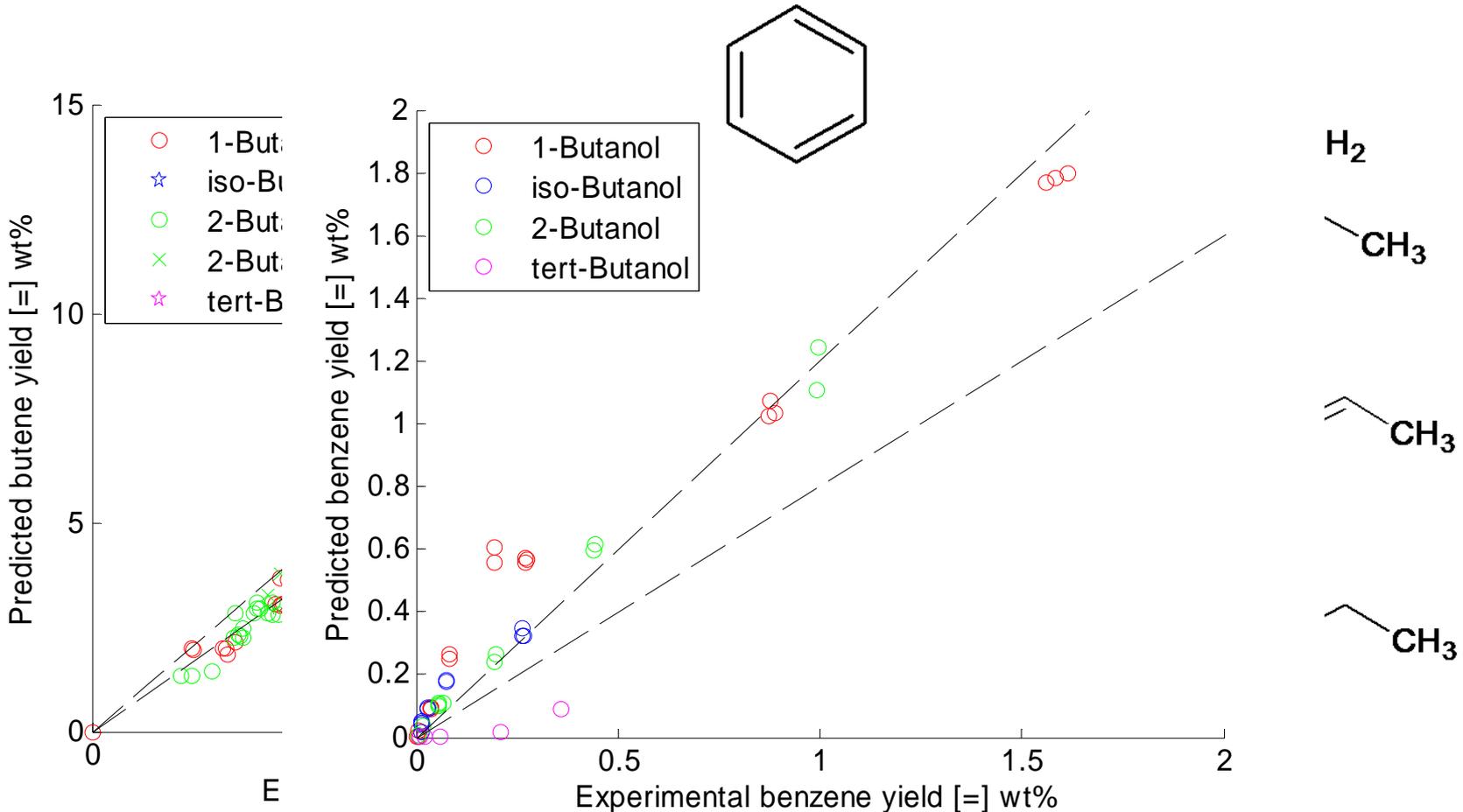
0.25% sec-BuOH



0.25% tert-BuOH

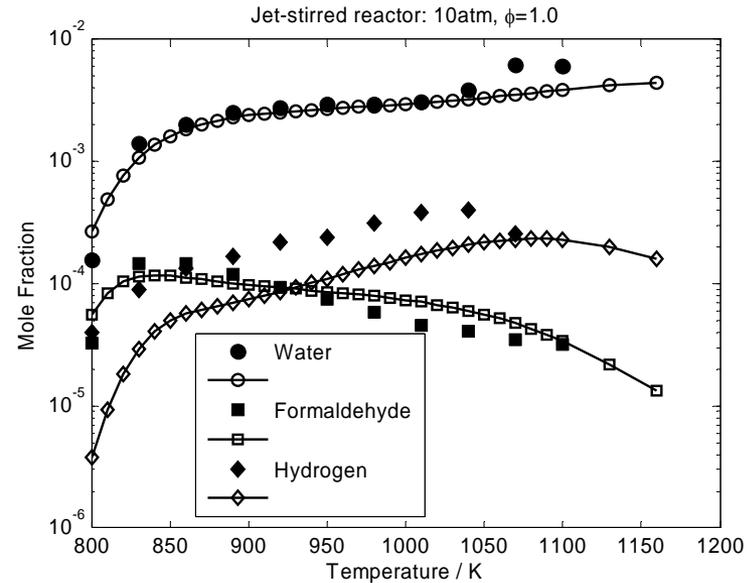
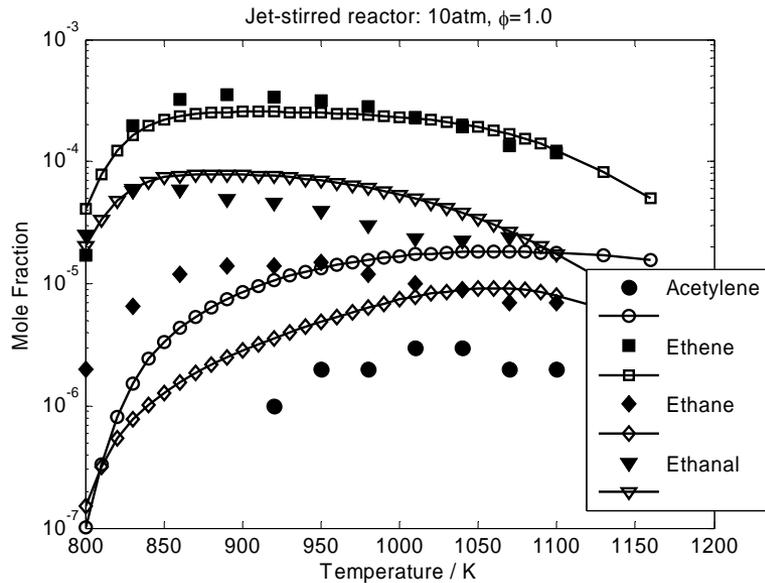
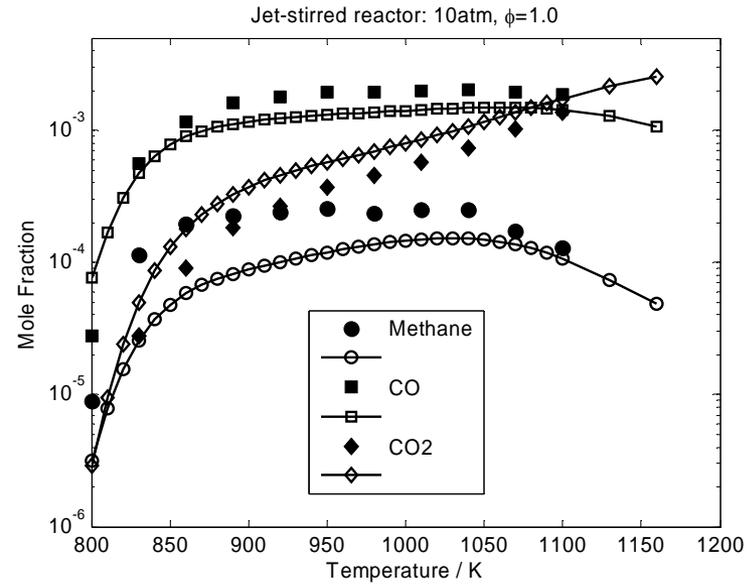
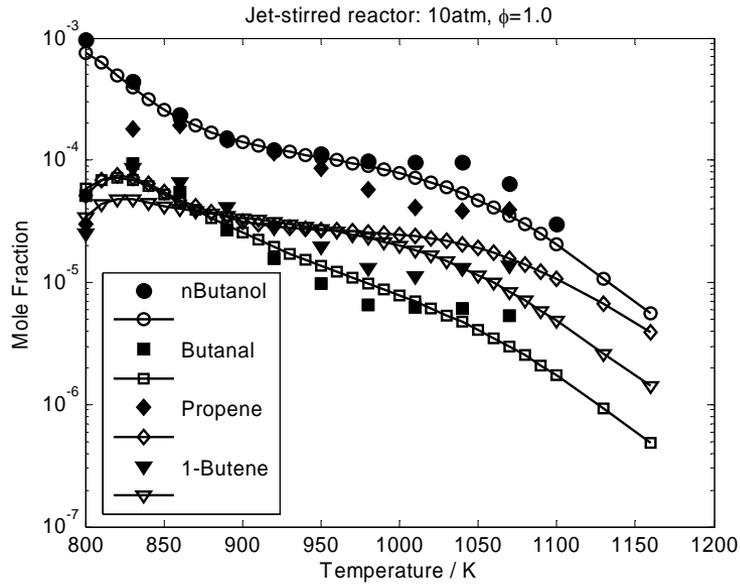


The kinetic model also predicts the **pyrolysis** product distribution well, including benzene and small aromatics



Butanol model predictions vs. Jet-Stirred Reactor Data

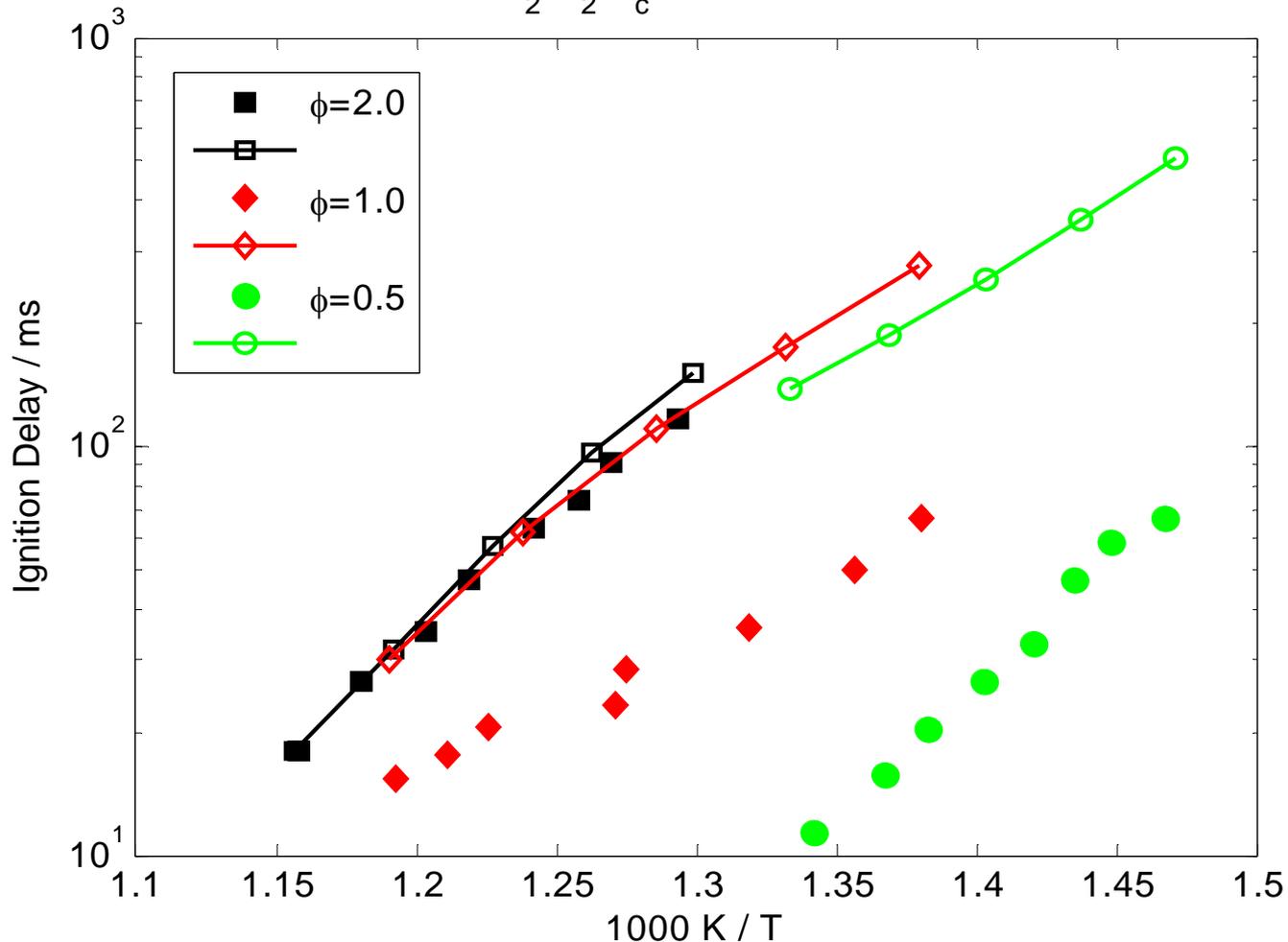
$\phi=1.0$, $P=10$ atm



Expts of Dagaut et al. PCI (2009)

Model accurate at many conditions... ...but wrong at low T, high [O₂]

n-Butanol/O₂/N₂ P_c=15bar 3.38% n-Butanol



Hypothesis:
Additional
Reactions
become
Important
for $T < 800$ K.

Now running
RMG to
grow the model
for $T = 700$ K

Data measured by Bryan Weber & C.J. Sung,
University of Connecticut

Butanols: Status

- 2 published models
 - 1-butanol *Combust. Flame* (2010)
 - *Ind. Eng. Chem. Res.* (2010)
 - 2-butanol + t-butanol + improved 1-butanol
- Latest (unpublished) model includes iso-butanol
- **Need to discuss team publication plans**
 - Team publication in *Science* (write article late 2010)
 - *If you have suggestions, please talk with Bill*
 - Numerous experimental publications
 - **Some by single PIs, probably using published models**
 - **Some jointly-authored with modelers (e.g. Hansen and I have agreed joint US Combustion Meeting paper).**
 - **Publish latest model including isobutanol back-to-back with experimental paper(s)?**

Proposal: wrap up butanol chemistry model (for now) around end of 2010, polish off publications in 2011. Someone (who?) reduce model for use in engine, multi-d flame simulations?

Main Challenge: Accurately Estimating/Computing Rates

- Worked on several rate-estimation issues this year:
 - Coupled hindered rotors (Truhlar)
 - Radical+Radical reactions (Klippenstein, Miller)
 - Automated NJB Green method for $k(T,P)$, better $\rho(E)$
 - Thermo for small molecules, fused rings
 - Biradicals (from ring-opening) with Piecuch
- Many CEFRC team members also working on rate computations, method development.

None of above issues is completely resolved

More Challenges

- Additional rate-estimation issues pending
 - **Roaming Radicals (fast estimates? Routine calcs?)**
 - **“H-bonding” (submerged) transition states: OH and carbonyl groups direct radicals, affect selectivities?**
 - **Small molecule reactions: How to resolve conflicting mechanisms? Should we calculate every reaction?**
- Memory problems for large mechanisms
 - **Has model-construction really converged?**
- Numerical Simulator issues for some experiments (esp. with large stiff mechanisms)
- Need better Version Control: big team, multiple models, multiple simulators & approximations, multiple versions of databases, multiple rate-estimation procedures.
- Need to upgrade error-propagation and model-data comparison, especially as discrepancies get smaller.