

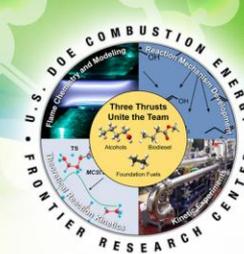
Making Fast Accurate Prediction of Alternative Fuels a Reality: The CEFRC Butanol Mechanism Thrust

William H. Green

MIT Chemical Engineering

Reporting collaborative work of 10 of the CEFRC PI's,
and about 3 dozen researchers

The Butanol team

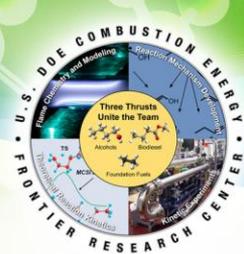


- William Green
- Michael Harper
- Shamel Merchant
- Mary Schnoor
- Jorge Aguilera-Iparraguirre
- John Alecu
- Amrit Jalan
- Everton Zanoelo
- Donald Truhlar
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- Tao Yu
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- Peng Zhang

External Collaborators:

- Kevin Van Geem (Ghent)
- Steven Pyl (Ghent)
- Guy Marin (Ghent)
- Marie-Francoise Reyniers (Ghent)
- Wing Tsang (NIST)
- Claudette Rosado-Reyes (NIST)

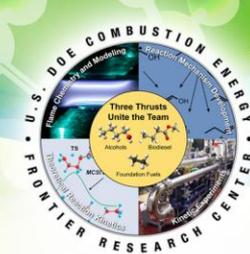
Motivation



- **Hundreds of molecules have been proposed as new alternative fuels, many from biology.**
 - How to assess which are worth pursuing? Not practical to run them all in comprehensive engine tests. Small scale expts and calcs instead?
 - Full engine experimental campaigns would require manufacturing large amount of each proposed new fuel and fuel blend...
- **Many new engine designs in development, not clear which engine to use to test future fuels.**
 - Experimentally building/testing each new engine is expensive and slow; fuel-in-engine experiments are relatively expensive and unreliable.
- **Fuel needs to work over broad range (T, P, composition).**
 - Hard to experimentally test over the whole range of conditions.

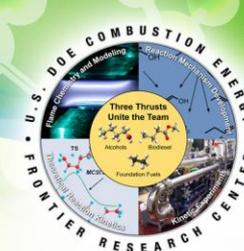
Ability to *predict* behavior of new fuels at many conditions, and in proposed engine designs, would be *very* valuable!

Goals / Philosophy



- Develop capability to ***predict*** fuel performance!
 - Faster, cheaper than testing all fuels at all conditions
 - How Accurate are Predictions? (And what accuracy is required?)
- “Right answers for the Right Reasons”
 - Consistent rate coefficients, don’t force fits.
 - Everything quantitatively correct:
 - CFD, numerics, error bars, ...
- Develop effective **strategy that can be used for other fuels**
 - Improve model-construction and validation technology
 - Methods for effective long-distance collaboration across disciplines
- **This is not just about butanol!**

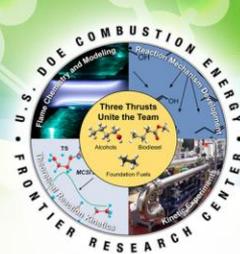
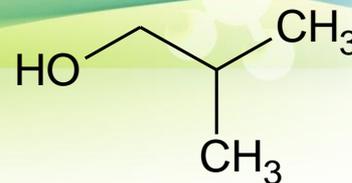
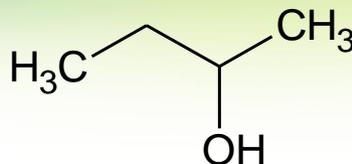
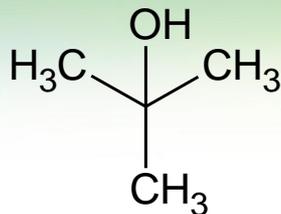
Where this Talk fits in to CEFRC effort



CEFRC: Activities, Products, and Linkages

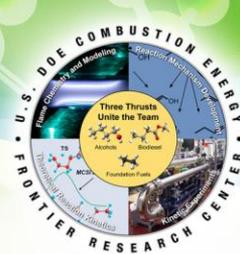


Why butanol as our test case?



- CEFRC wanted a single focus from the outset, to draw the geographically scattered team together.
- Why did we choose Butanol as our starting point?
 - **Real-World Impact:** n-butanol or iso-butanol expected to be commercialized soon in USA to beat ethanol “blending wall” and satisfy RFS2 standard
 - **Small:** convenient for quantum, mechanism builders/solvers
 - **Volatile:** convenient for experiments
 - **Realistic:** exhibit complications expected in other biofuels, e.g. isomers, multiple conformers, k(T,P), second O₂ addition.

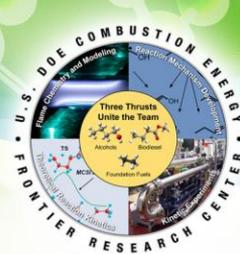
Many Experimental Data on Butanol Combustion/Oxidation/Pyrolysis; majority measured by CEFRC team in 2010-2011



- Ignition Delays
 - Shock tube (**Stanford**, RPI, Galway, Aachen)
 - Rapid compression machine (**U.Conn.**)
- Flame Speeds & Extinction Strain Rates
 - spherical and flat flames (**USC, Princeton**)
 - Turbulent flame balls (**Princeton**)
- Individual Rate Coefficients
 - Shock Tube (**Stanford**)
- Speciated Data from:
 - Flames (Yale, **Princeton, USC**, Bielefeld, Hefei, **ALS**)
 - Flow reactors (**Ghent, Princeton**)
 - Jet-Stirred Reactors (France)
 - Rapid Compression Facility (U.Mich.)
 - Species time profiles in shock tube (**Stanford**)
 - Single-pulse shock tube (**NIST**)

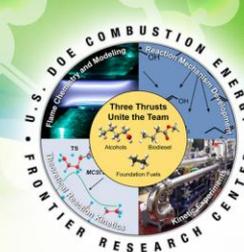
We test our butanols model against *all* these experiments

Our Model Development Process



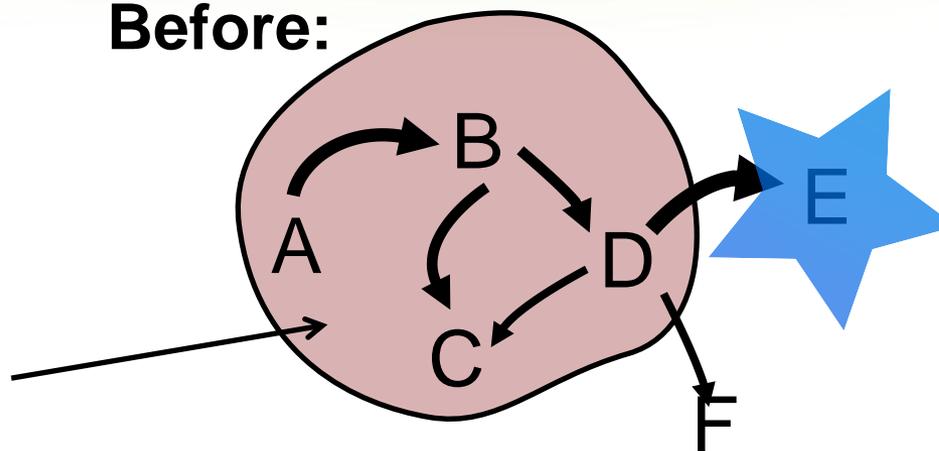
- **Computer assembles large kinetic model** for particular condition(s) using rough estimates of rate coefficients. (open source RMG software)
 - Start from model derived for other conditions, so appending new reactions and species.
 - Automated identification of chemically activated product channels, and computation of $k(T,P)$.
- If sensitive to k derived from rough estimate, recompute that k using **quantum chemistry**.
 - Generalize from quantum to improve rate estimation rules.
- *Iterate* until not sensitive to rough estimates.
- Compare with **experiment**.
 - Big discrepancies? Look for bugs or typos.
- Match OK? *Repeat* for different conditions.

RMG algorithm: Faster pathways are explored further

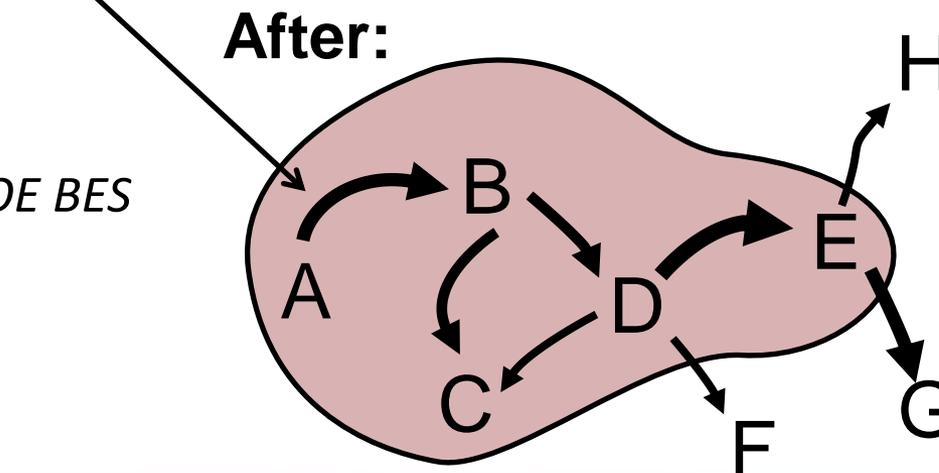


“Current Model” inside.
RMG decides whether
or not to add species to
this model.
Final model typically
~500 species, 5000 rxns

Before:

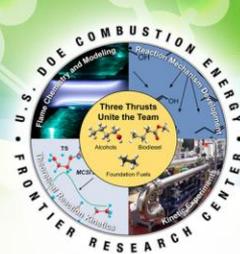


After:



*RMG software originally
developed by a separate DOE BES
grant (Chemical Physics
program).*

Chemical Activation is a major complication

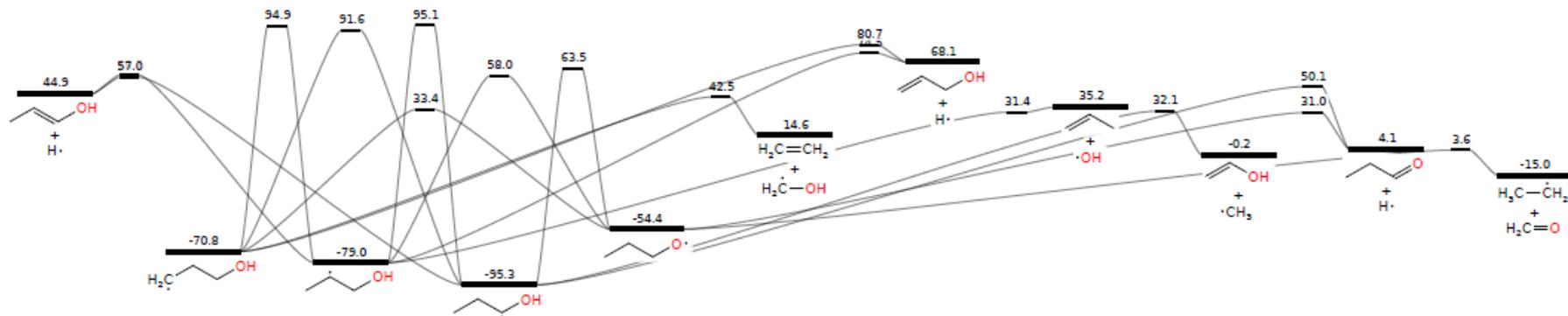


Reactions faster than thermalization:
Initial product immediately reacts

Thermalization rate increases with pressure: $k(T,P)$

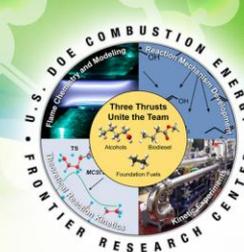
A+B can lead to many possible products due to “well skipping”
RMG automatically tracks down all the channels.

Example: H-catalyzed keto-enol tautomerism of propenol

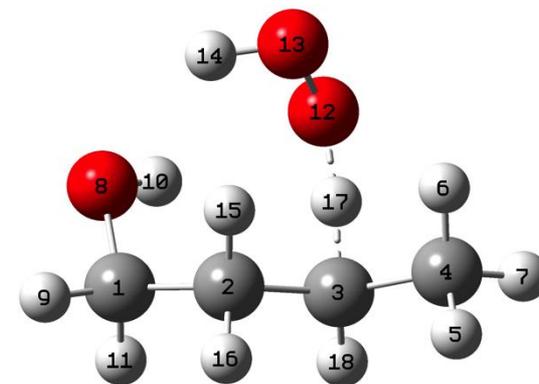


Instead of 2 possible products, 10 are formed. Instead of 2 TS's, must compute 16 TS's.

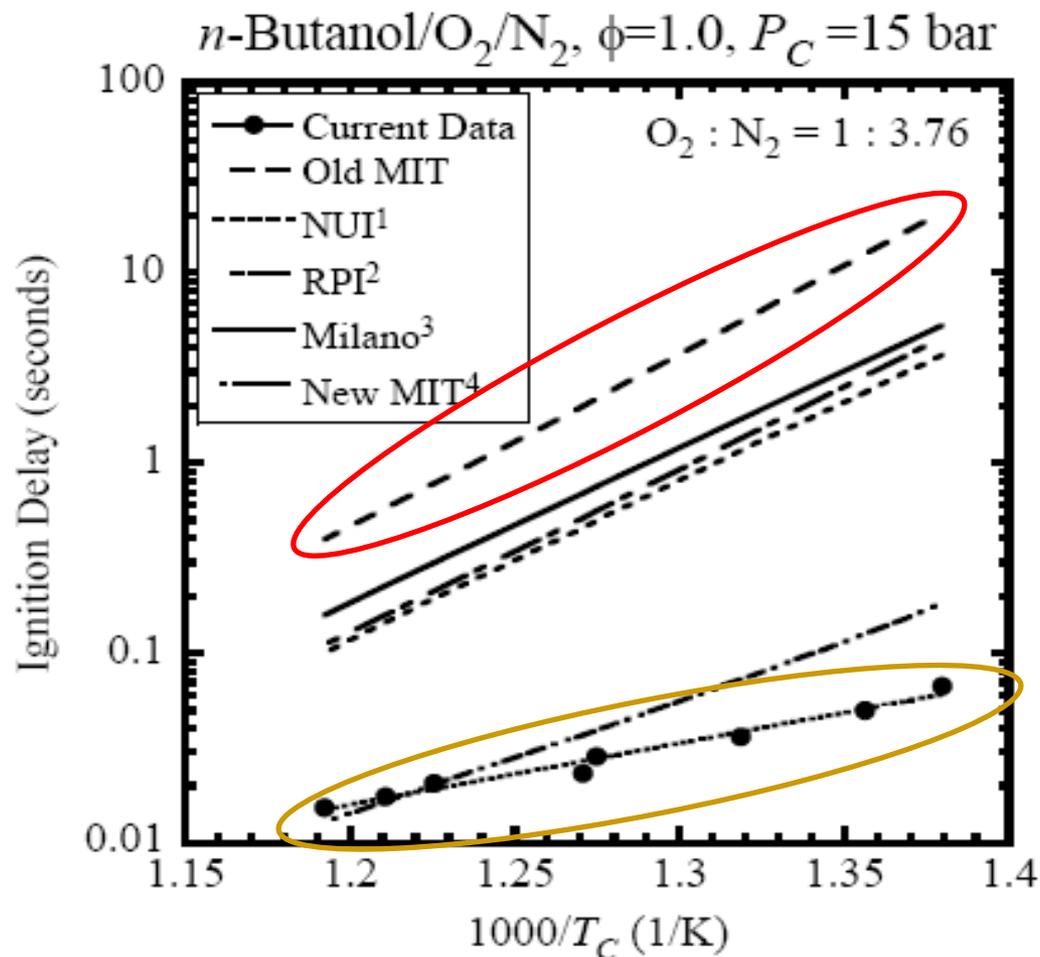
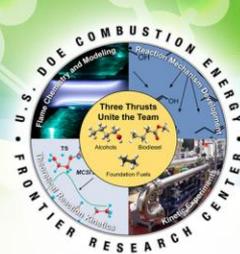
Large Models built by combining many components



- “Foundation Fuels” small molecule chemistry
 - Big molecules break down to small ones!
 - Many observables are most sensitive to the small molecule reactions
 - We start from the high-accuracy H₂/O₂ model of Ju, Dryer & Klippenstein
- Biofuel chemistry involves intramolecular (and intermolecular) H-bonding; many molecules and transition states have multiple conformations.
 - Conventional approach was separable rotor approximation: $V = \sum V_n(\phi_n)$
 - Green: separable approx is not accurate!
 - Truhlar invented MS(T) method
- Quantum chemistry is key for important steps
 - CCSD(T), CASPT2, MRCI... for large molecules!
- Functional Group extrapolations fill in the rest



2009 model way off: did *not* predict fast n-butanol ignition <900 K!

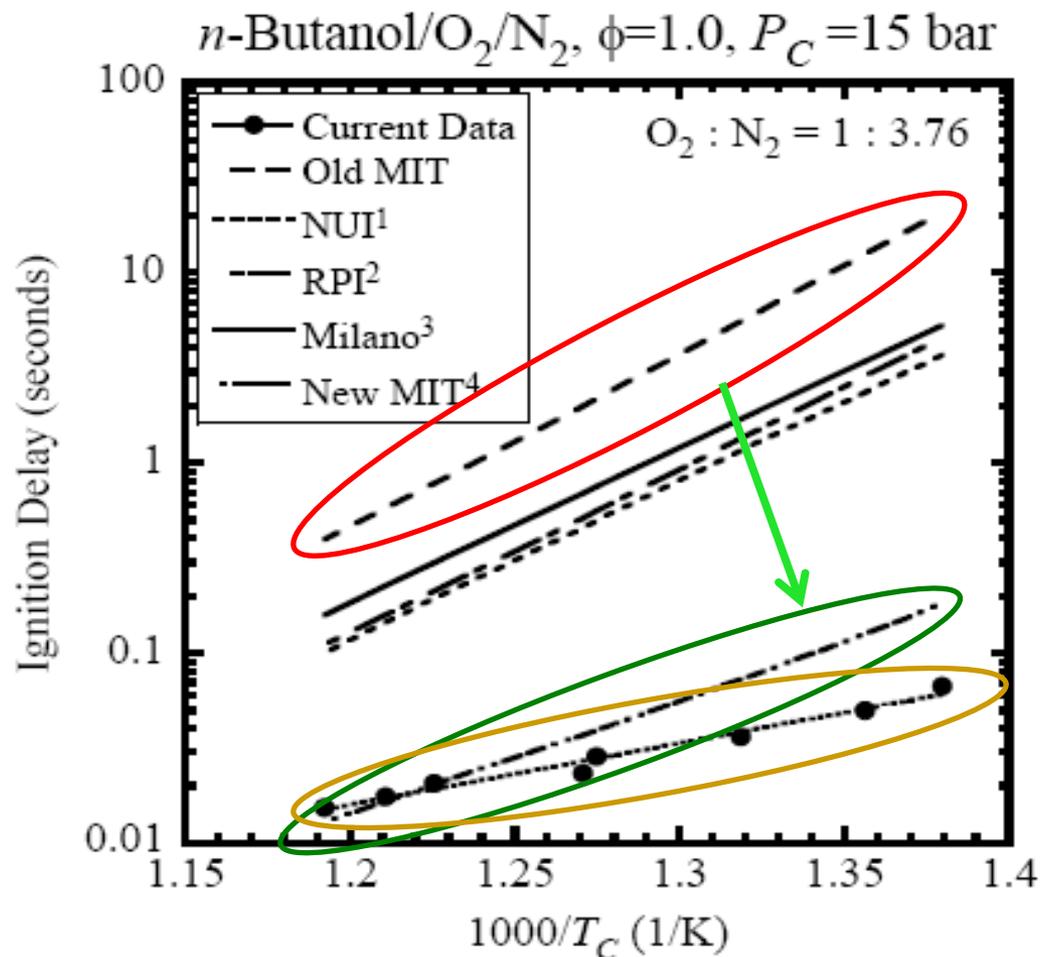
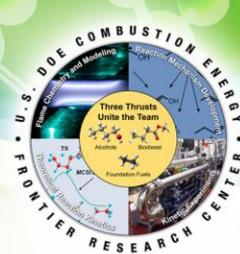


Model was built automatically at MIT using computer “expert system” at the outset of the project (Aug 2009), no butanol-specific inputs (quantum nor expt).

Due to bug in reaction classification system used by expert system, initial model wildly mis-estimated barriers for all $R + H_2O_2 = RH + HO_2$ reactions.

Experimental validation is Critical... in this case, bug identified immediately by Weber & Sung RCM expt.

After removing the bug in 2009 model, 2010 model predicts reasonable ignition delay



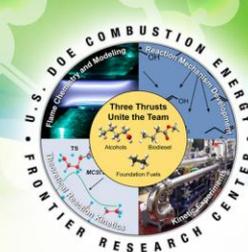
Models were built automatically at MIT using computer “expert system”, no butanol-specific inputs (quantum nor expt).

Due to bug in reaction classification system used by expert system, 2009 model wildly mis-estimated barriers for all $R + H_2O_2 = RH + HO_2$ reactions.

Experimental validation is *Critical...* in this case, bug identified, rectified in less than 2 months.

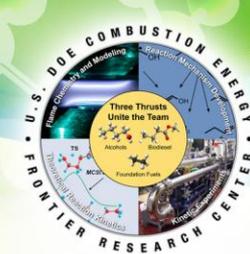
Model & expt still not quite in agreement for low T ignition

No adjustment of parameters to match experiments we are modeling



- Main Goal: Assess how accurately we can **predict** chemistry of new fuels
 - ...and which **quantum chemistry calculations** or experiments would be most helpful.
- Too many parameters in most biofuel models for adjustment-to-fit-experiment to be sensible
 - Very different from small-model situation e.g. H_2/O_2
- Model improved by doing better $k(T,P)$ calculations based on higher levels of quantum chemistry & rate theory (see next talk and posters).

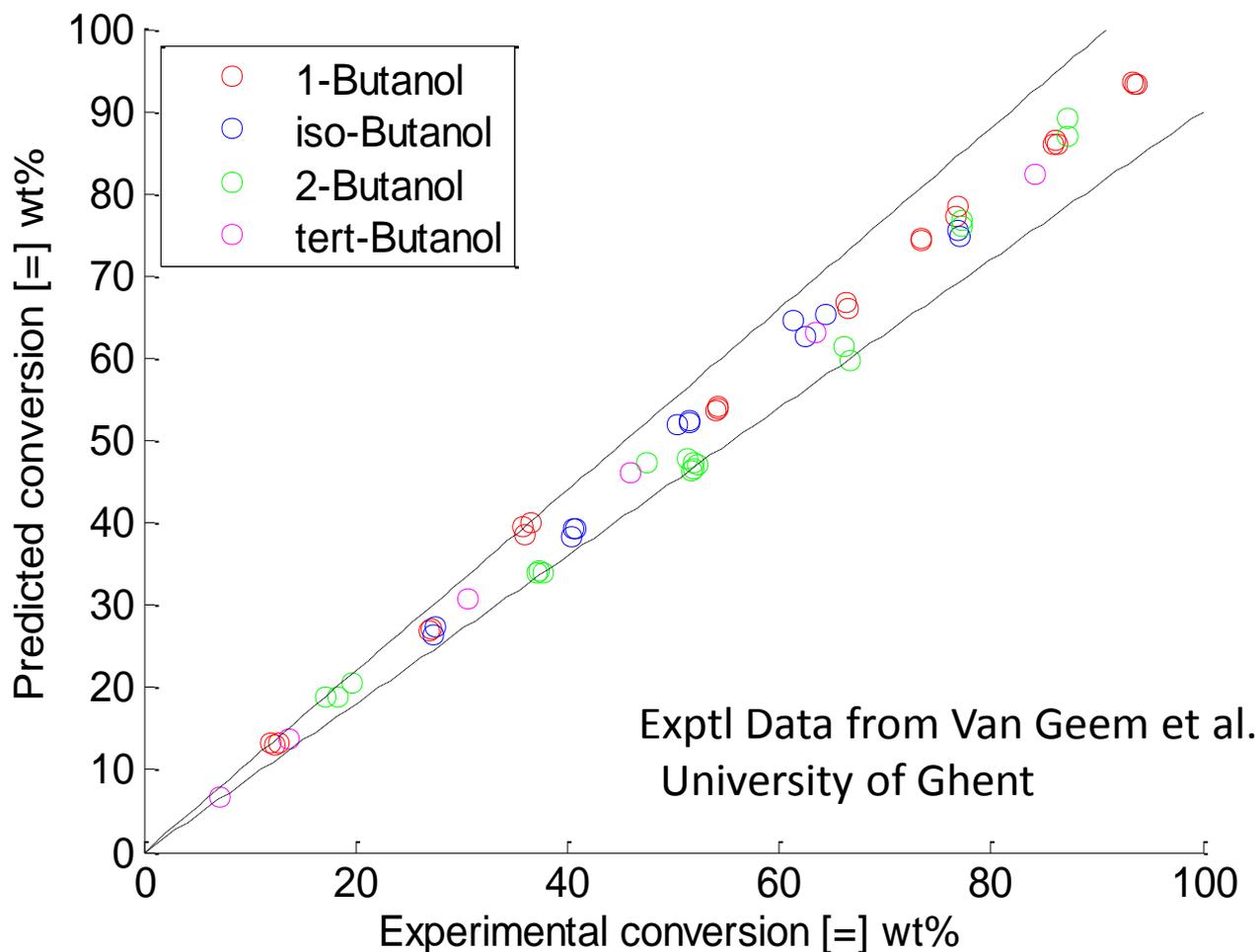
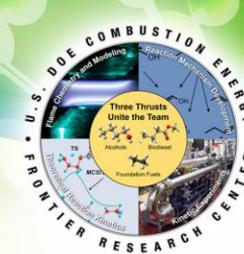
We do not expect perfect agreement: currently feasible quantum calculations for rate coefficients are typically uncertain by factor of 2-3, so expect comparable errors in model predictions



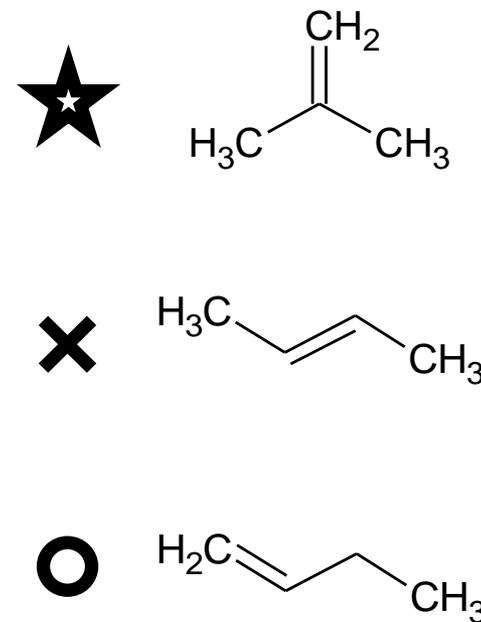
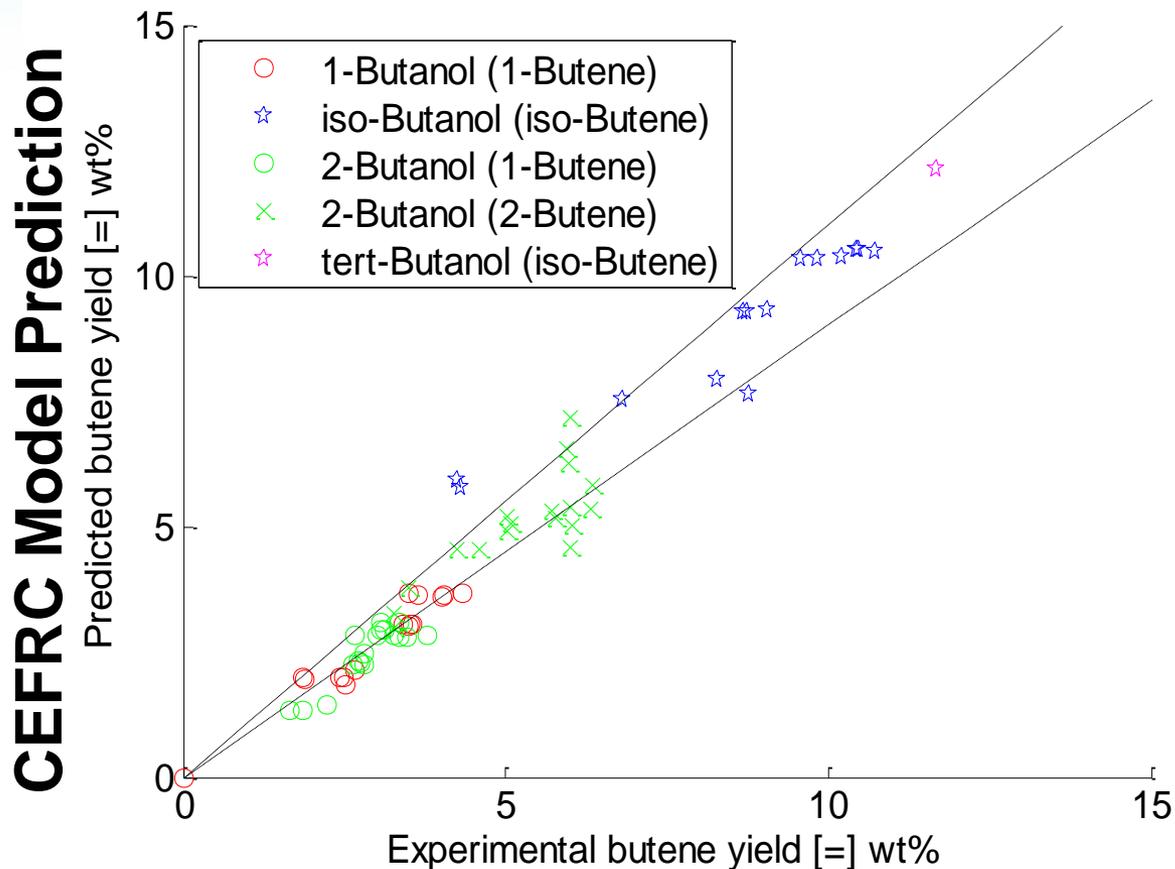
Ghent Flow Reactor, Stanford and NIST Shock Tubes,

BUTANOL PYROLYSIS

Butanol model's predicted conversion agrees well with ~ 1000 K flow-reactor *pyrolysis* measurements

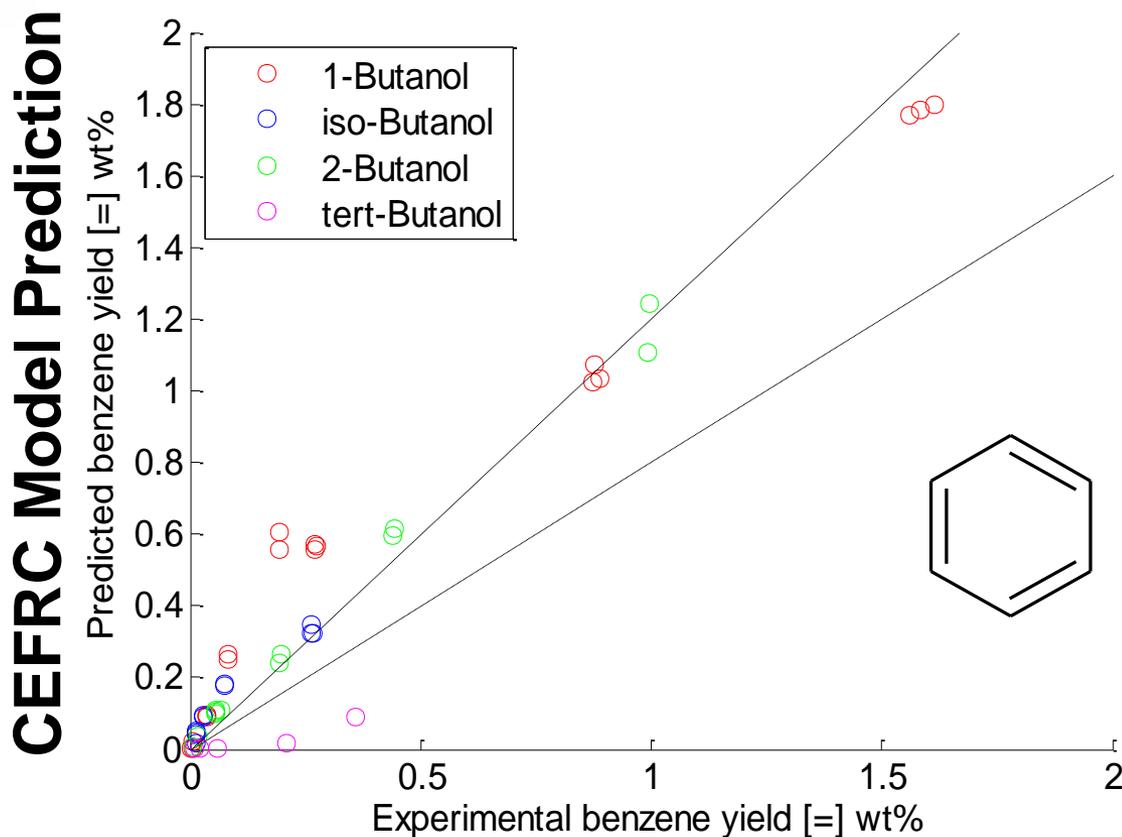
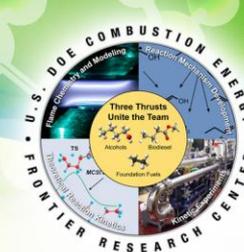


Model predicts most products quantitatively, e.g. butene isomers from various butanols



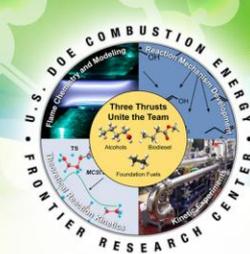
Experimental Data, Univ. Ghent

But model generally overestimates benzene...
...Something odd with t-butanol...



Model also missing some polycyclic aromatic (and Soot) formation....

Stanford Multi-Species Time-Profile Experiment

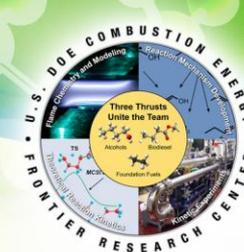


- Most experiments measure either a single observable at many times ($N_{\text{timepoints}}$), or many species at a single time (N_{species}).
- New Stanford experiment measures several species at many times: ($N_{\text{timepoints}} * N_{\text{species}}$) data
- Great for thoroughly testing the kinetic model!

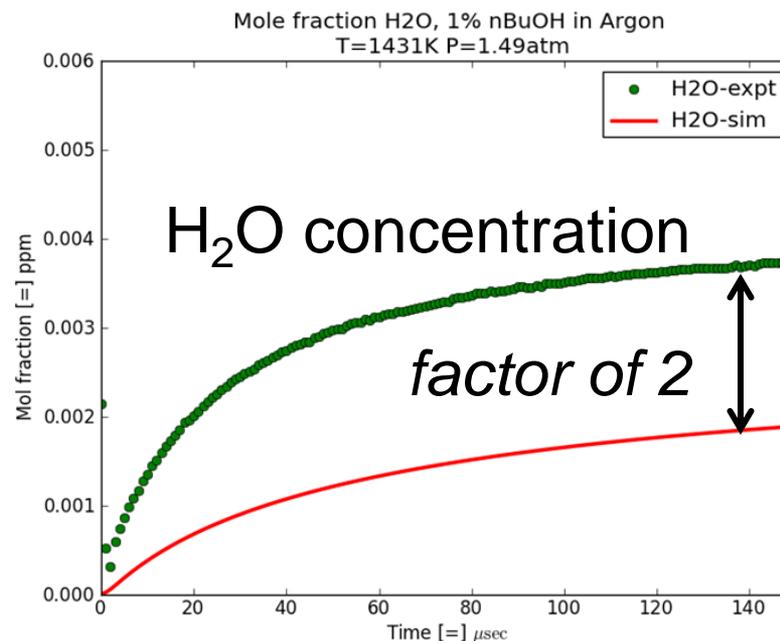
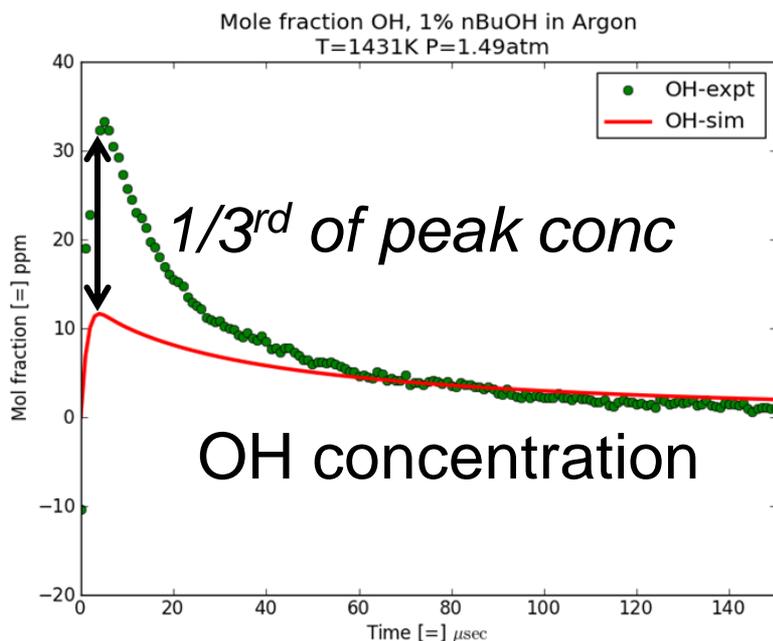


Stanford Shock tube

2010 model predictions not so good for OH and H₂O formation from fast pyrolysis

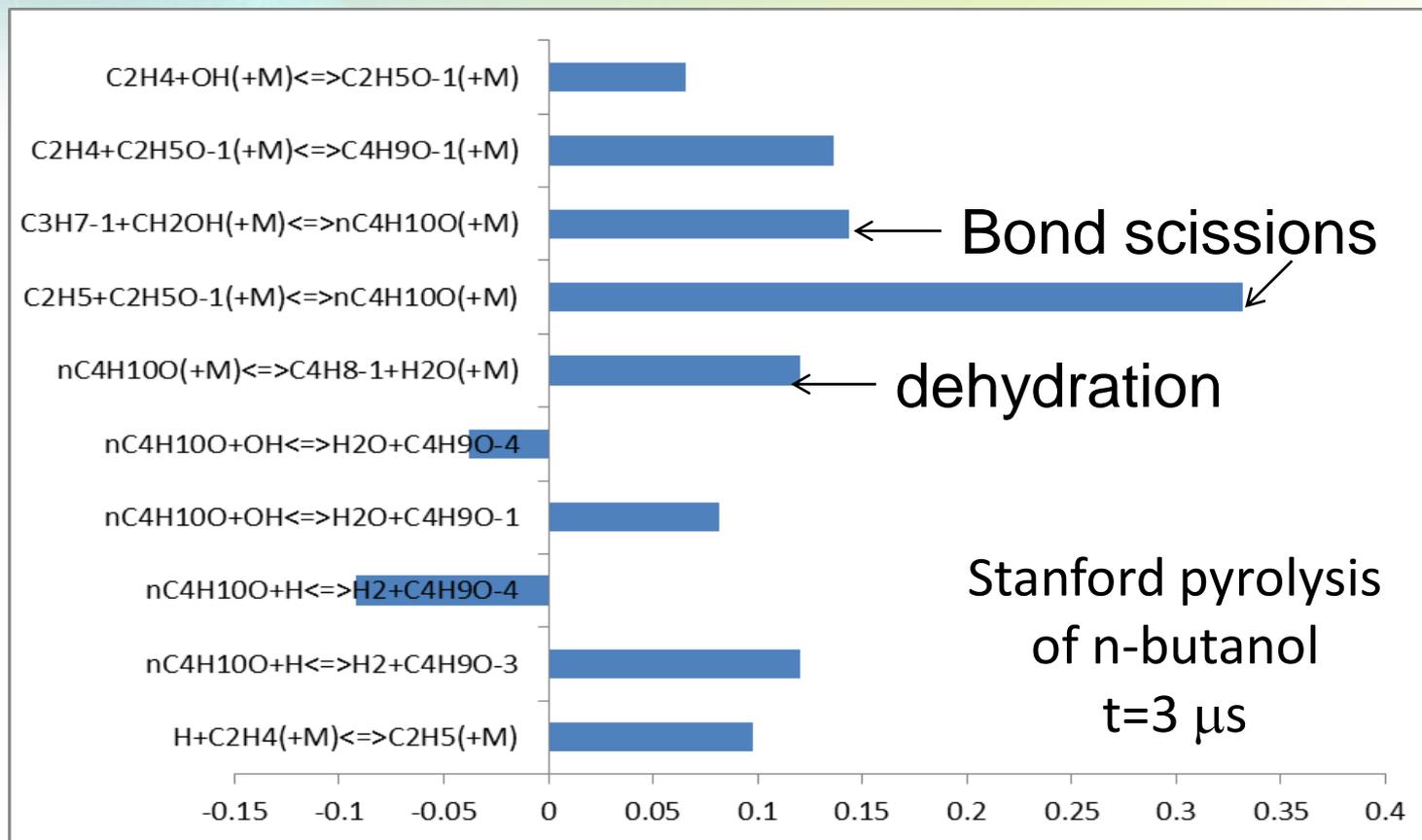
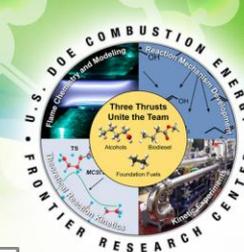


Initial Model Predictions (no quantum calcs)

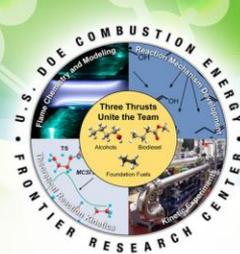


Stanford group multispecies experiments: Cook R. *et. al*, Multi-Species Laser Measurement of n-Butanol Pyrolysis behind Reflected Shock Waves, *Int. J. Chem. Kinet.*, **2012 (accepted)**.

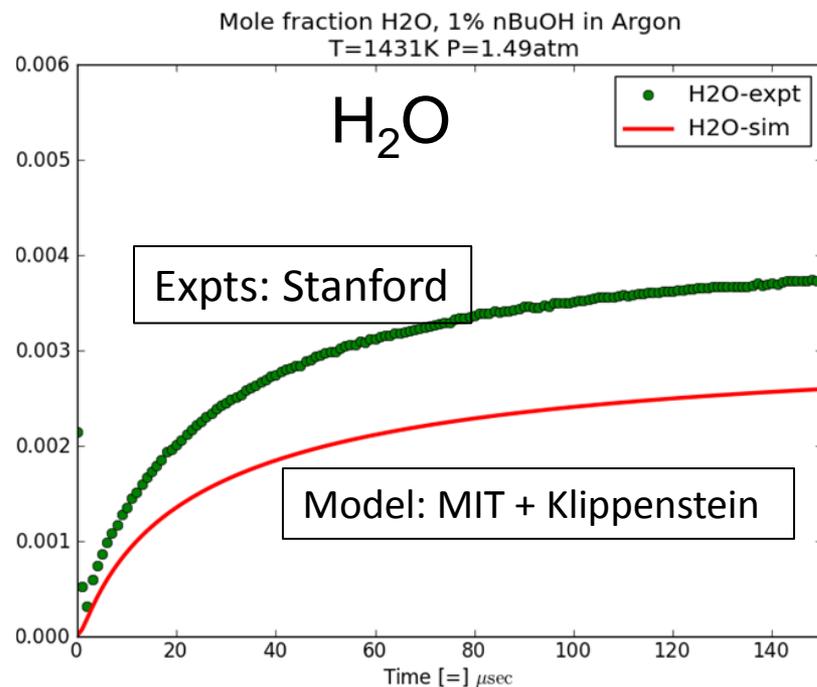
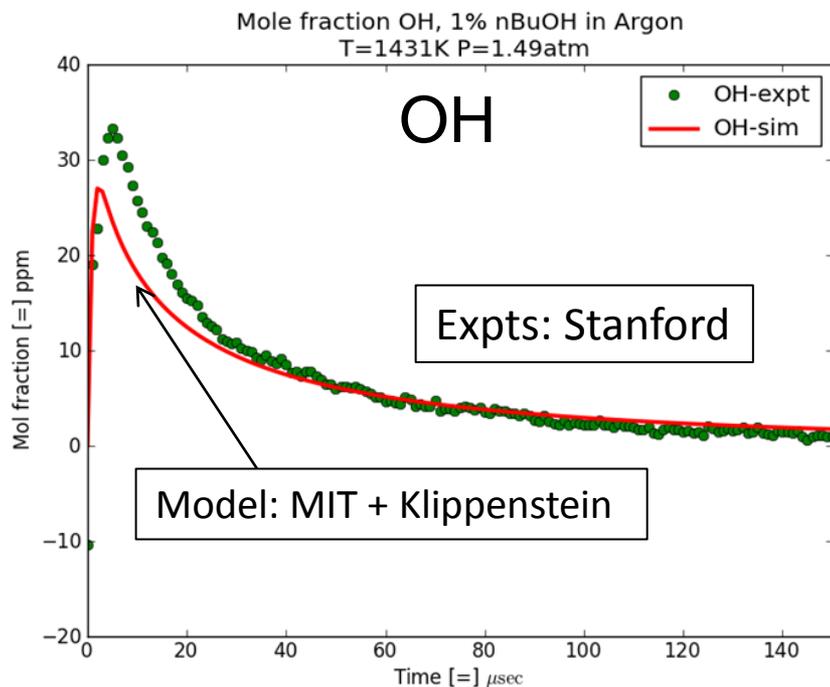
H₂O formation sensitive to butanol bond scission and dehydration



So... Klippenstein computed bond scissions, and MIT computed dehydration using quantum chemistry.

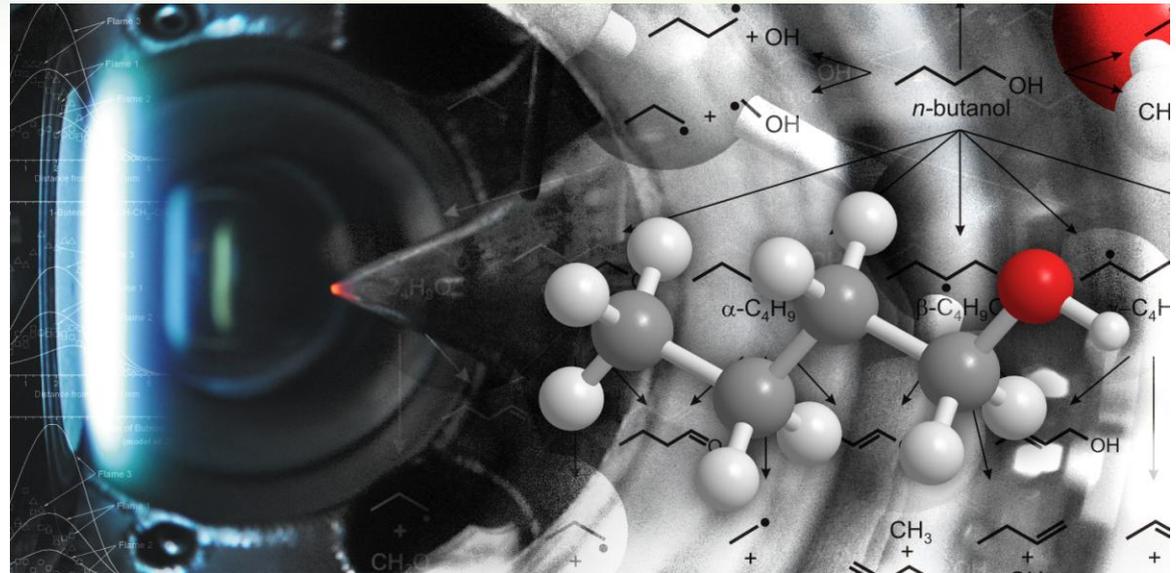
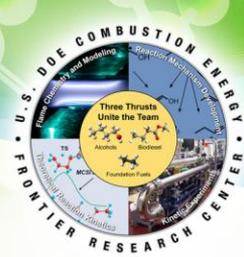


nBuOH Pyrolysis Model, with quantum $k(T,P)$: predictions much closer to experimental data



Several new experiments and calculations have been done to try to resolve this discrepancy (Hanson, Rosado-Reyes & Tsang, Alecu, Klippenstein, Truhlar)

About a factor of 2 discrepancy for some rate coefficients,
about what we would expect

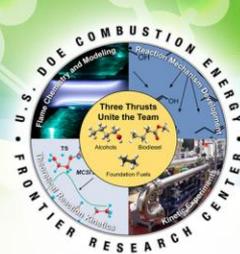


MBMS: Advanced Light Source

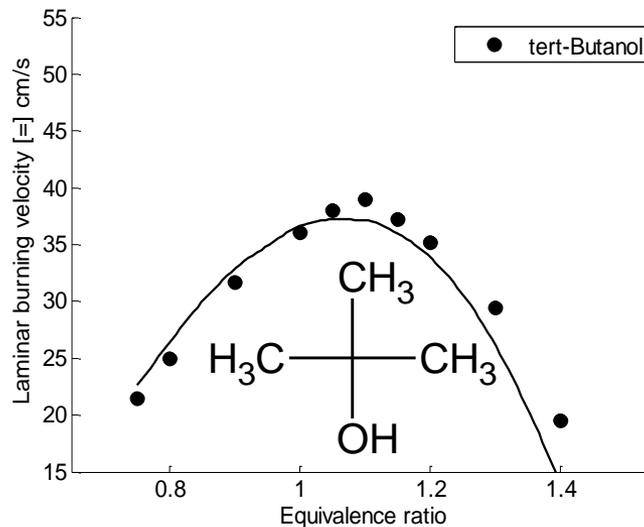
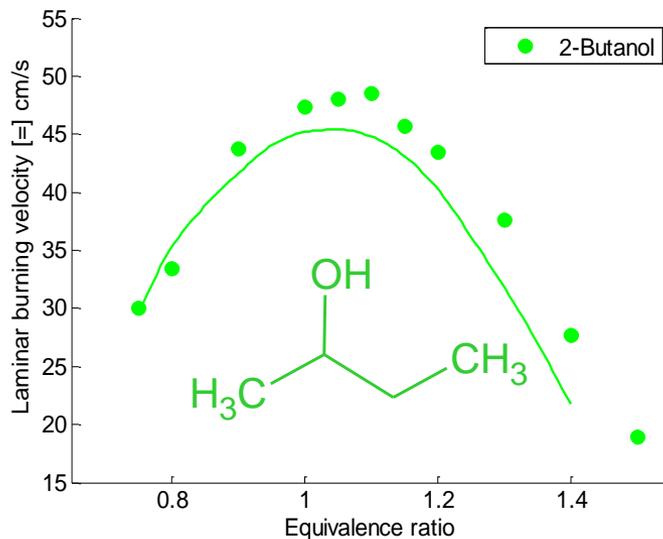
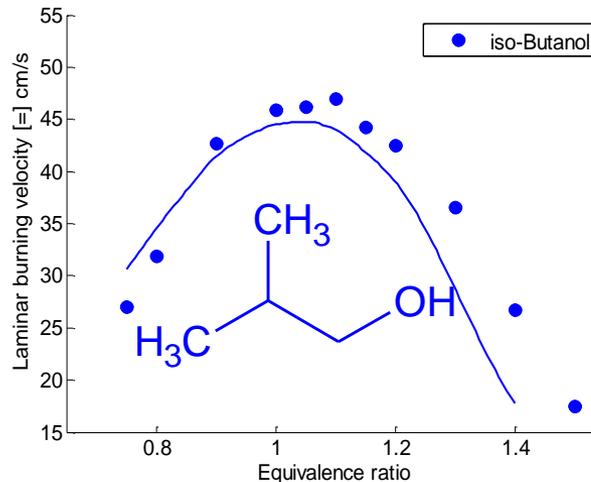
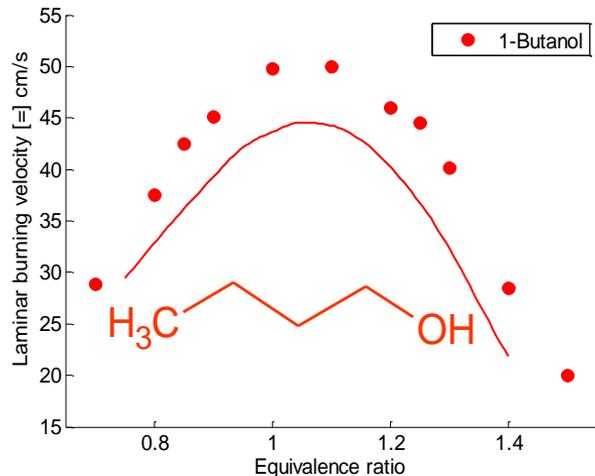
MBMS: Bielefeld, China

Flame Speeds measured at USC and Princeton

BUTANOL IN FLAMES



Flame Speed predicted pretty well by all the models



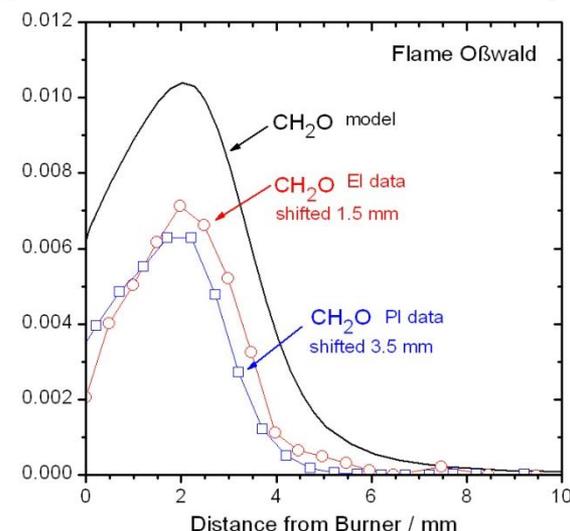
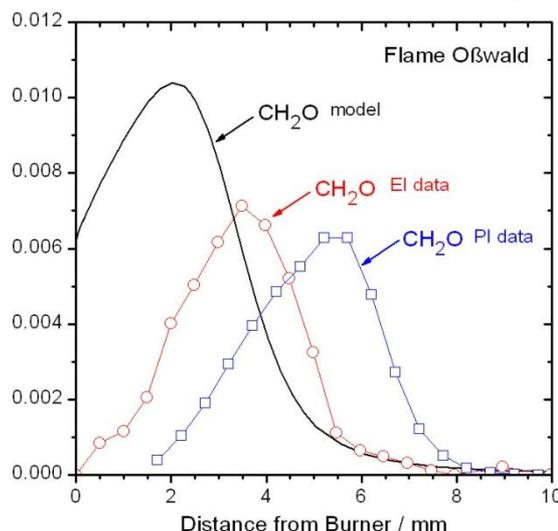
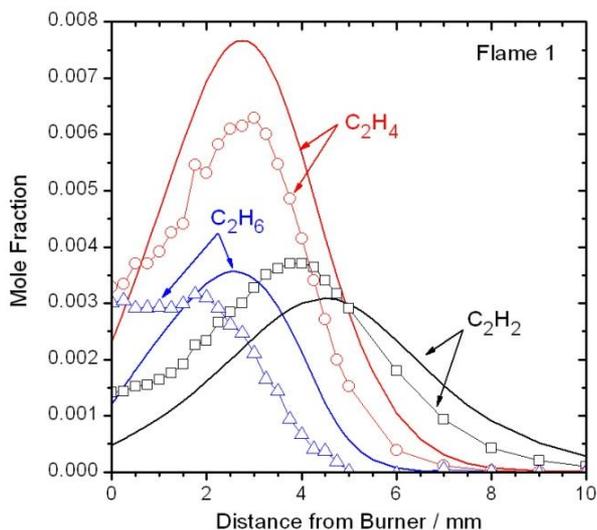
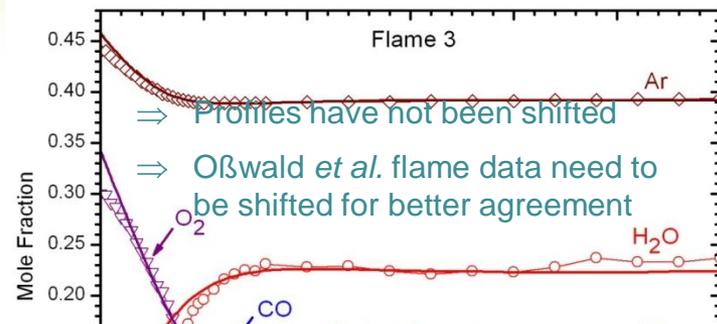
This data from USC. Related expts done at Princeton, with different geometry and strain rate.

Cross-Comparison of expts clarified, confirmed strain-rate extrapolation

Advanced Light Source (ALS) Flat Flame Data: Detailed Test of the Model's Predictive Capabilities

Hansen, Harper, Green PCCP (2011)

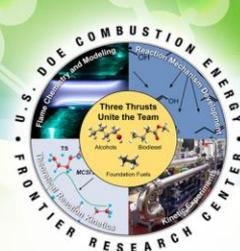
- ✓ Mole fraction profiles of the major species are predicted accurately
- ✓ A more powerful test is provided by comparing modeled and experimental profiles of intermediate species



Only a few of the many data traces shown here... most show good agreement

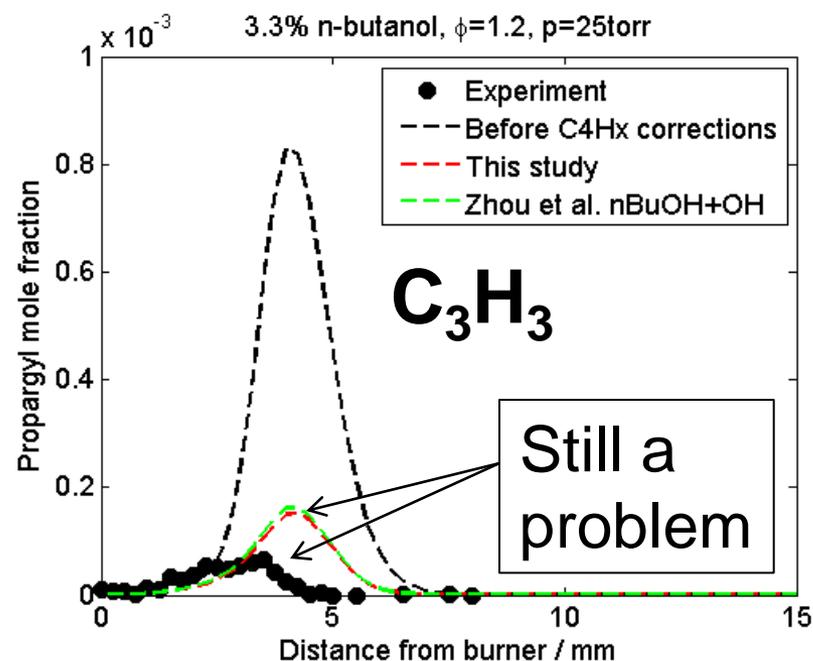
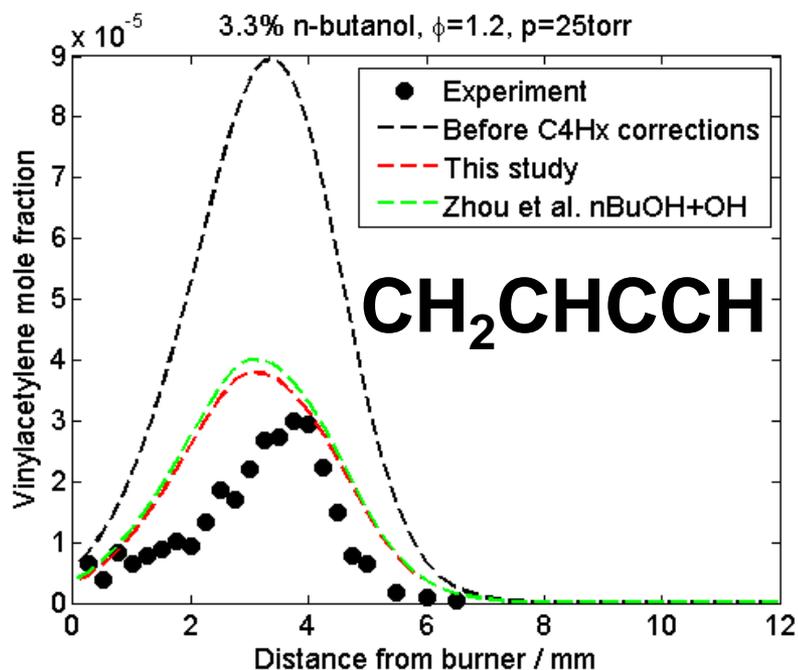
Oswald, Guldenberg, Kohse-Höinghaus, Yang, Yuan, Qi, *Combust. Flame* (2011)158, 2

You learn more from discrepancies! C_4H_4 and C_3H_3 overpredicted

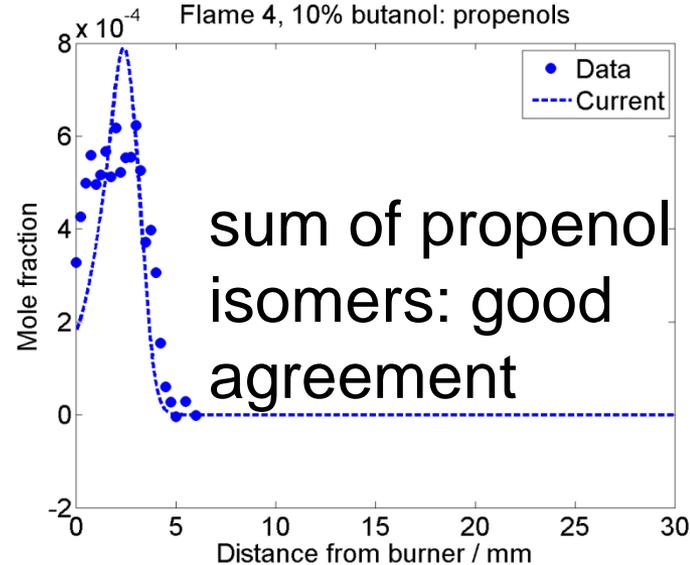
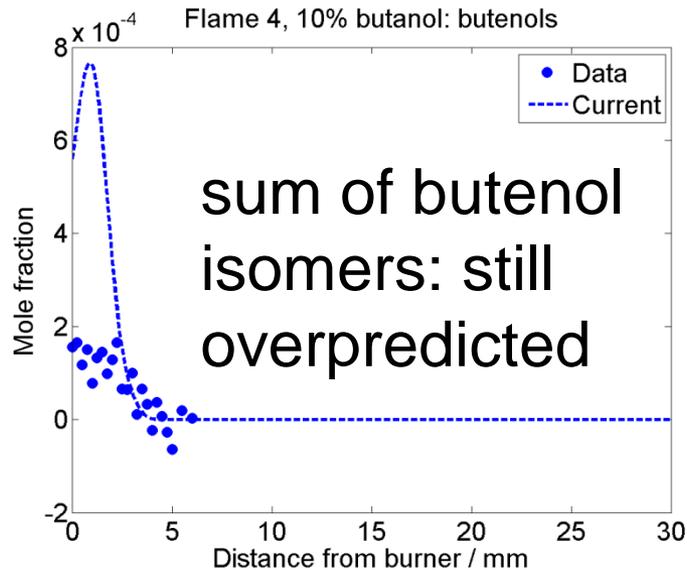
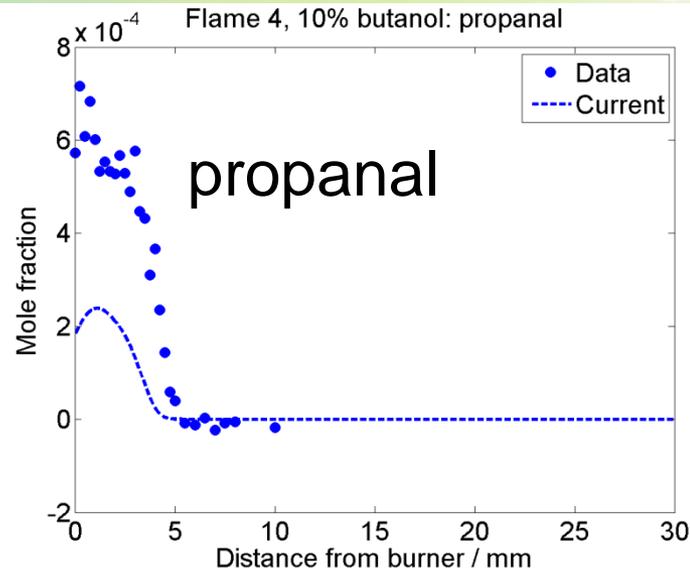
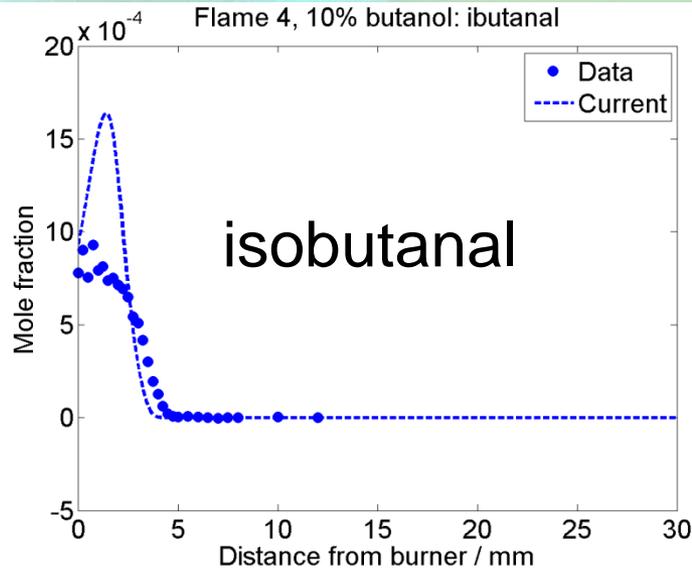
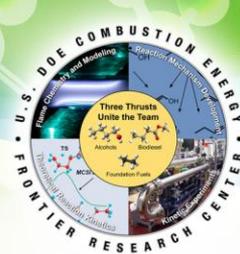


Sensitive to mistake in C_4H_5 Thermochemistry

- Simulations of the ALS flames are sensitive to the enthalpy of $i-C_4H_5$ ($CH_2=CH-\bullet C=CH_2 \leftrightarrow \bullet CH_2-CH=C=CH_2$). None of the other available experimental data are sensitive to this number.
- This radical's enthalpy value was incorrect in the MIT database. Correcting to the accepted literature value partially resolved the discrepancy.



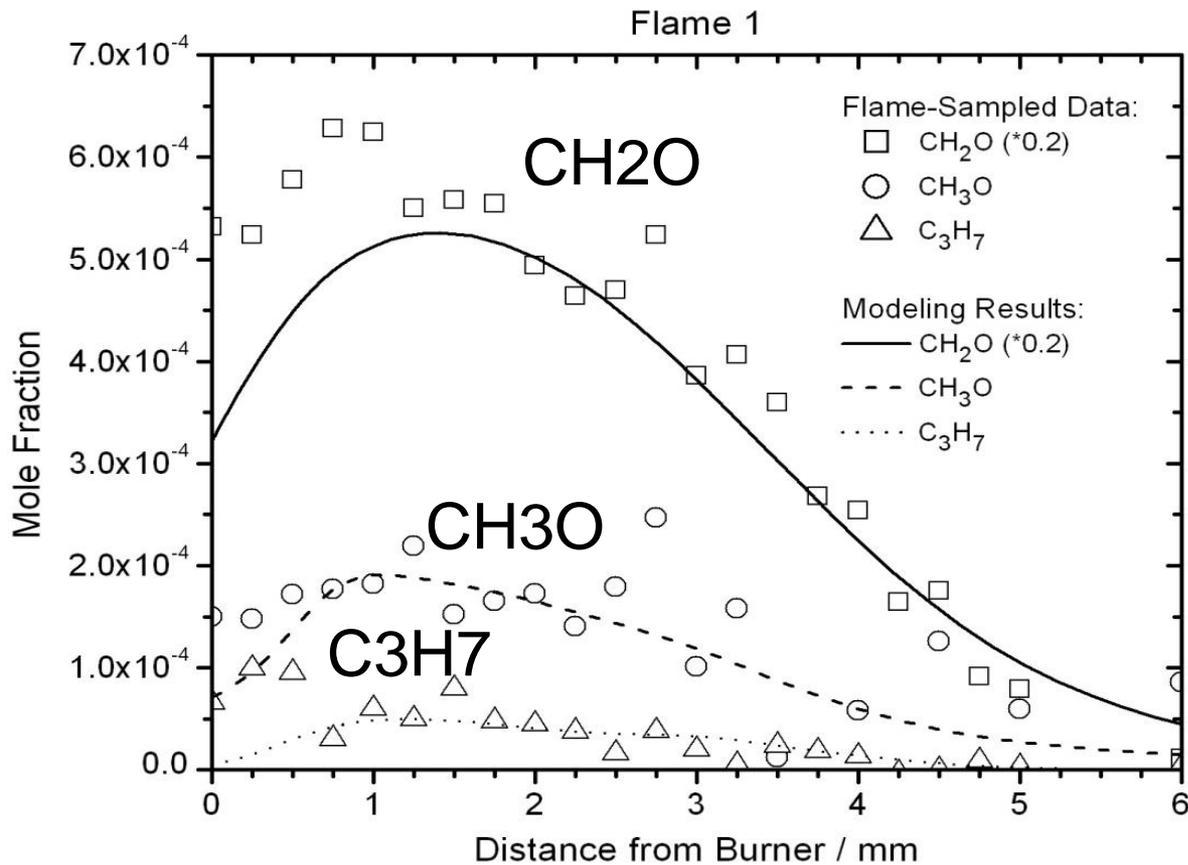
Updated Quantum $k(T,P)$ for H-catalyzed keto-enol isomerization resolves some discrepancies for enols.



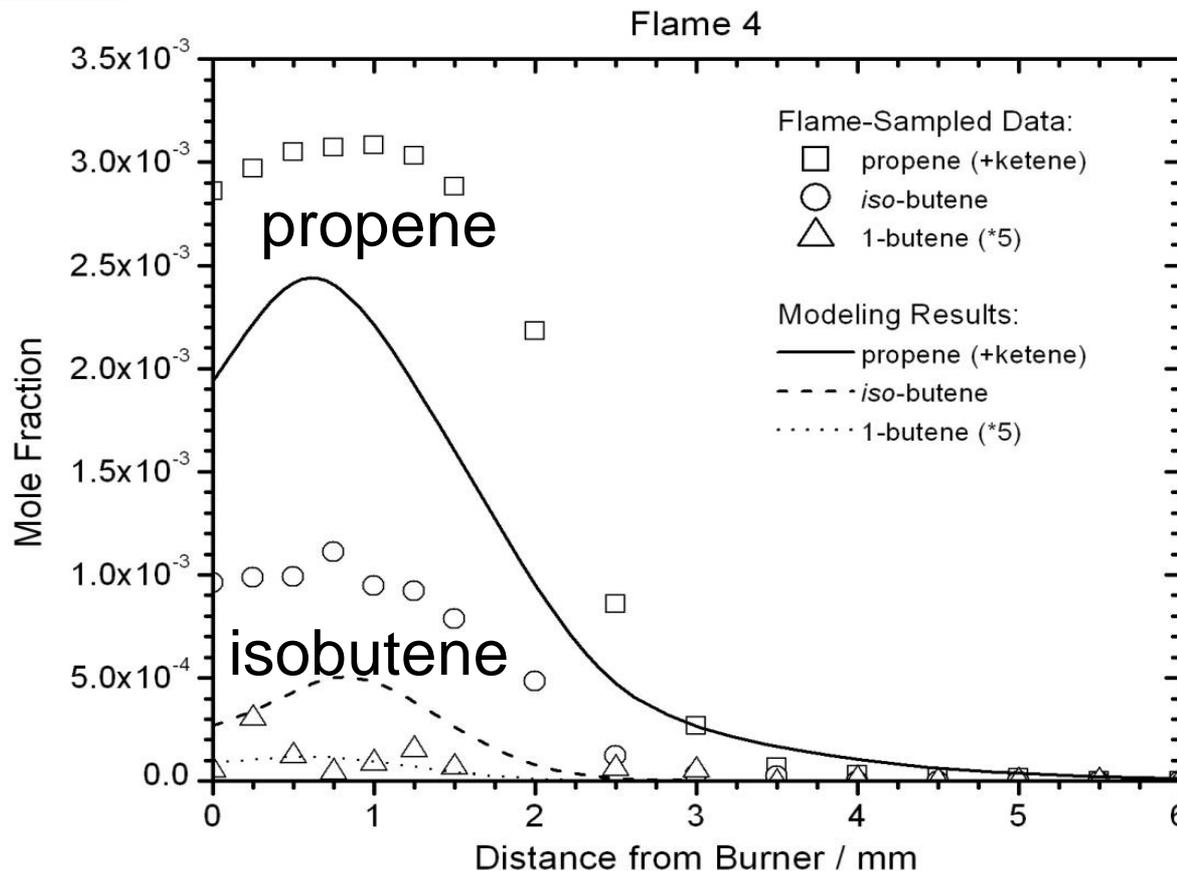
Data from Nils Hansen rich isobutanol flat flame Measured at ALS.

MIT model (2012) predictions. All existing models mispredict some enols.

Predict propyl and CH_3O radicals as accurately as we can measure them (isobutanol flame, 2012 model)



But discrepancies of about a factor of 2 are common, as expected



Hansen, Merchant, Harper, and Green (about to be submitted)



Stanford Shock Tube, RPI Shock Tube and Univ. Conn. RCM

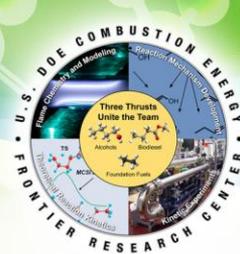
IGNITION DELAY

A CRUCIAL PART OF FUEL CHEMISTRY

Stranic I. *et. al*, Shock tube measurements of ignition delay times for the butanol isomers, *Combust. Flame*, **2012**, 159 (2), 516-527.

Moss J. T. *et. al*, An Experimental and Kinetic Modeling Study of the Oxidation of the Four Isomers of Butanol, *J. Phys. Chem. A*, **2008**, 112 (43), 10843–10855.

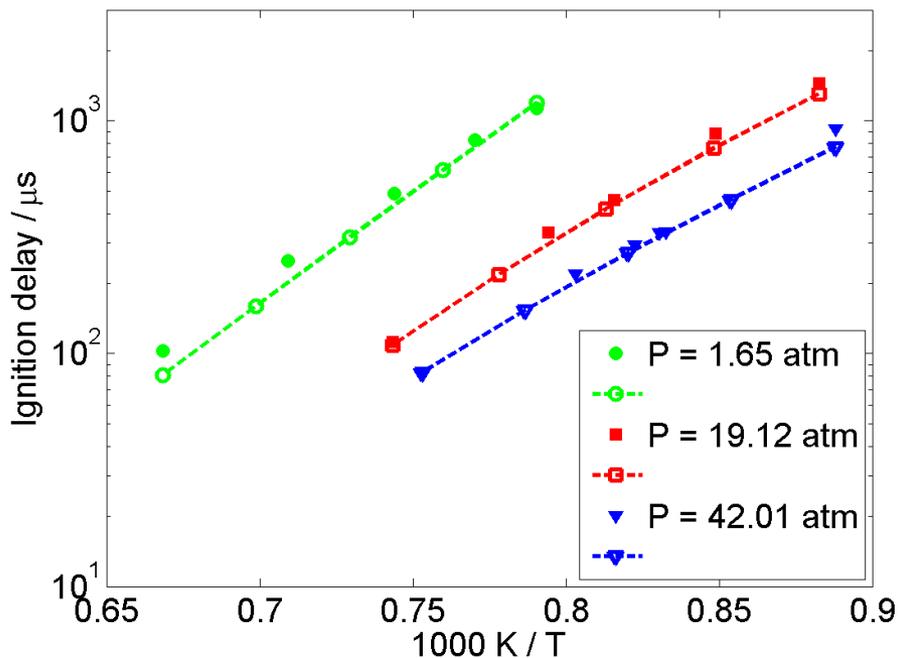
Very important fuel performance property: ignition delay



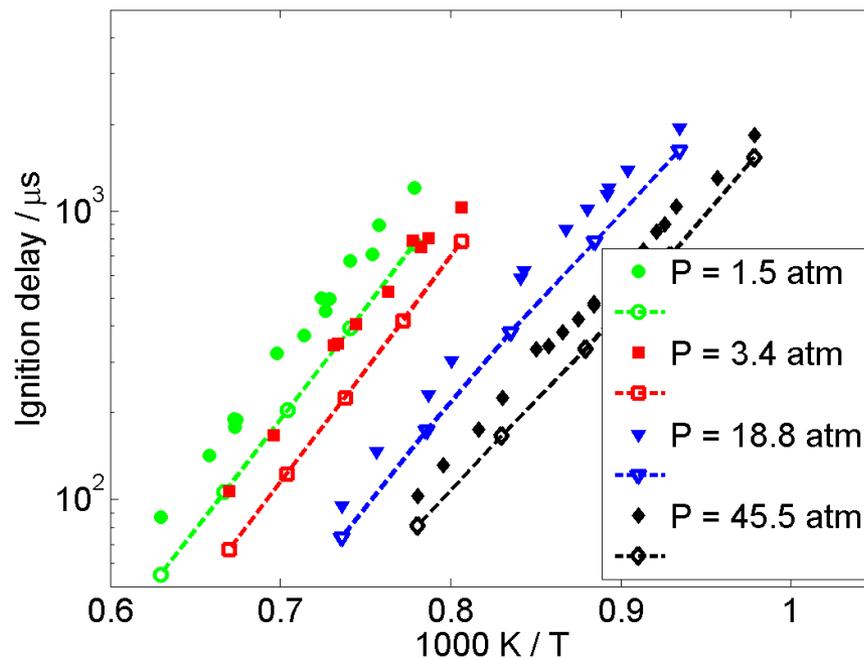
- Gasoline “Octane Number”
- Diesel “Cetane Number”
- Small changes in fuel make big changes in ignition:
 - sensitive to molecular structure!
- New engines even more sensitive to ignition
 - Potential for big gains...
 - ... but only if the fuel ignition delay matches engine requirements

High T isobutanol ignition delay: model predictions consistent with recent experiments by Stanford group

iso-Butanol: 4% O₂, $\phi = 0.5$



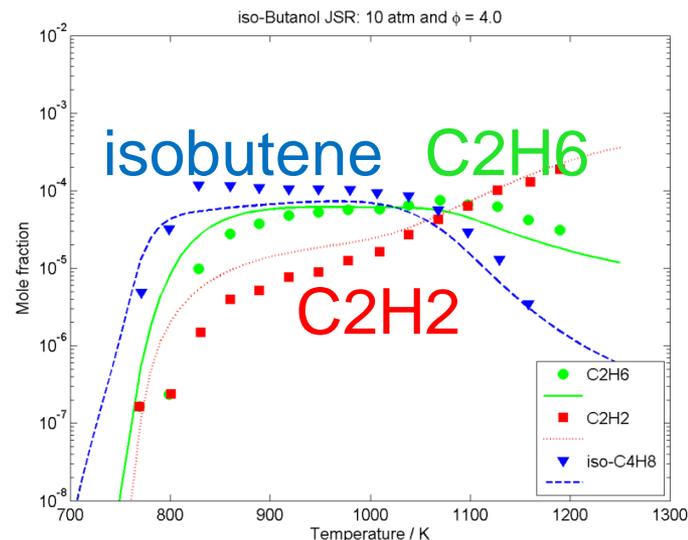
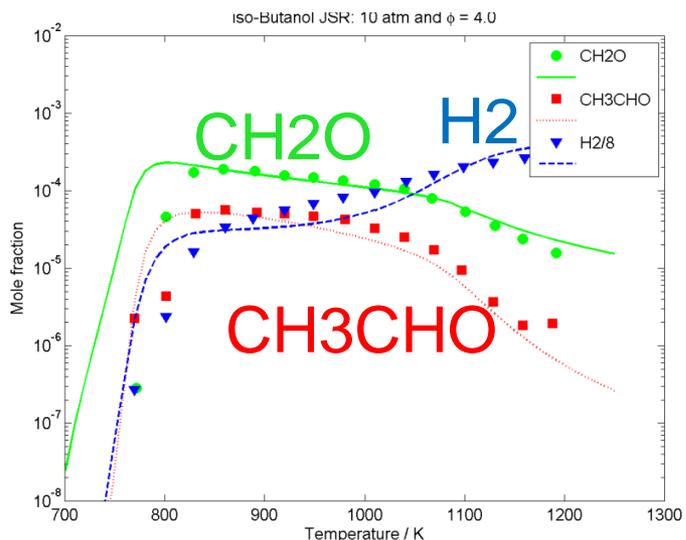
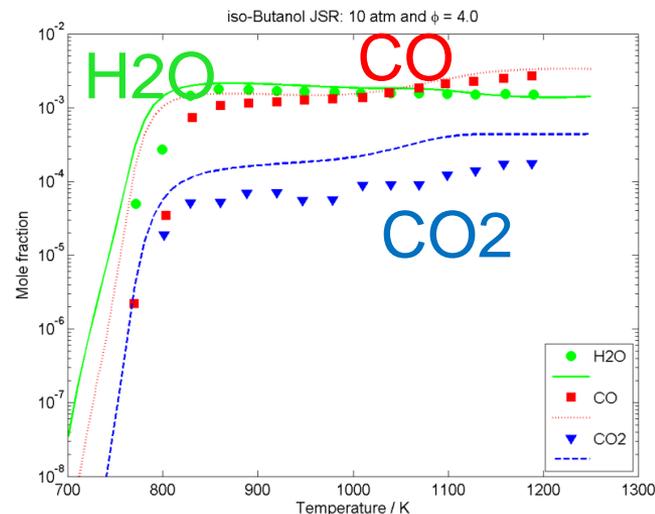
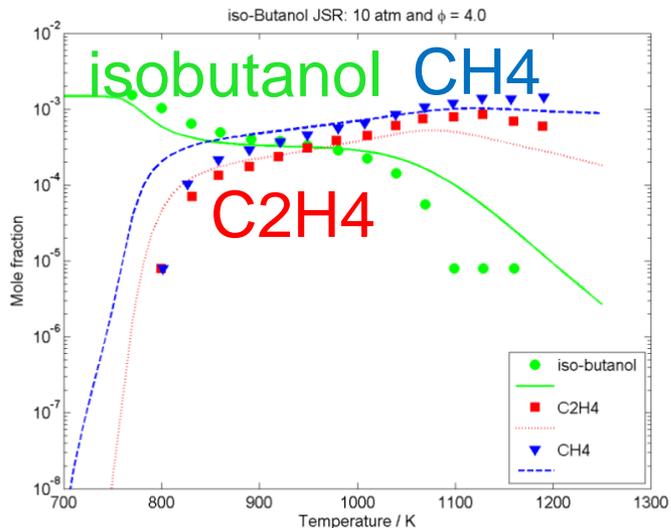
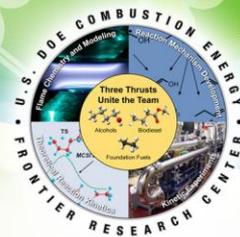
iso-Butanol: 4% O₂, $\phi = 1.0$



Model Predictions quite close to experiment, better than factor of 2:
lucky? Sensitive to Foundation Fuels rates: some H₂/O₂ rate coefficients
very accurate

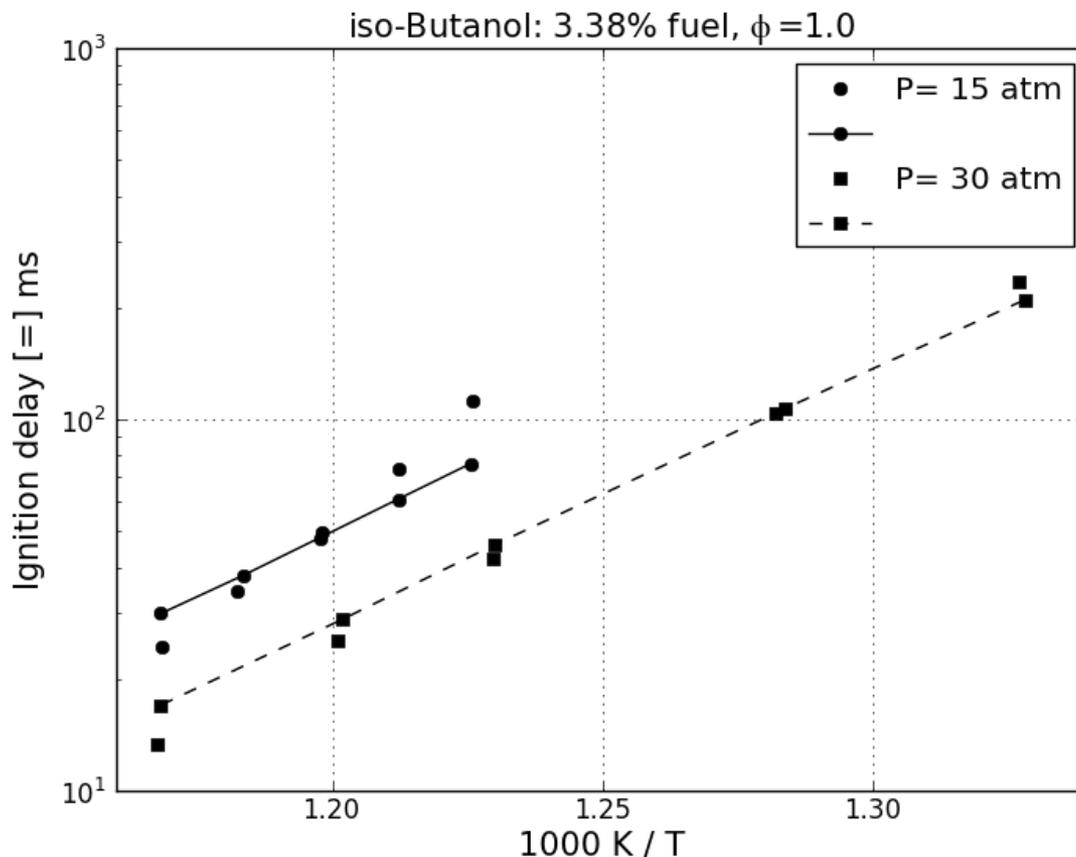
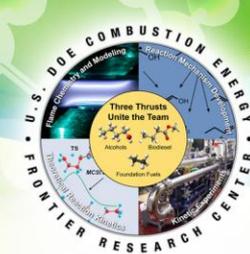
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Model agrees with most low T oxidation expts (e.g. iso-butanol Jet-Stirred Reactor)



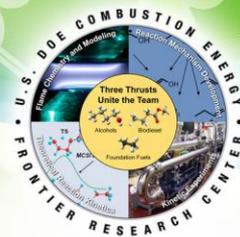
C. Togbé et. al., *Energy Fuels*, 2010, 24, 5244-5256. [Dagaut group, Orleans]

2012 model accurately predicts ignition delay of stoichiometric iso-butanol/air mixture, even at 750 K

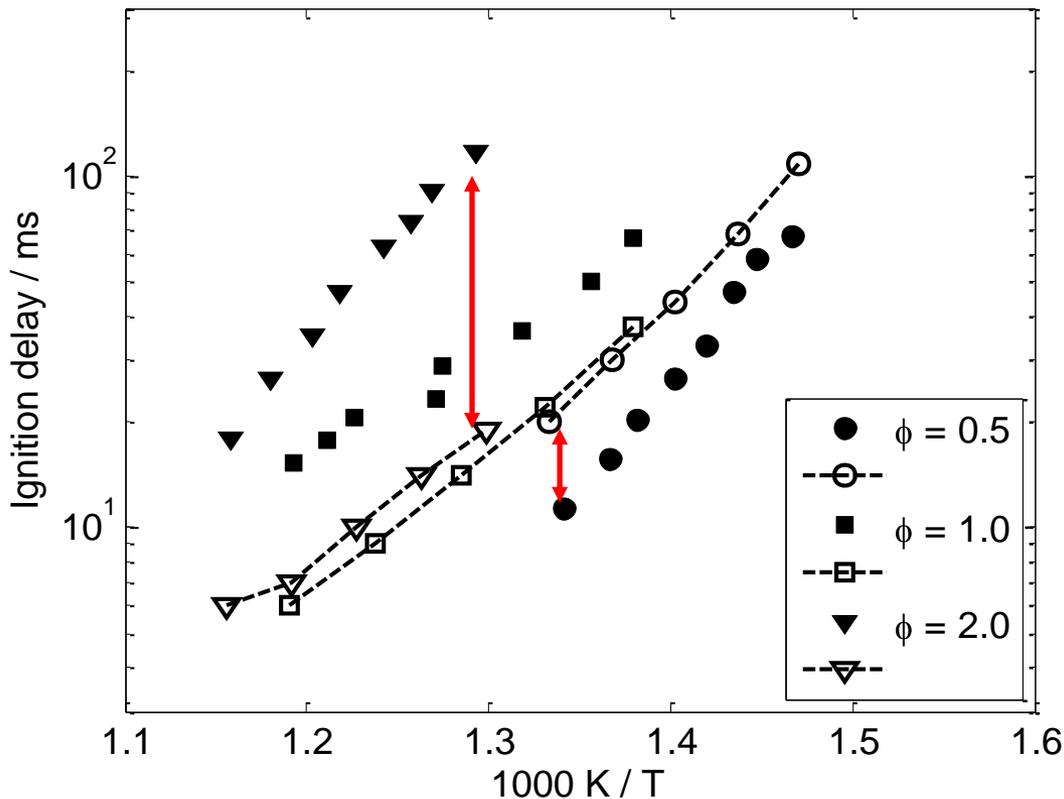


Experiments of Weber et al., model of Merchant et al.

But all models wildly mispredict $[O_2]$ effect on low T ignition of n-BuOH !!



3.38% n-butanol, P = 15 bar

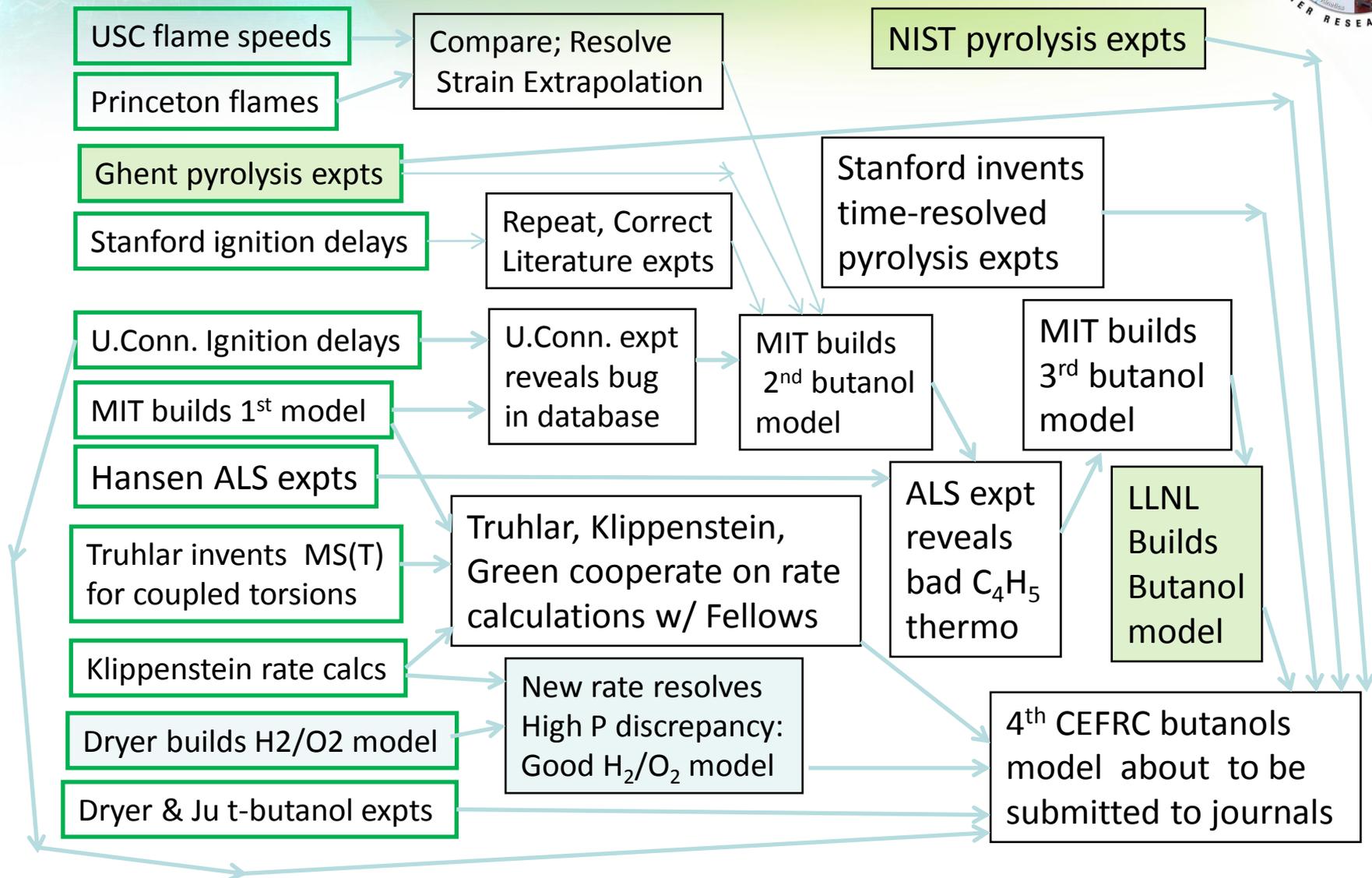
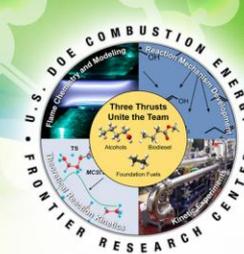


Exptl Data (Solid symbols)
Bryan Weber &
C.J. Sung, U.Conn.

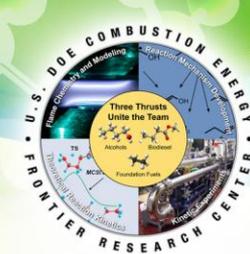
MIT model (open symbols)

CEFRC chemistry theory team is pursuing several different angles, including new chemistry. See next talk.

CEFRC Butanol Thrust: First 2.5 years

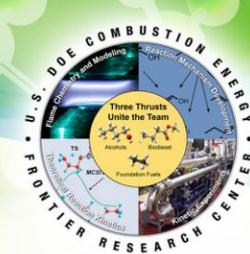


Predicting Alternative Fuel Chemistry: Technical Capability Today



- **Big comprehensive detailed combustion chemistry models can be built pretty quickly.**
 - Current capability: ~500 species, ~10,000 rxns in final model.
 - Current database: C,H,O + some Sulfur
- **Iterative refinement using quantum chemistry** is not automated, takes a few months. Challenging for large molecule (> 10 carbons) reactions (but see recent advances in CEFRC by Carter). Possible to automate, run in parallel?
- **P-dependence and hindered rotor / multiple conformation issues** are significant sources of error in computed k's. CEFRC has made important advances, but more work is needed.
- **Comparison with published experiments is often difficult**, primarily because complete kinetic data is not routinely available in useful electronic formats. Very nice to work in a collaborative team!

Predicting Alternative Fuel Chemistry: Accuracy Today



- Predictions from kinetic models based on quantum chemistry + rate estimates are semi-quantitatively accurate for wide range of combustion/oxidation/pyrolysis experiments.
 - without any adjustment to match experiment
- Occasional big errors due to bugs, holes in database, or missing reactions
 - Discrepancies identify holes in understanding
 - Low T ignition delays
 - PAH formation around 1000 Kelvin
 - Experiments and team-mates great for catching errors!
- As we eliminate the big errors, starting to reach accuracy limits of current quantum chemistry.
 - Better experimental numbers coming (e.g. from Hai Wang, Greg Smith, Ron Hanson, Fred Dryer, Michael Burke & SJK)
 - Quantum chemistry/rate calculations continuing to improve (e.g. Carter, Klippenstein, Truhlar)



QUESTIONS/COMMENTS?