
Massachusetts Institute of Technology

# Combustion Chemistry of a New Biofuel: Butanol

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# Assessing Alternative Fuels: The Challenge of Predicting Performance

- **Hundreds of possible alternative fuels:**

  ***What do we want?***

  - **We can specify the fuel composition**
    - **Sometimes precise control: bioengineering, catalysis from H2**
  - **Which fuels give special performance advantages?**
  - **Do any enable advances in engine technology?**
  - **Performance gain could help biofuel enter market.**
- **Predict performance of a new fuel in a new engine?**

  **…or do we need to experimentally test every possible engine/fuel combination?**

  - **Computer simulations of combustion becoming practical.**
  - **Rate constants, thermo from quantum calculations**
  - **Validate predictions with experiments**

# CEFRC's First Test Case: Butanol
# Why Butanol?

- Bio-butanol is about to be commercialized
  - Strong demand for an accurate computer model
- Butanol has some advantages over ethanol
  - More soluble in gasoline
    - Can be used at higher blending ratios
    - Can be shipped in gasoline pipelines
  - Lower vapor pressure: less smog
- When CEFRC started, very few data or models available on butanol combustion
- Small molecule, but big enough
  - Simpler chemistry than e.g. diesel range fuels
  - Feasible to do high-accuracy quantum chemistry
  - Experimentally convenient: easy to vaporize
  - Interesting: Several isomers with quite different chemistry

# Dozens of Center members all studying butanol in parallel

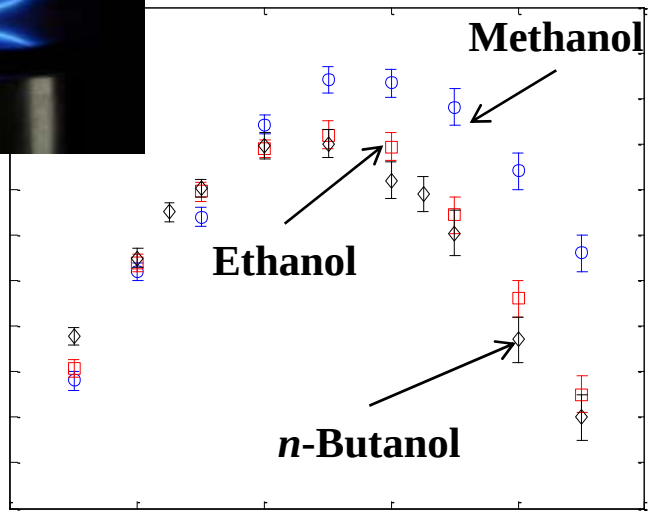
***Tied together by connections with the MIT team assembling the kinetic model***

**As examples, here we show data and calculations from these groups:**

- C.K. Law (Princeton) flame speeds, flame ball
- F. Egolfopoulos (USC) flame speeds, extinction
- Nils Hansen (Sandia, ALS) species in flames
- S. Klippenstein (Argonne) quantum chemistry
- Ron Hanson (Stanford) ignition delays, species
- C.J. Sung (Connecticut) ignition delays

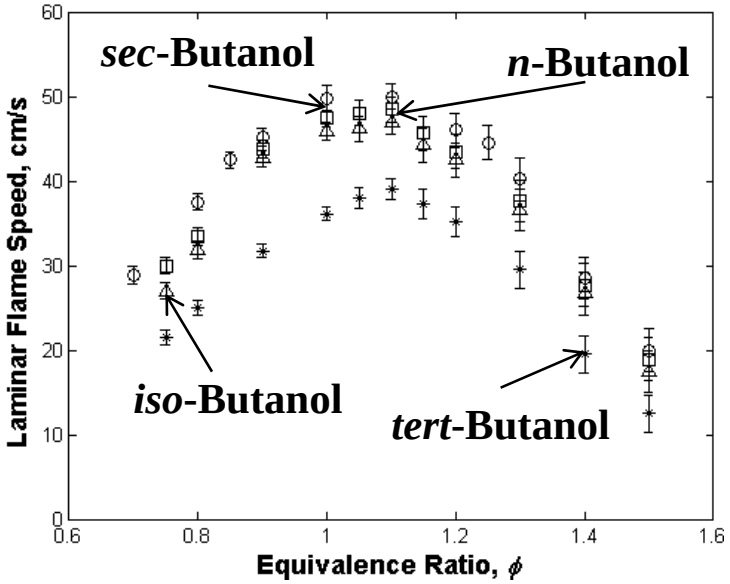
Other data and calculations not shown because of the time…

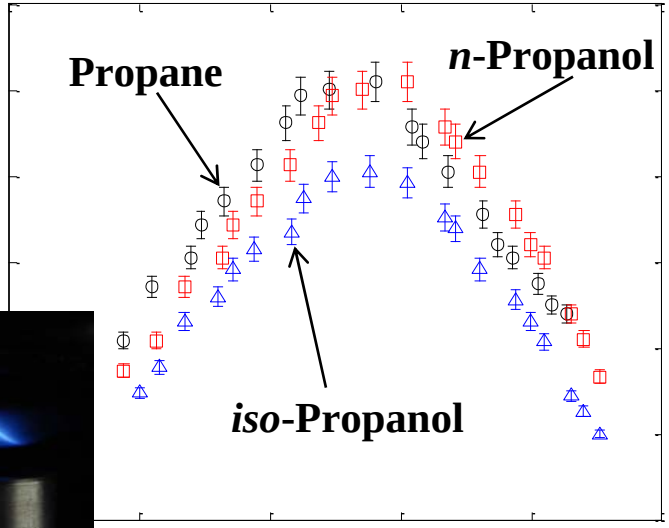
# Flame Speeds for Different Fuels: Not Intuitive. Need a Model!

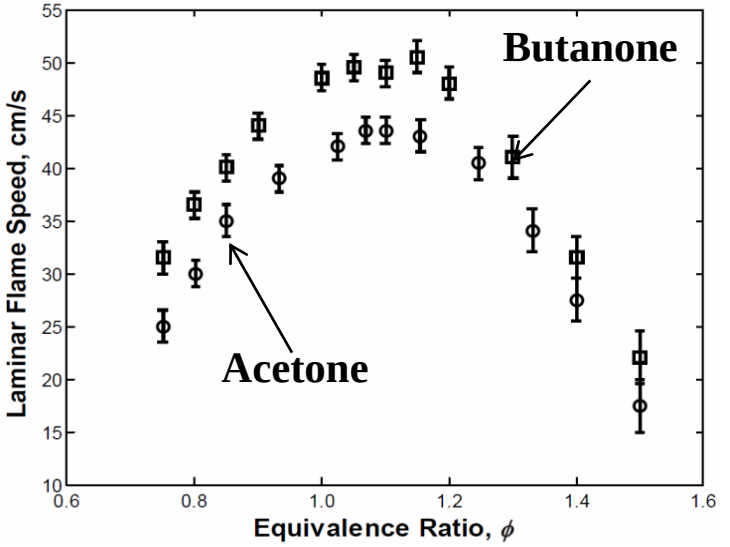



Flame Speed

Equivalence Ratio

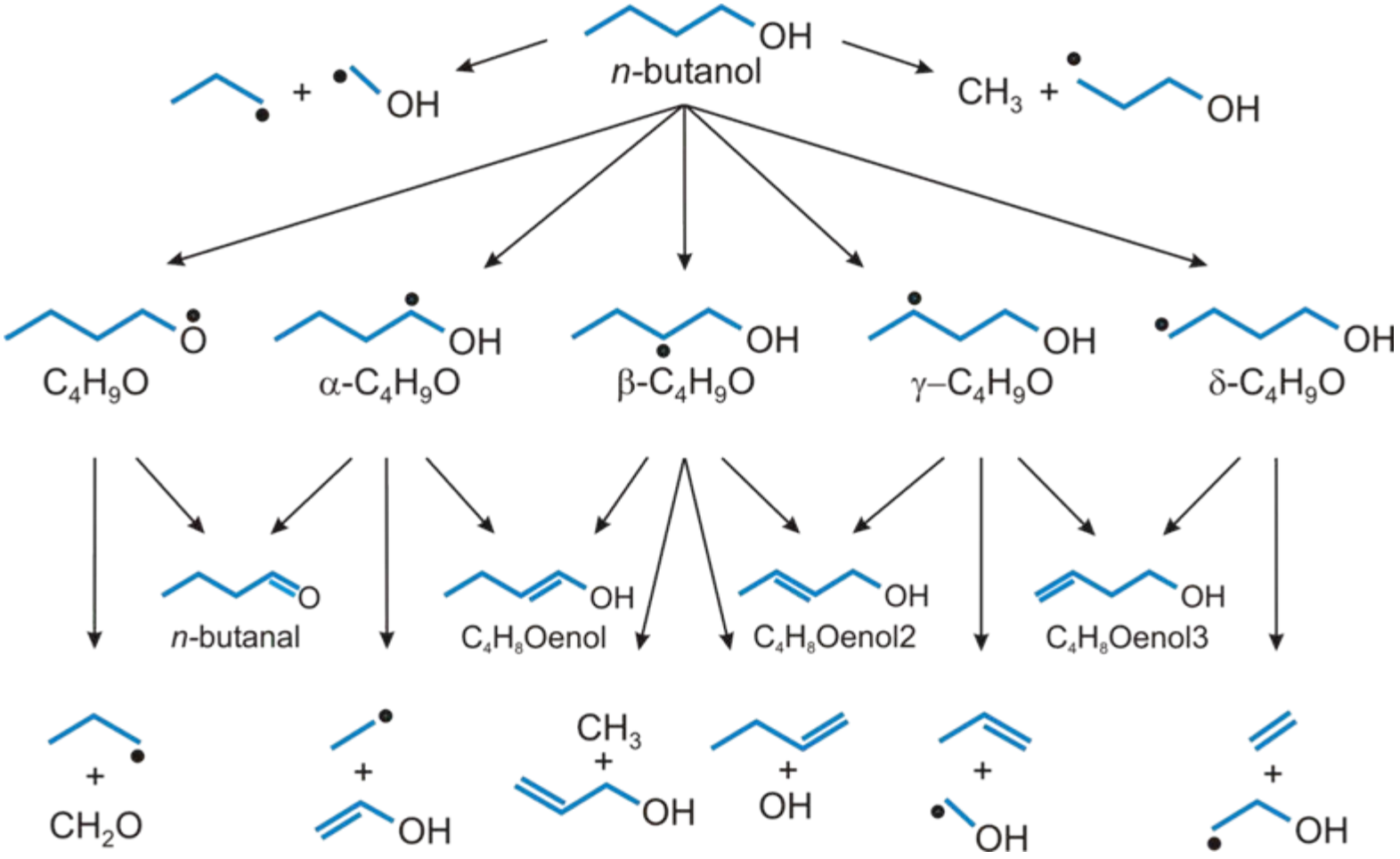


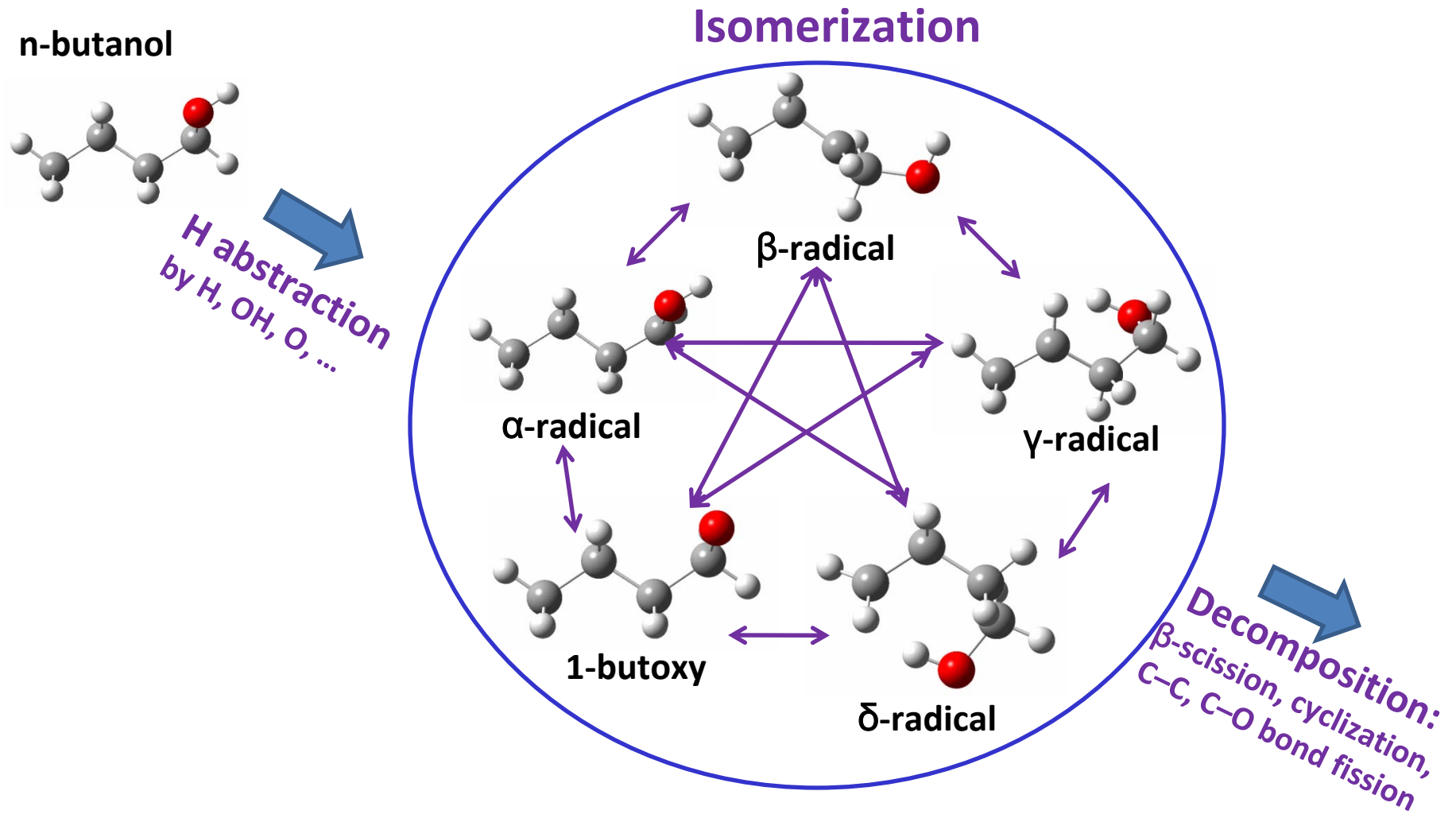

**Measured in Egolfopoulos lab (USC). Air, 1 atm.**

# Different Reaction Paths Important at different combustion conditions

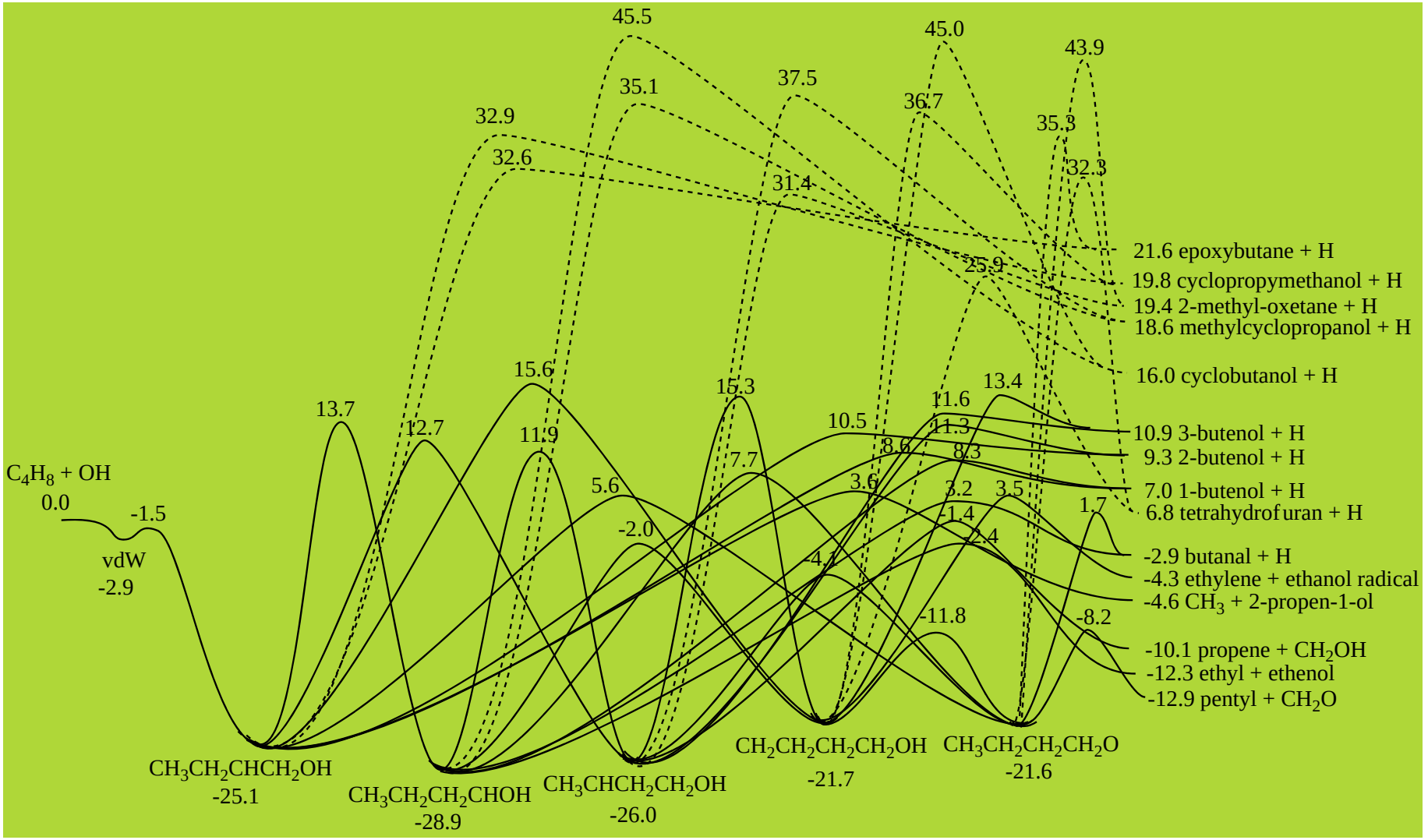



**Big consequences: ignition, soot-formation, toxic emissions**

# Thermal Decomposition of $C_4H_9O$ radical critical in n-butanol combustion



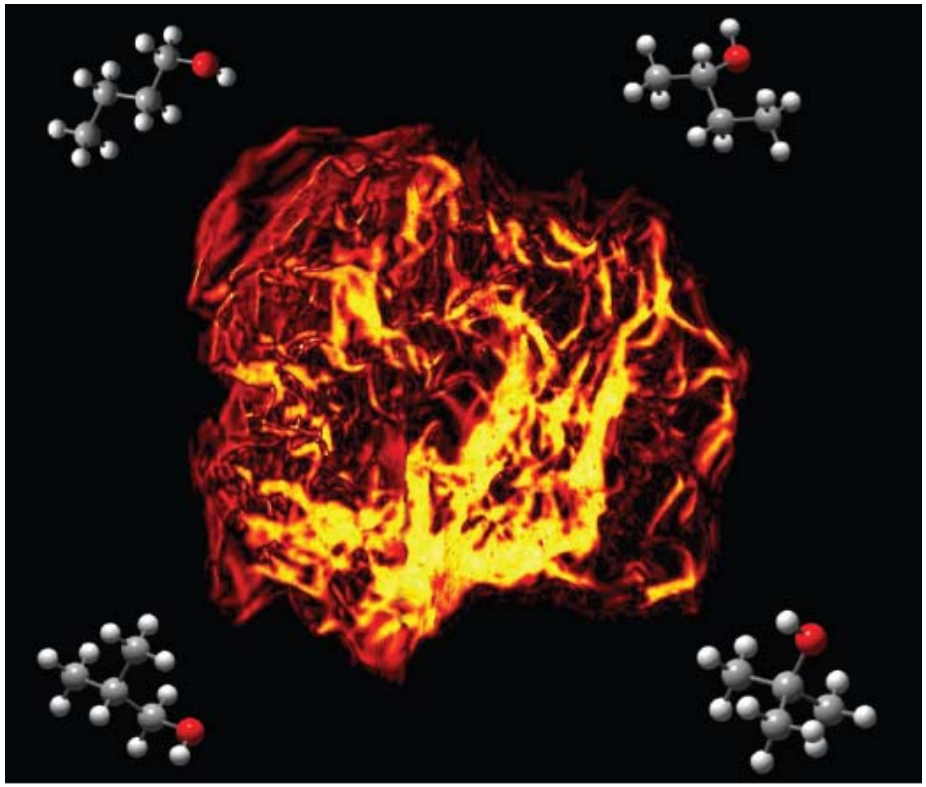
# Quantum Chemistry allows us to compute rates k(T,P) of all $C_4H_9O$ Decomposition Reactions




**CASPT2 (3e,3o)/ADZ** **B3LYP/6-311++G(d,p)**

Calcs by S. Klippenstein (Argonne)

# Combustion has been studied for a long time, but still quite challenging



**Photograph of a Butanol/Air flame in internal combustion engine conditions (measured in C.K. Law's lab, Princeton)**

Current CEFRC Chemistry Model:

334 species reacting via 7113 reactions

4288 of the reactions have complicated non-Arrhenius k(T,P)

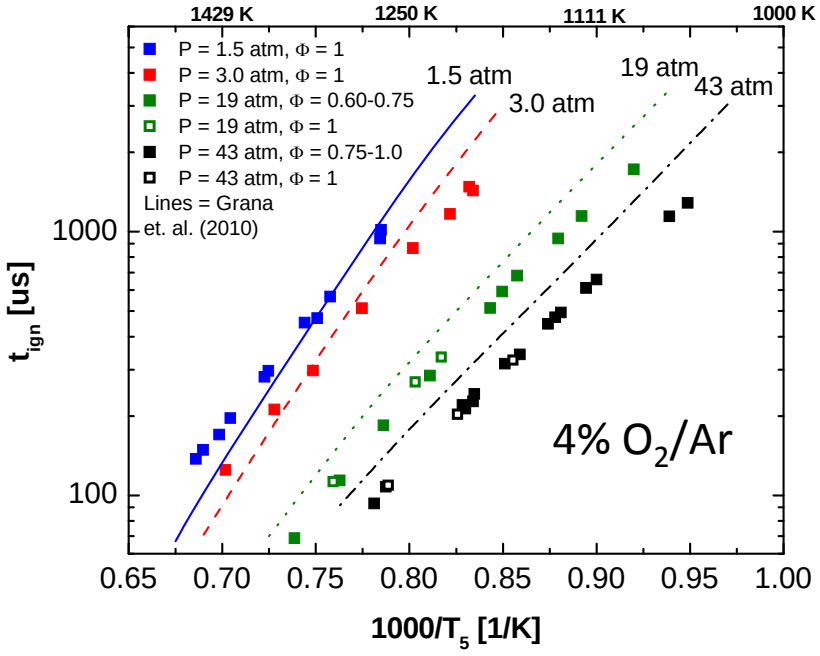
***Numerical issues in solving the model, but possible to do it. Tricky to know true boundary conditions in many combustion experiments.***

# Most important fuel performance property: ignition

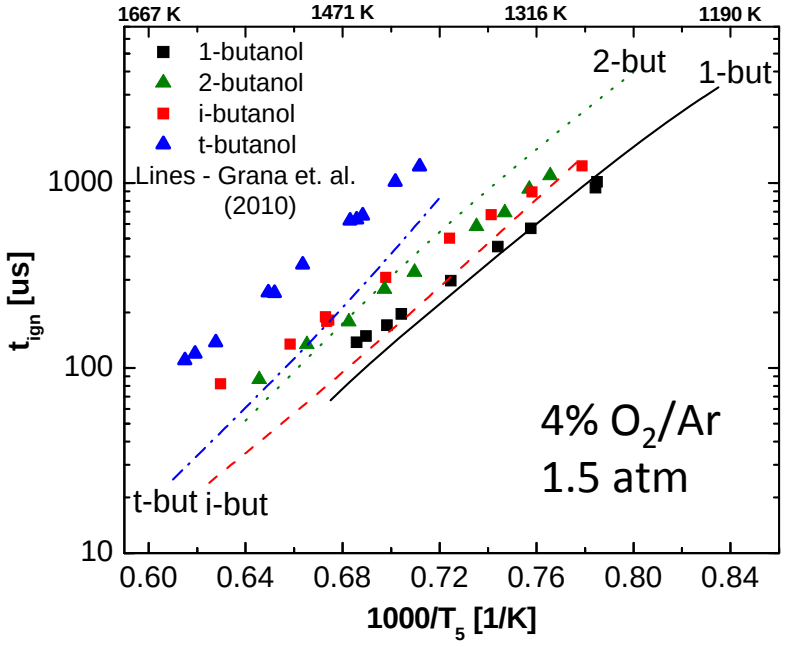
- Gasoline “Octane Number”
- Diesel “Cetane Number”
- Small changes in fuel make big changes in ignition: sensitive to molecular structure!
- New engines under development are even more sensitive to ignition
  - Potential for big gains… but only if the fuel ignition delay time matches engine requirements

# Stanford Shock Tube Measurements: Butanol Ignition Delay Time

## N-Butanol

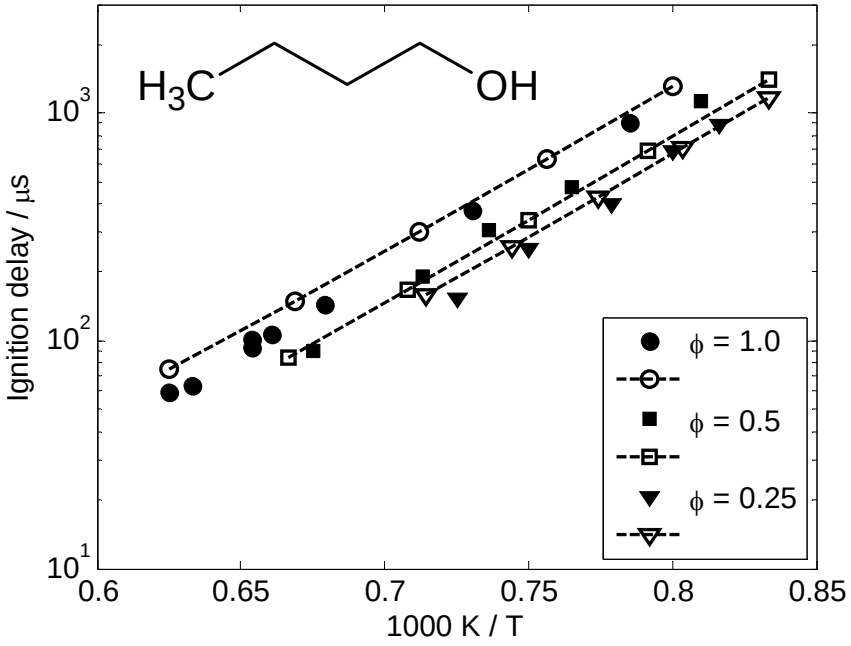


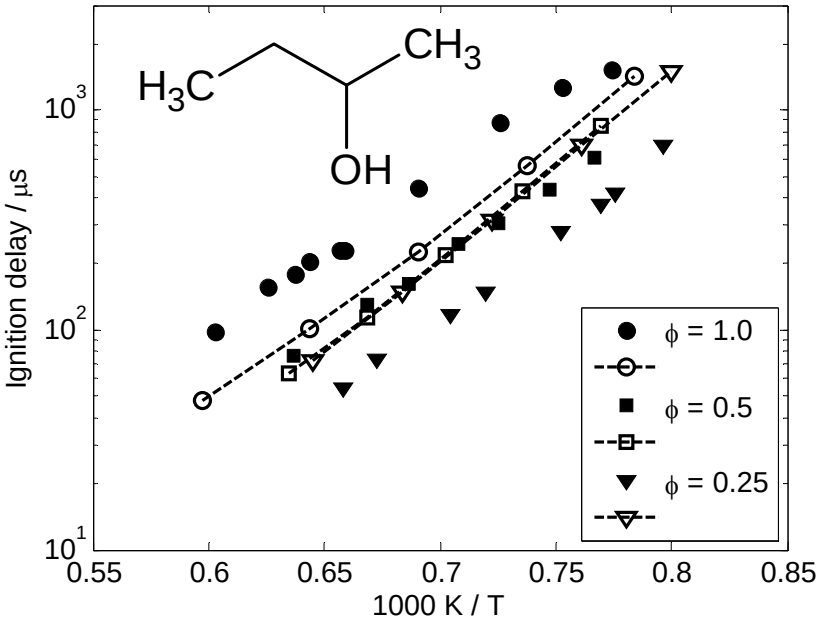

## Butanol Isomers

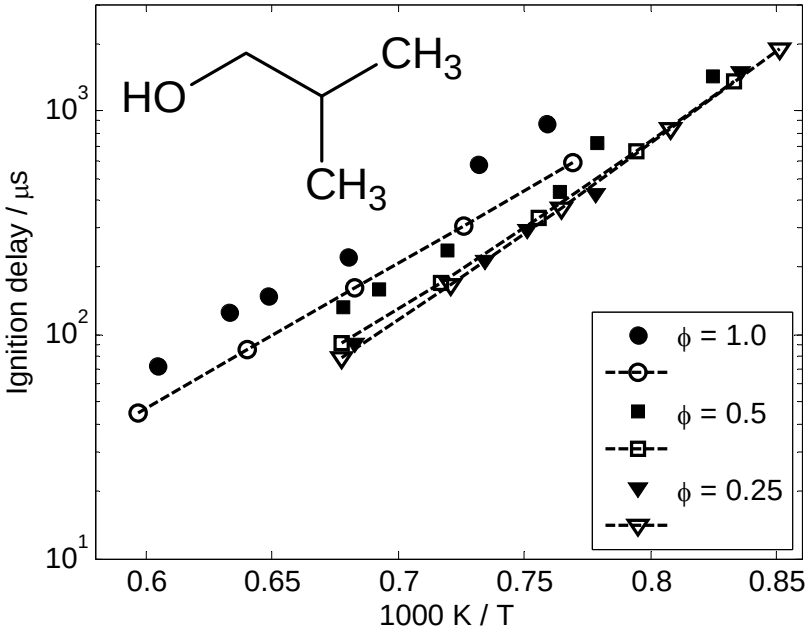


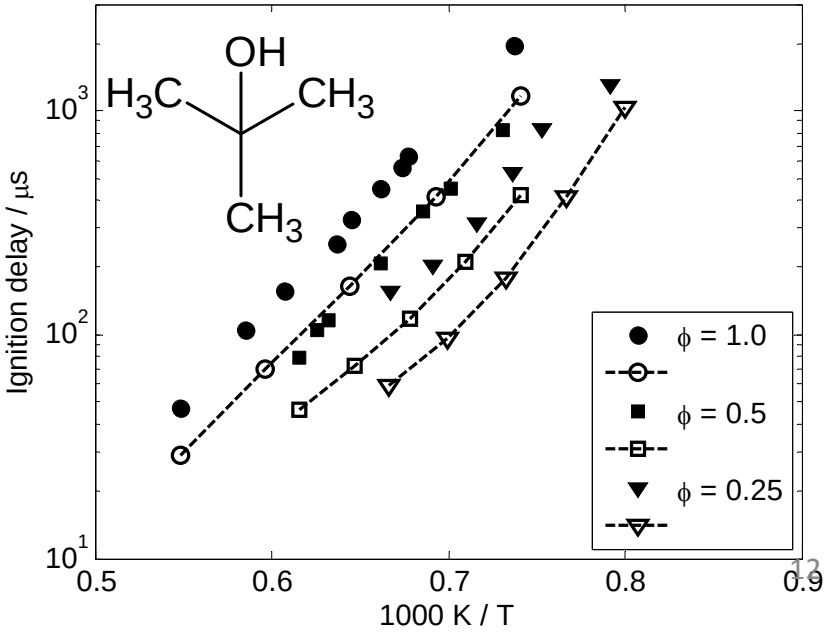

- Ignition delay time database provides wide coverage of pressure and temperature
- **Tert-butanol** has significantly **longer ignition delay times** than other isomers

# Model accurately predicts Stanford high-T ignition delays



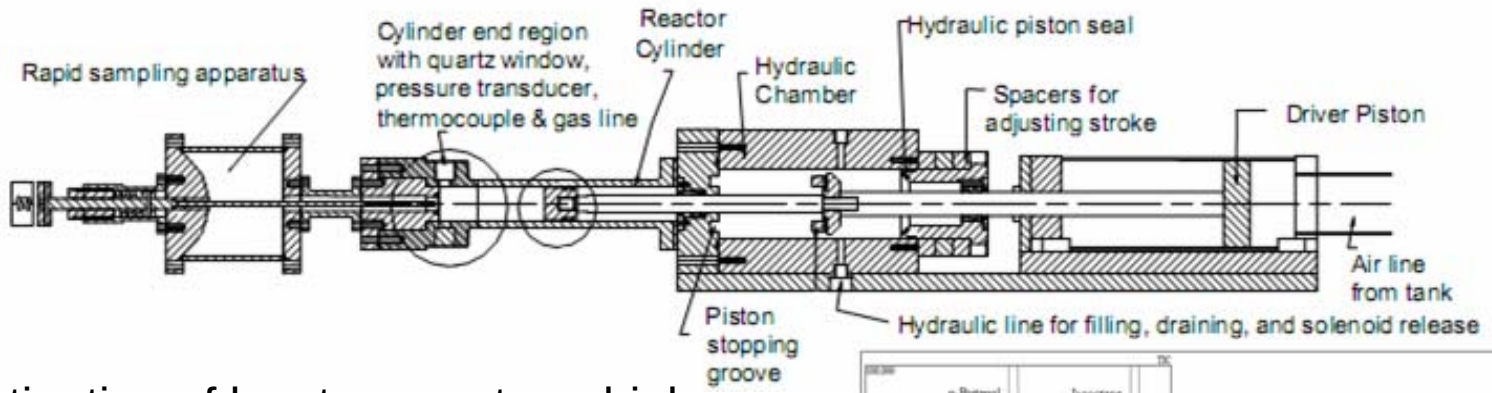



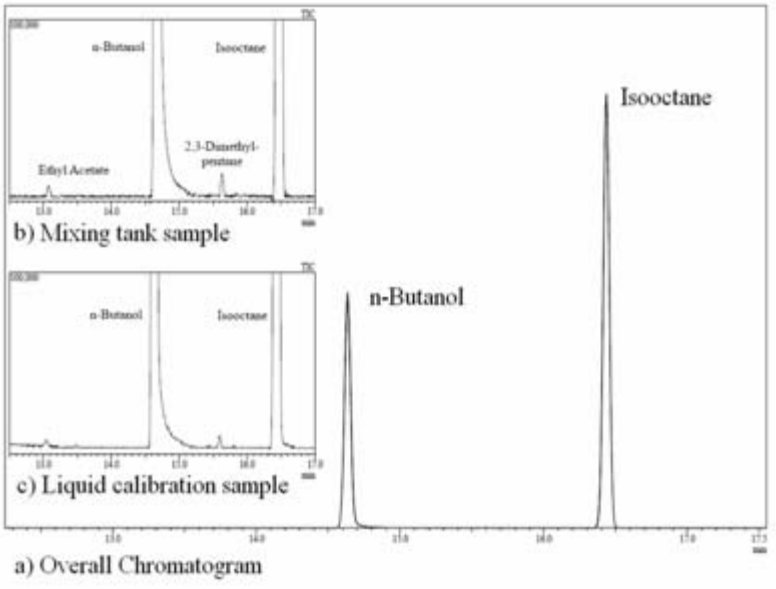



# Engines Sensitive to Ignition at High Pressure and "Low" Temperature

## Rapid Compression Machine

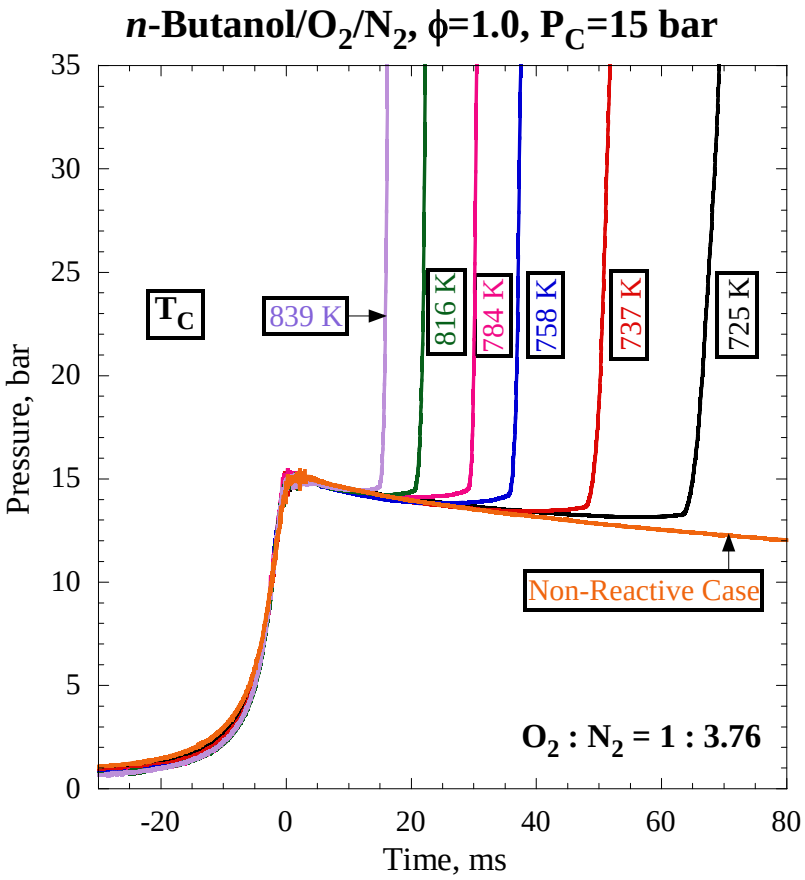


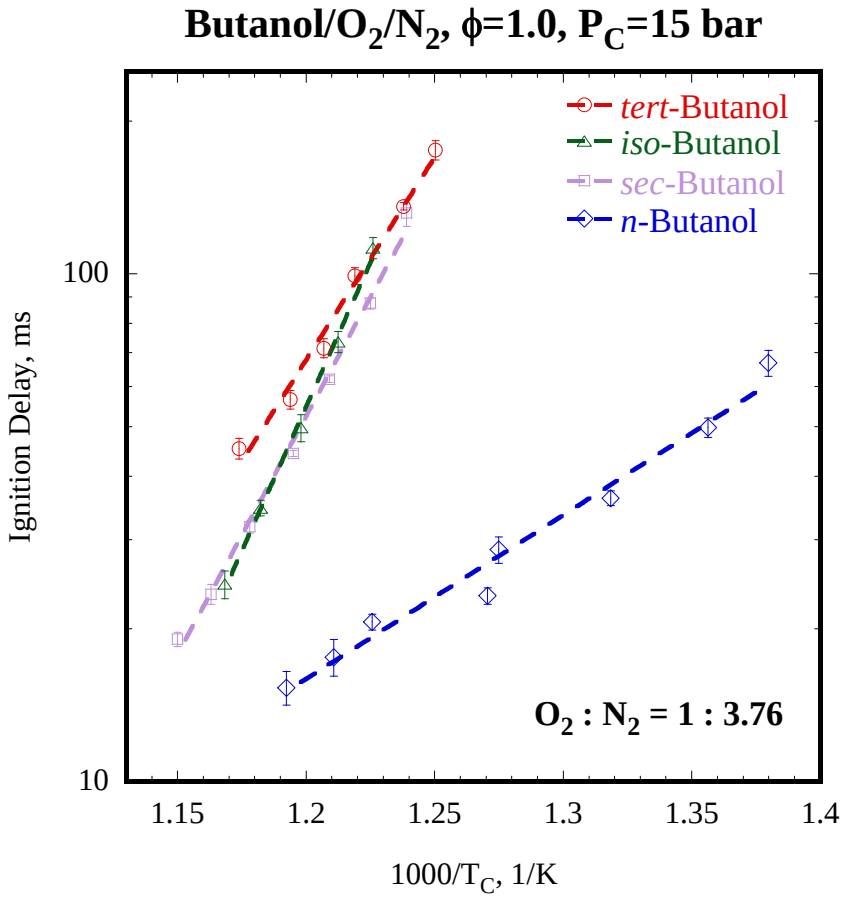

- Investigation of low-temperature, high-pressure autoignition is relevant to many emerging engine technologies
- GCMS sampling results prior to experiments confirm mixture composition preparation procedure when handling liquid fuels
- Gas samples from the reaction chamber for GC-MS/FID analysis allow identification and quantification of important species during autoignition




***C.J. Sung group, U. Conn.***

# Autoignition Studies of Butanol Isomers at High Pressure and Low Temperature



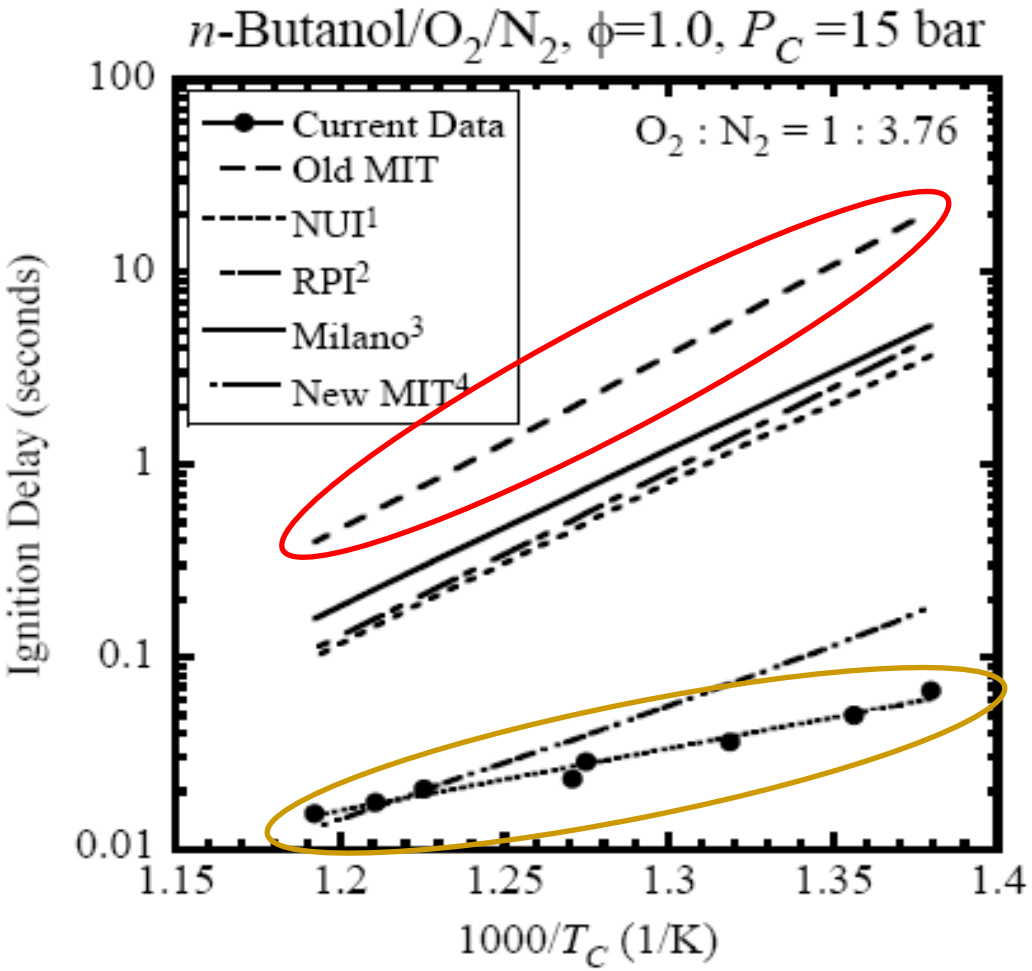




**_n_-butanol ignition is _much_ faster than the other butanol isomers for T< 900 K**

**Measured in C.J. Sung lab (U.Conn.)**

# Big Discrepancy: Model did *not* predict the fast n-butanol ignition observed at T < 900 K!

University of Connecticut




**Model was built automatically using computer "expert system"**

**Due to mistake in rate database used by expert system, model wildly mis-estimated barrier for HO2 + C-H reactions.**

# Big Discrepancy: Model did not predict the fast n-butanol ignition at T < 900 K!

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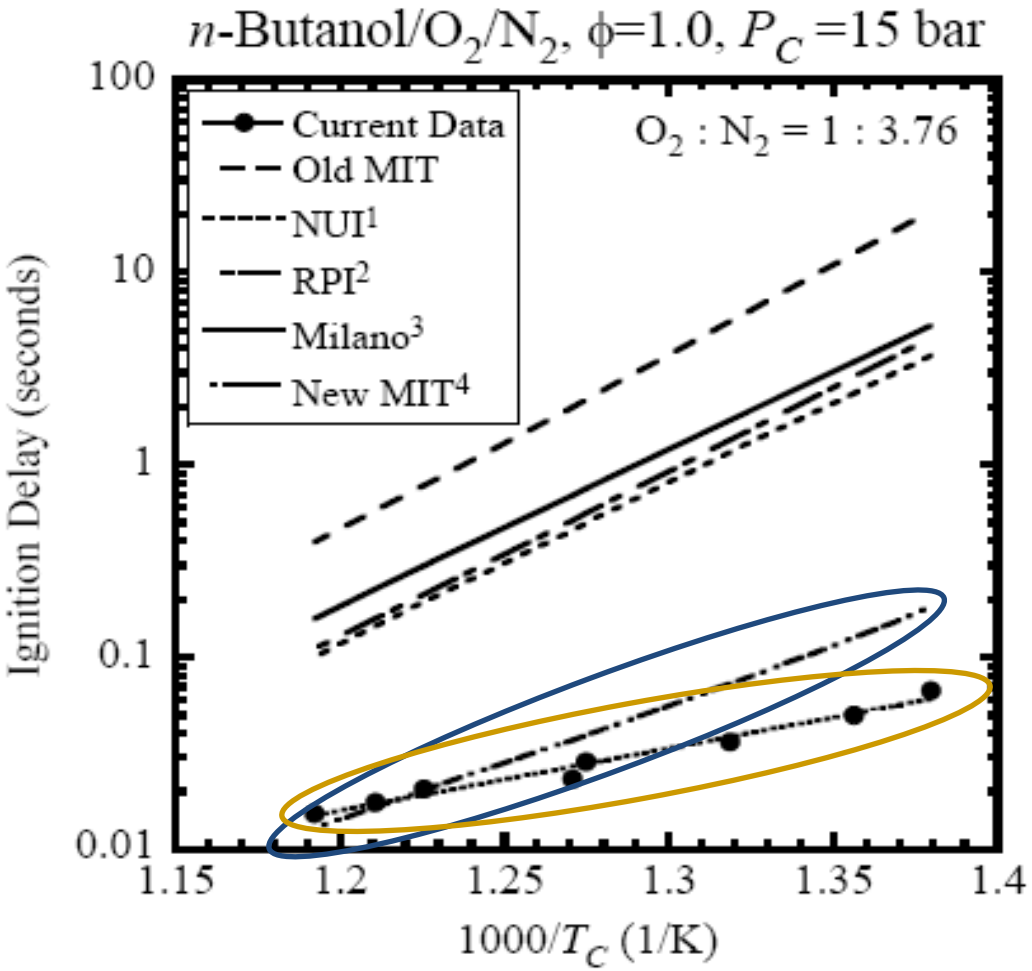


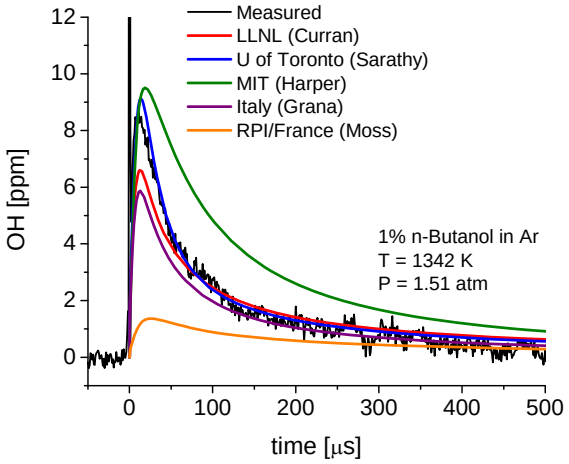

**Model was built automatically at MIT using computer "expert system"**

**Due to mistake in rate database used by expert system, model wildly mis-estimated barrier for $HO_2$ + C-H reactions.**

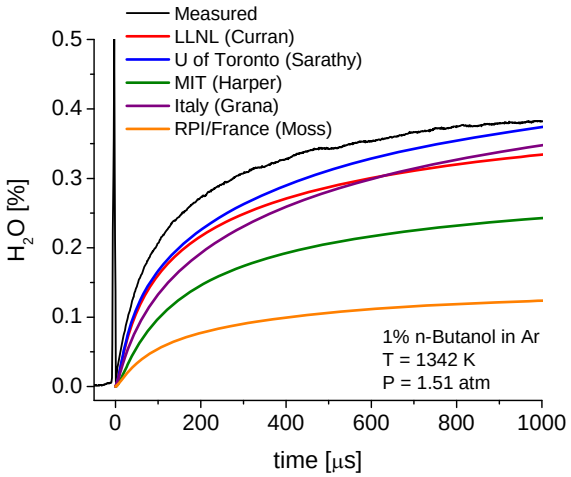
**After correcting that big mistake, current CEFRC model is much closer…**
**…but still not quite right at lowest temperatures.**
**Work continues…**

# Multi-Species Time-Histories Provide Stronger, More Informative Tests of Model: n-Butanol Pyrolysis

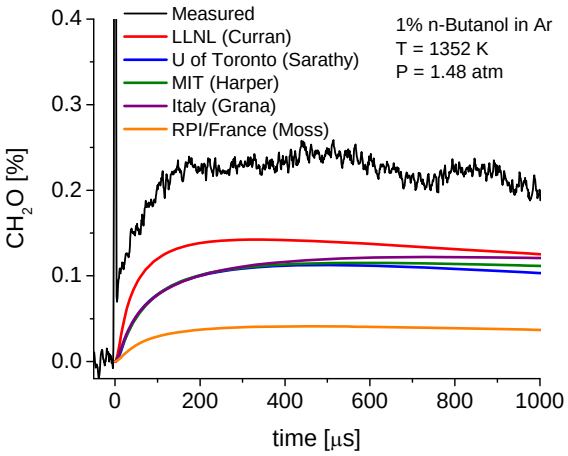
## OH




## $H_2O$




## $CH_2O$

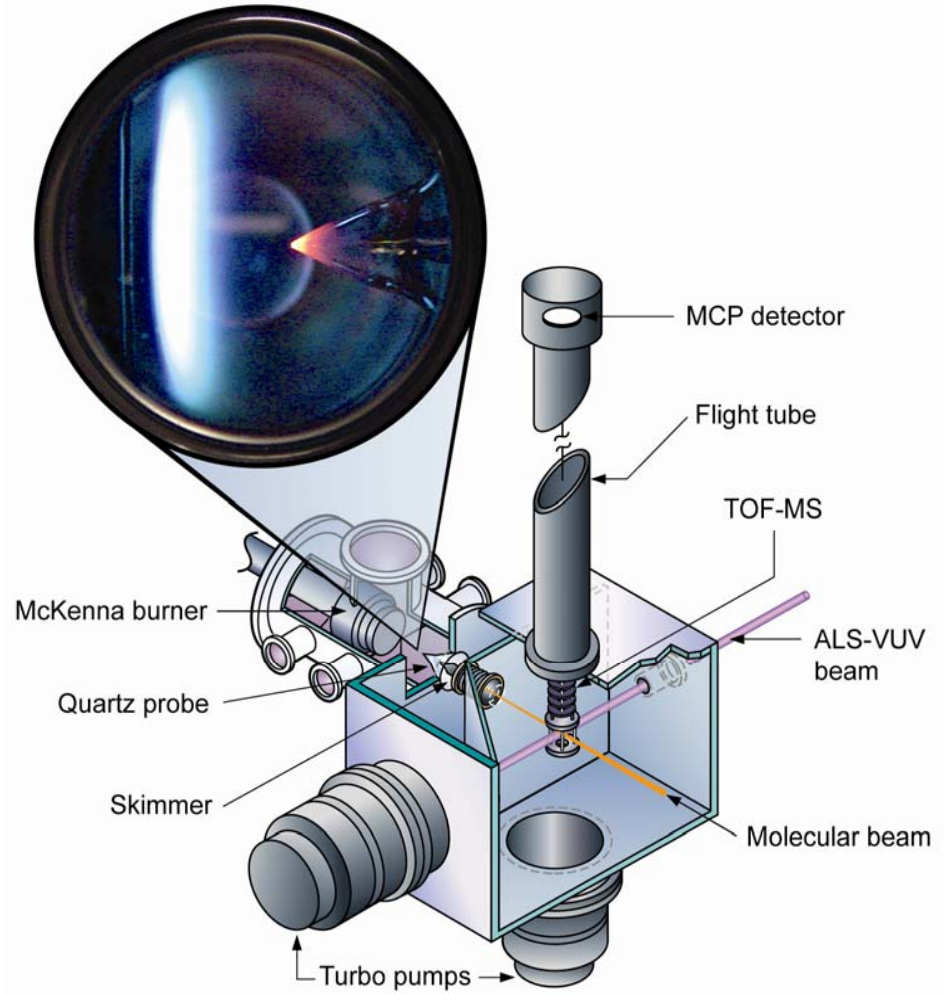



- **Current status:** Stanford species time-history measurements for OH, $H_2O$ and $CH_2O$
- **Next step:** laser absorption measurements of CO and $C_2H_4$

- **All models underpredict formaldehyde and $H_2O$** formed in high-T *n*-butanol pyrolysis

# Advanced Light Source allows direct detection of *dozens* of species including key radicals

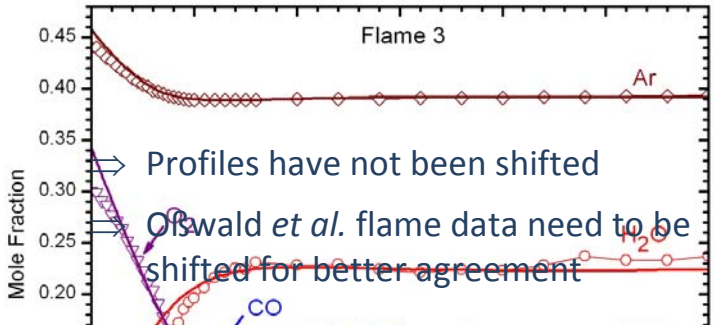
## Photoionization Molecular Beam Mass Spectrometry

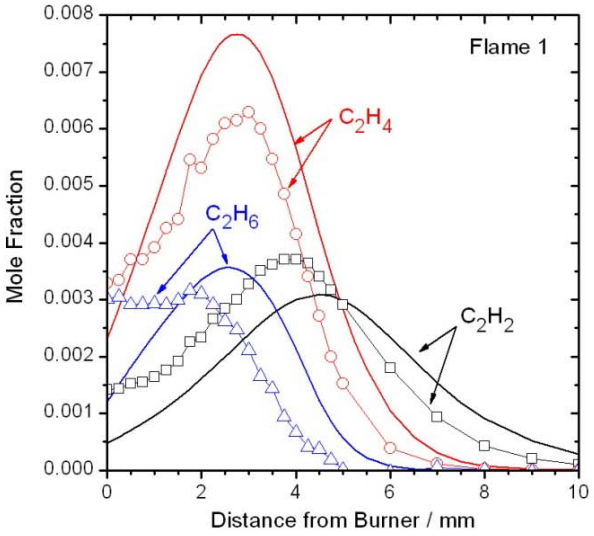


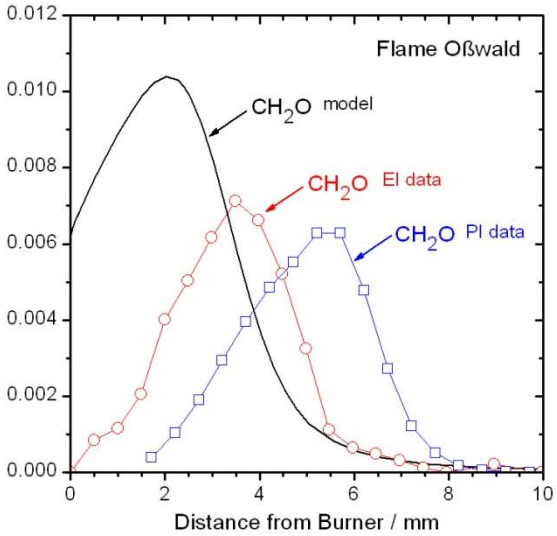

- Flames are analyzed with molecular beam time-of-flight mass spectrometry
- Photoionization with tunable synchrotron-generated VUV photons allows identification of species
  - by mass
  - by ionization energy
- Experimental mole fraction profiles are compared with flame model predictions and reaction path and sensitivity analysis are performed

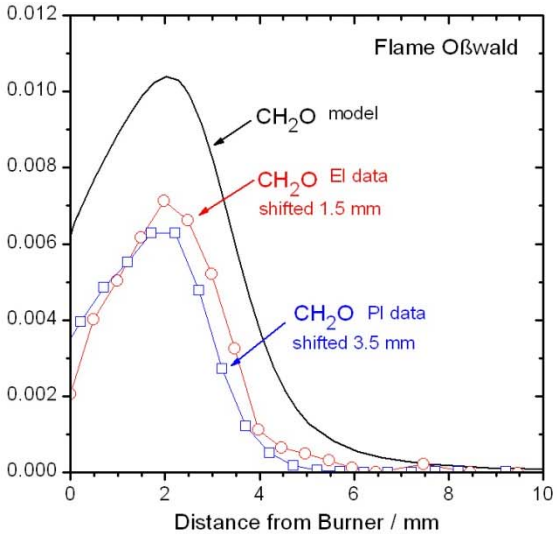
# Advanced Light Source (ALS) Flame Data:
## Detailed Test of the Model's Predictive Capabilities

- ✓ 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



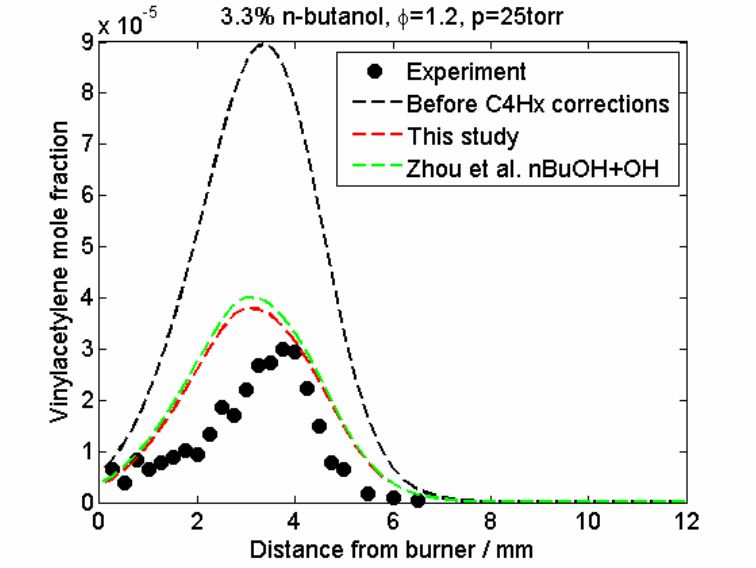



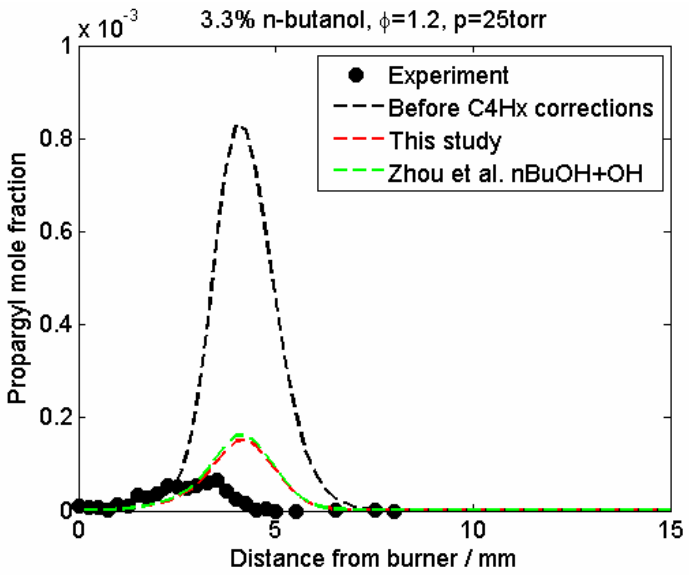

Only a few of the many data traces shown here… most show good agreement

# One big discrepancy identified between model and ALS data: $C_4H_4$ and $C_3H_3$ overpredicted

## *Sensitive to $C_4H_5$ Thermochemistry*

- Simulations of the flames studied by ALS are sensitive to the enthalpy of formation of *i*-$C_4H_5$ ($CH_2$=CH-•C=$CH_2$ ↔ •$CH_2$-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 largely resolved the discrepancy.




**Now investigating origins of smaller discrepancies…**

# Conclusions

- **Teams can move fast!**
  - **In less than 2 years, went from zero to quite good model for butanol combustion, comprehensively validated by many different types of experiments.**
  - **Contrast: sequential single-investigator model-building and comprehensive validation usually takes decades.**
  - **Certainly we can do it even faster next time through**
  - **Very promising for other alternative fuels: do you have a fuel we should model?**
- ***Focus on the discrepancies*** **(models vs. expts, and expts vs. expts.): that is where there is an opportunity to learn something!**
  - **Don't be shy: expose the discrepancies to your EFRC team-mates!**