Combustion Chemistry of a New Biofuel: Butanol

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!

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 C₄H₉O radical critical in n-butanol combustion

n-butanol

H abstraction by H, OH, O, ...

Isomerization

β-radical

α-radical

γ-radical

δ-radical

1-butoxy

Decomposition: β-scission, cyclization, C–C, C–O bond fission
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.

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

- 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

![Graphs showing ignition delays for different fuels and equivalence ratios](https://example.com/graphs)
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/O$_2$/N$_2$, $\phi=1.0$, $P_C=15$ bar

$n$-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 $T < 900 \text{ K}$!

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!

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 $\text{HO}_2 + \text{C-H}$ reactions.

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

- **Current status**: Stanford species time-history measurements for OH, H$_2$O and CH$_2$O
- **Next step**: laser absorption measurements of CO and C$_2$H$_4$
- **All models underpredict formaldehyde and H$_2$O formed in high-T \textit{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

Profiles have not been shifted
Oßwald et al. flame data need to be shifted for better agreement

Only a few of the many data traces shown here... most show good agreement
One big discrepancy identified between model and ALS data: C₄H₄ and C₃H₃ overpredicted

*Sensitive to C₄H₅ Thermochemistry*

- Simulations of the flames studied by ALS are sensitive to the enthalpy of formation of $i$-C₄H₅ (CH₂=CH-•C=CH₂ ↔ •CH₂-CH=C=CH₂). 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!