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## Motivation

- The butanol isomers are second generation biofuels under active investigation by the Combustion Energy Frontier Research Center (CEFRC).
- Butanols can be synthesized from lignocellulosic biomass.
- Butanols have greater energy density, absorb less water, and evaporate less than ethanol.
- *t*-Butanol is already an EPA High-Production Volume (HPV) chemical, with more than 1 million lbs. produced every year.

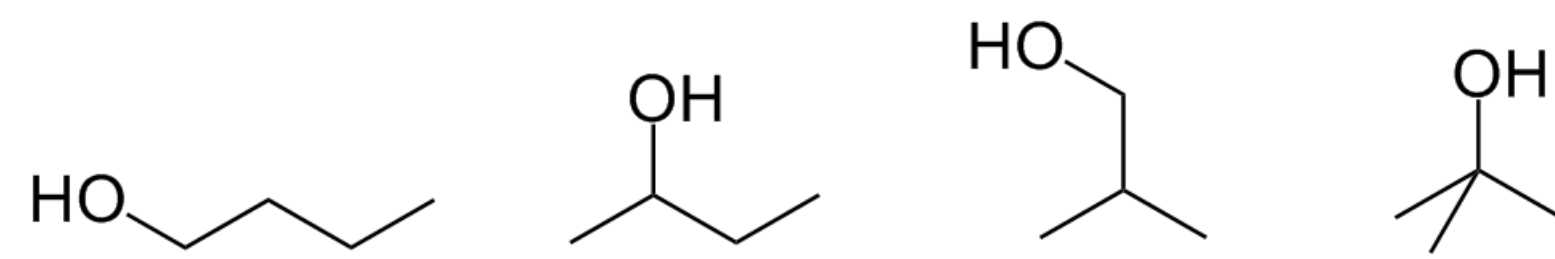


Figure 1. Isomers of butanol. Beginning from the left is *n*-butanol, *sec*-butanol, *iso*-butanol, and *t*-butanol.

## Background

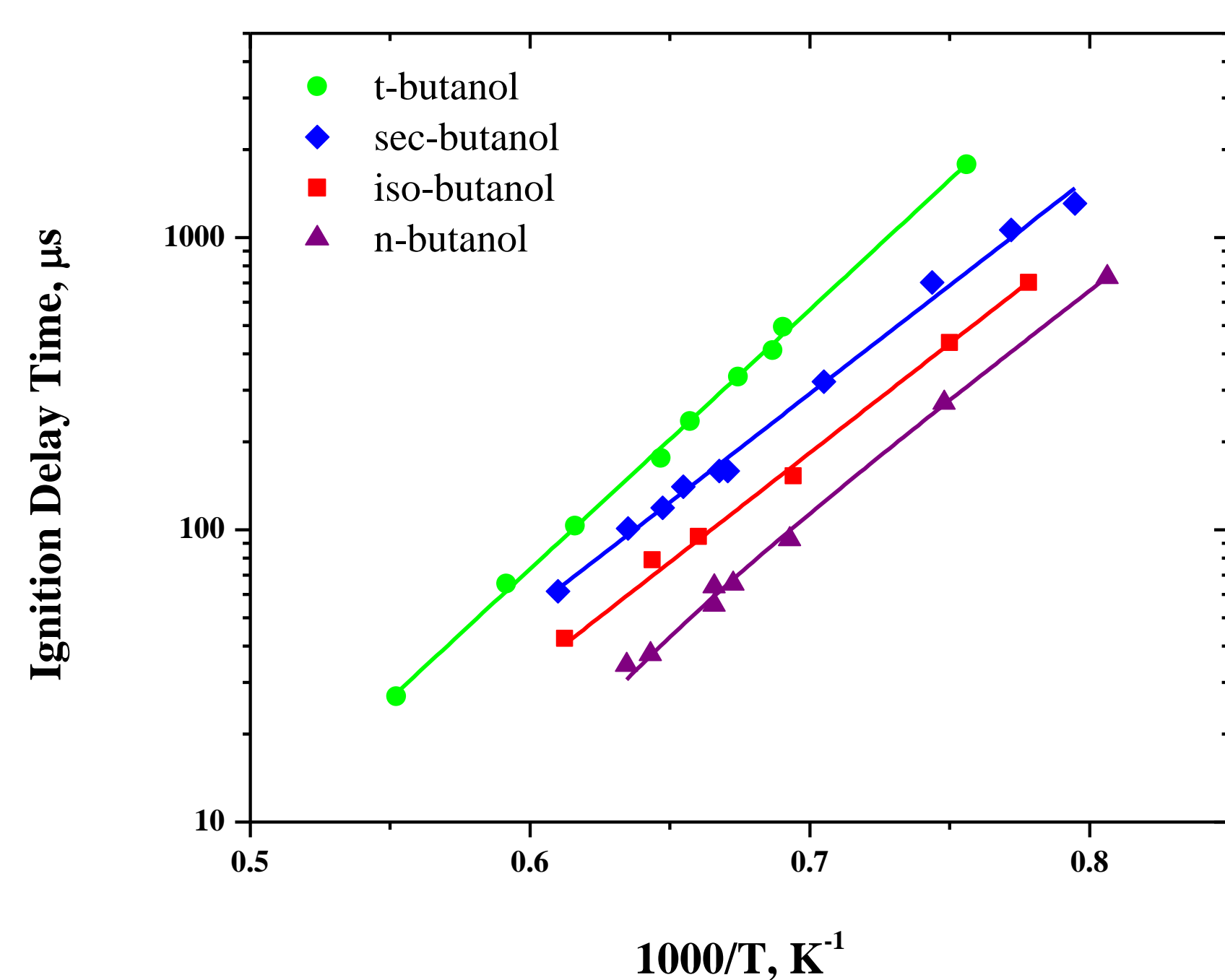


Figure 2. Ignition delay times as a function of inverse temperature for all the butanol isomers at  $\Phi = 1$ , 93% Ar.gon, at 1 bar [1].

- The ignition delay times of the butanol isomers were measured by Moss et al. [1], and *t*-butanol was found to have the slowest chemistry, see Figure 2.
- They determined that the long ignition delay time was due to the comparatively high activation energy for the decomposition reactions of *t*-butanol as well as the slow reactions of its primary intermediate, *iso*-butene.

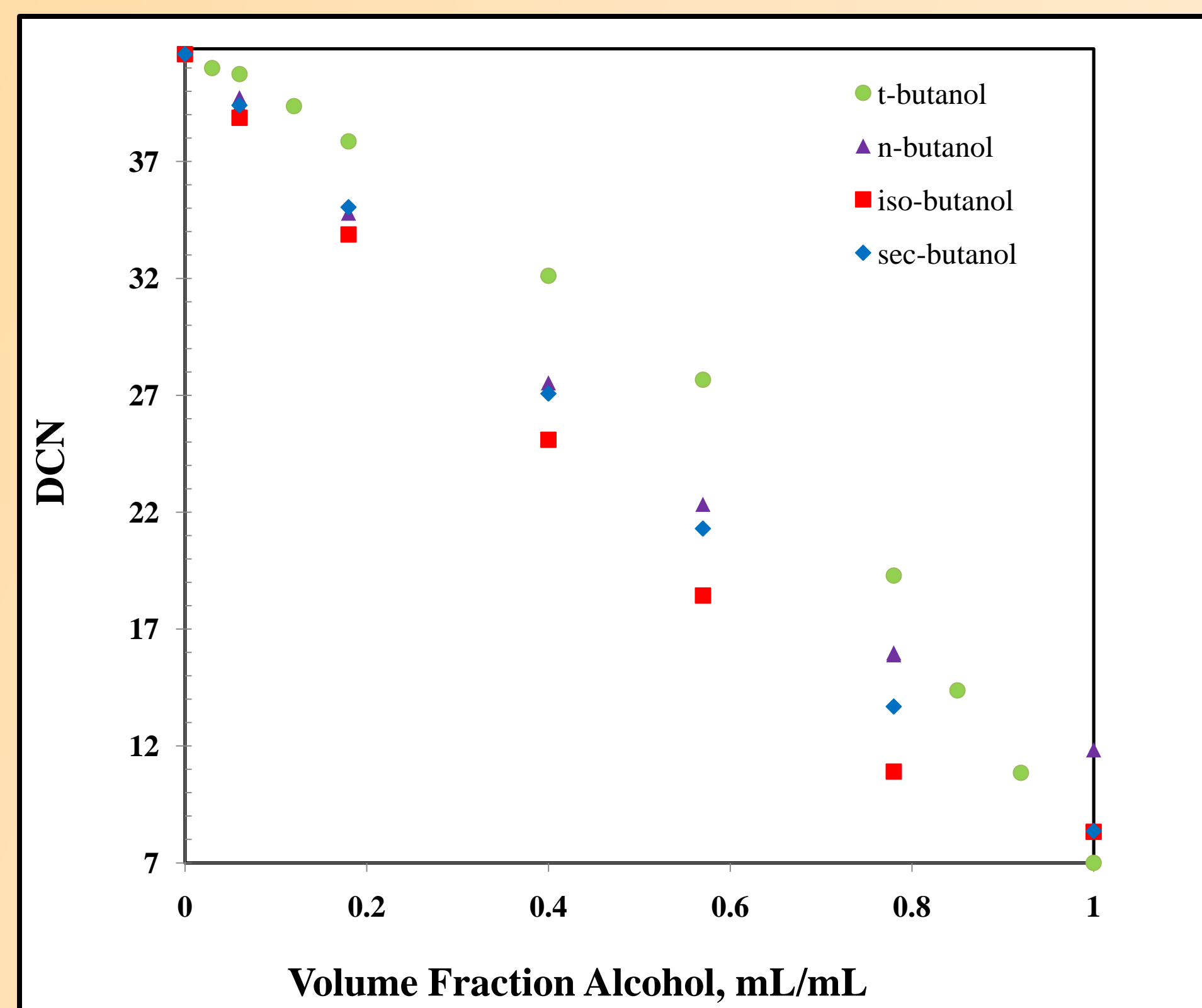


Figure 3. Derived cetane number (DCN) as a function of blending ratio of the butanol isomers in *n*-heptane [2].

- In blends with *n*-heptane, Haas et al. [2] found *t*-butanol to react faster than the other isomers when in blends of less than 80% alcohol, see Figure 3.
- They concluded that *t*-butanol does not participate in the ignition chemistry of *n*-heptane to the same extent as the other isomers, thus detracting the least from the ignition quality of the alkane.

## Flux Analysis

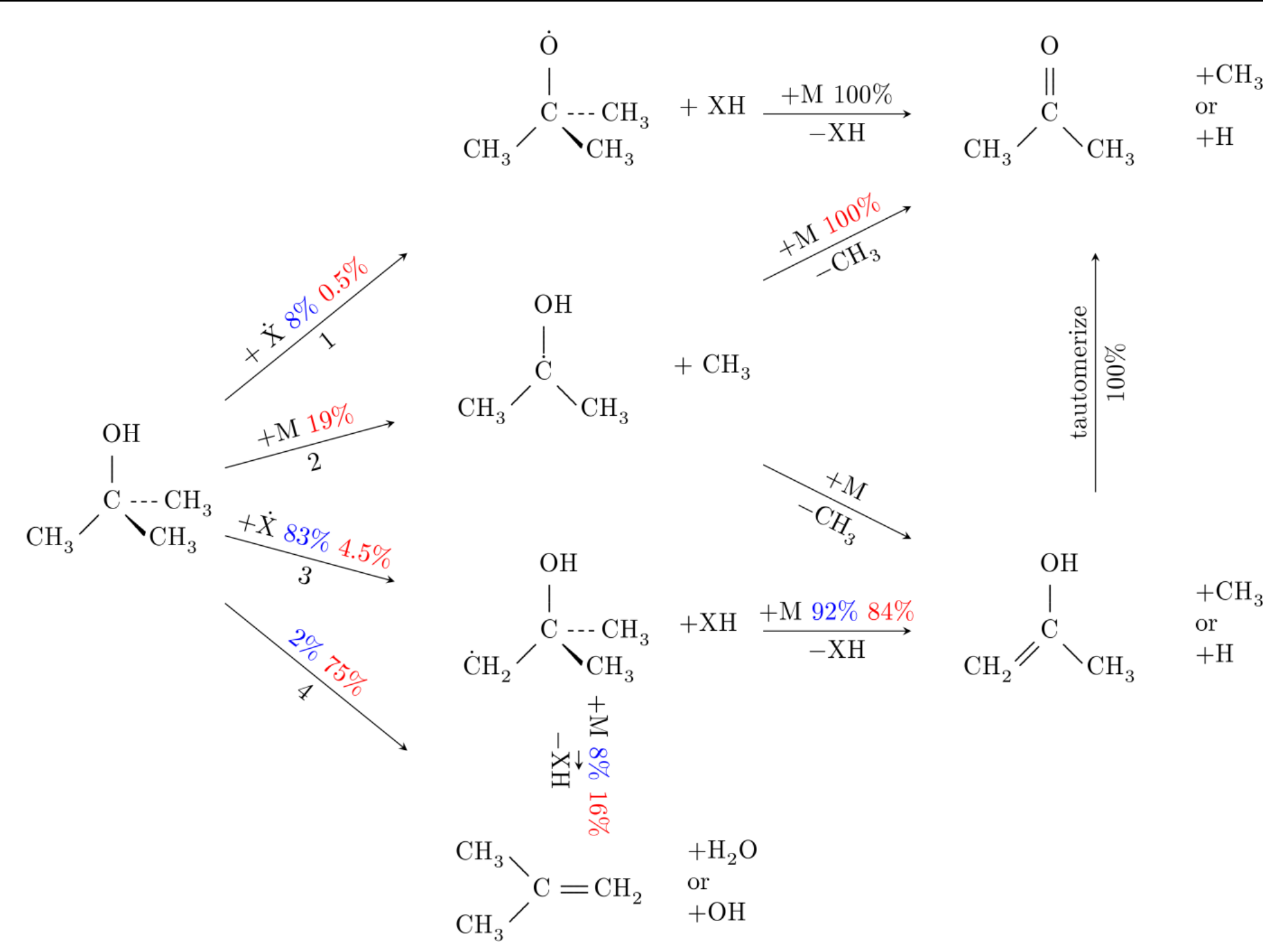


Figure 3. Flux analysis for *t*-butanol using the Grana et al. model [3]. Blue numbers indicate flow reactor simulations at 775 K, 12.5 atm, and  $\phi = 1.0$ ; red numbers indicate diffusion flame simulations at  $X_f = 0.3$ ,  $a = 100\text{s}^{-1}$ .

- The symmetry of *t*-butanol allows for only two stable intermediate species: acetone and *iso*-butene.
- At low temperatures, *t*-butanol was predicted to decompose primarily via hydrogen abstraction/alkyl beta-scission reactions to mostly acetone and methyl radicals.
- At high temperatures, the primary decomposition route shifted drastically to the dehydration reaction to form *iso*-butene and water.

## Experiment: Variable-Pressure Flow Reactor

- Experimental approach:
- Species distributions as a function of initial conditions at a constant residence time.
  - Near-adiabatic or isothermal (high dilution) operation.

- Conditions run for this study
- $P = 12.5$  atm
  - $500\text{ K} < T < 1000$  K
  - $\tau_{\text{res}} = 1.8$  s

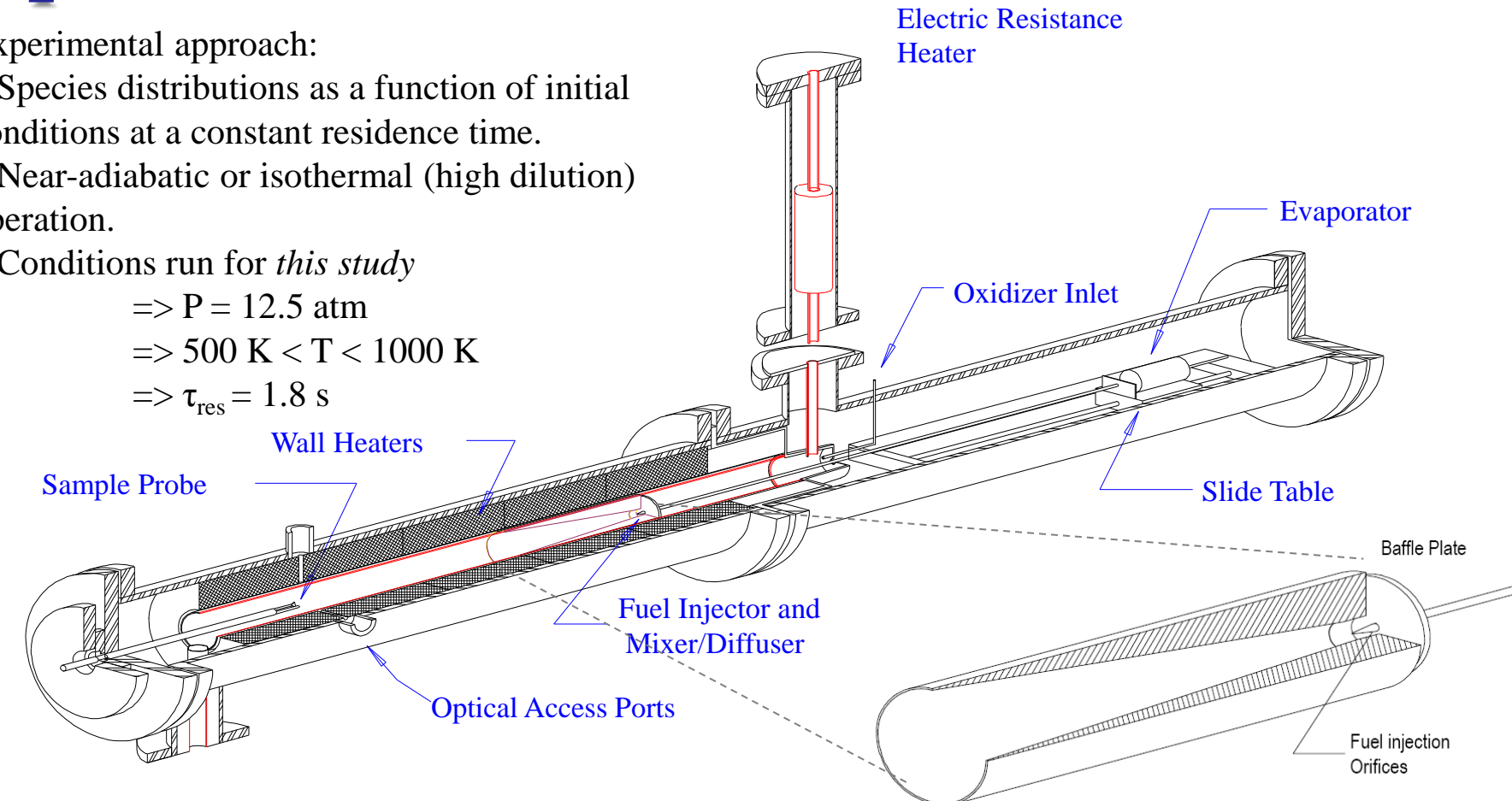


Figure 4. Princeton Variable-Pressure Flow Reactor (VPFR)

Reactor Duct Material: Fused Silica  
Pressure: 0.2 - 20 atm  
Temperature: 500- 1200 K  
Reactor Section Dia.: 10 cm  
Mass Flow rate: 10 - 30 grams/sec  
Residence Time: 0.015 - 5 sec

## VPFR Results

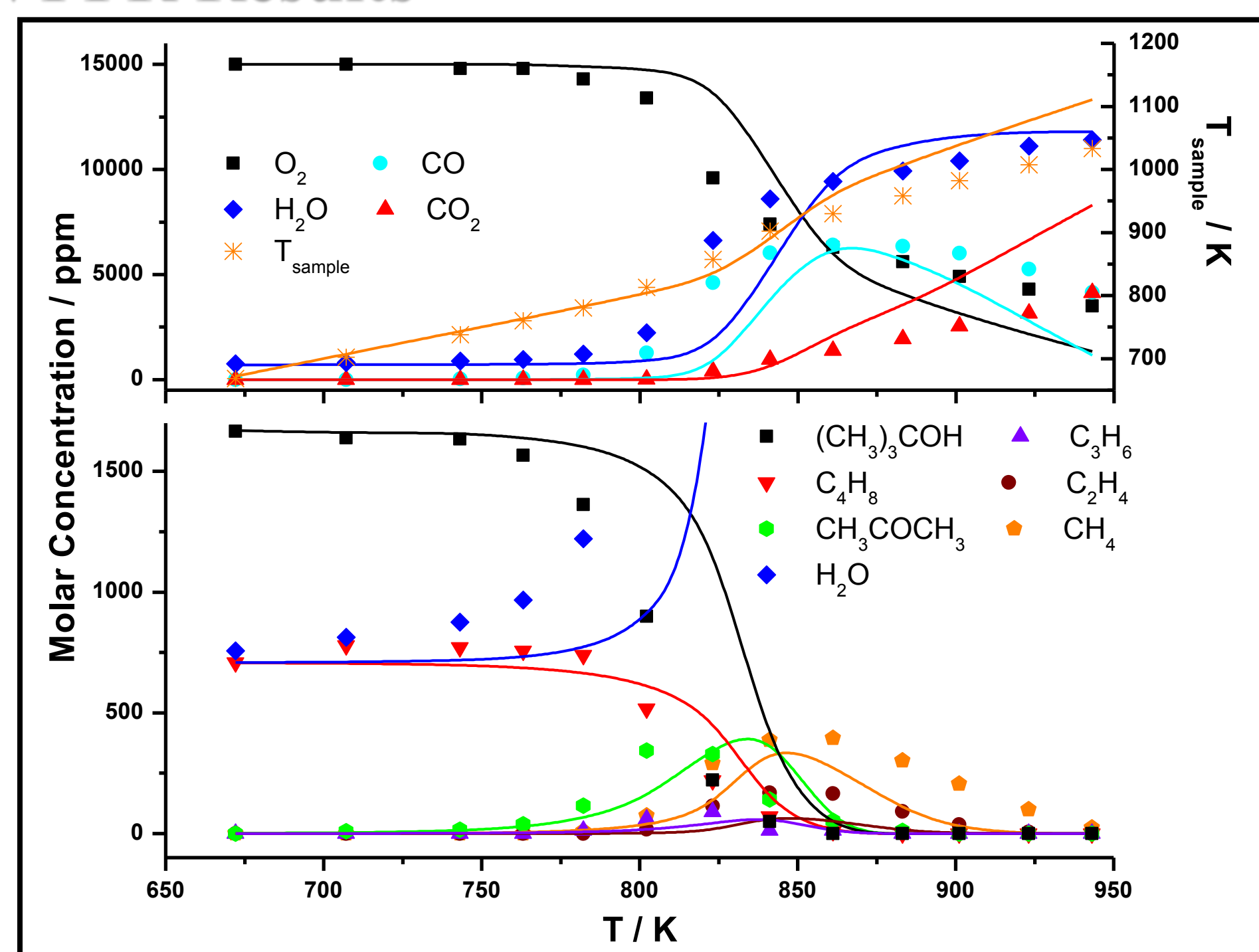


Figure 5. Flow reactor oxidation of *t*-butanol/ $\text{O}_2/\text{N}_2$  2500/15000/982500 ppm at 12.5 atm and a residence time of 1.8 seconds. Experimental data are symbols and lines are Grana et al. [3] kinetic model computations.

- Onset of gas phase chemistry at approximately 775 K.
- Acetone and methane are found to be the most abundant intermediate species, indicates that hydrogen abstraction/alkyl radical beta-scission reactions dominate *t*-butanol decomposition at low temperatures.
- Model predicts experiments well in terms of overall species concentrations. However, it is too fast between 800-900 K.

## Experiment: Counterflow Diffusion Flame

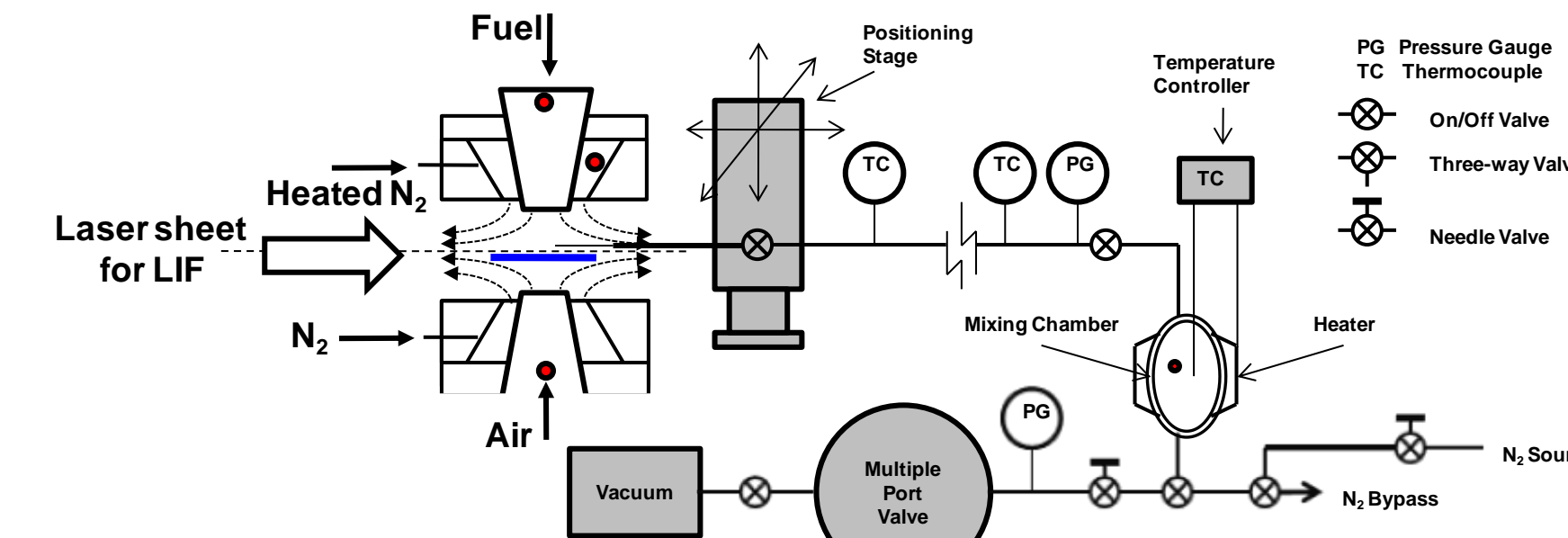
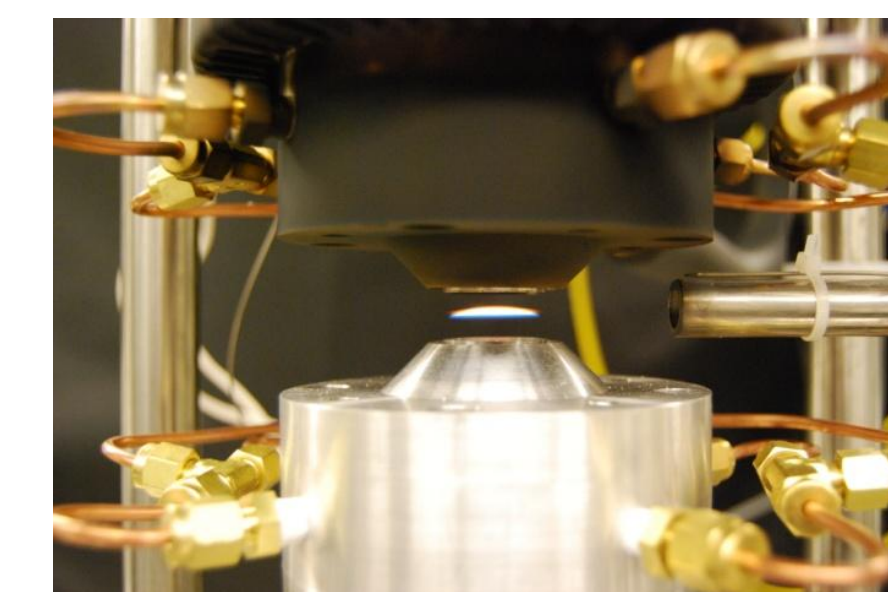


Figure 5. Schematic of counterflow burner at Princeton University

Experimental approach:

- Measure chemical species within flames
  - Provide detailed mechanistic information on flame oxidation.
- Measure extinction strain rate
  - Fuel reactivity.
  - Diffusive-kinetic coupling.
- Conditions run for this study
  - $P = 1$  atm
  - $T_{\text{fuel}} = 400$  K,  $T_{\text{oxi}} = 300$  K
  - $100 < a < 500$   $\text{s}^{-1}$



## Counterflow Results: Speciation

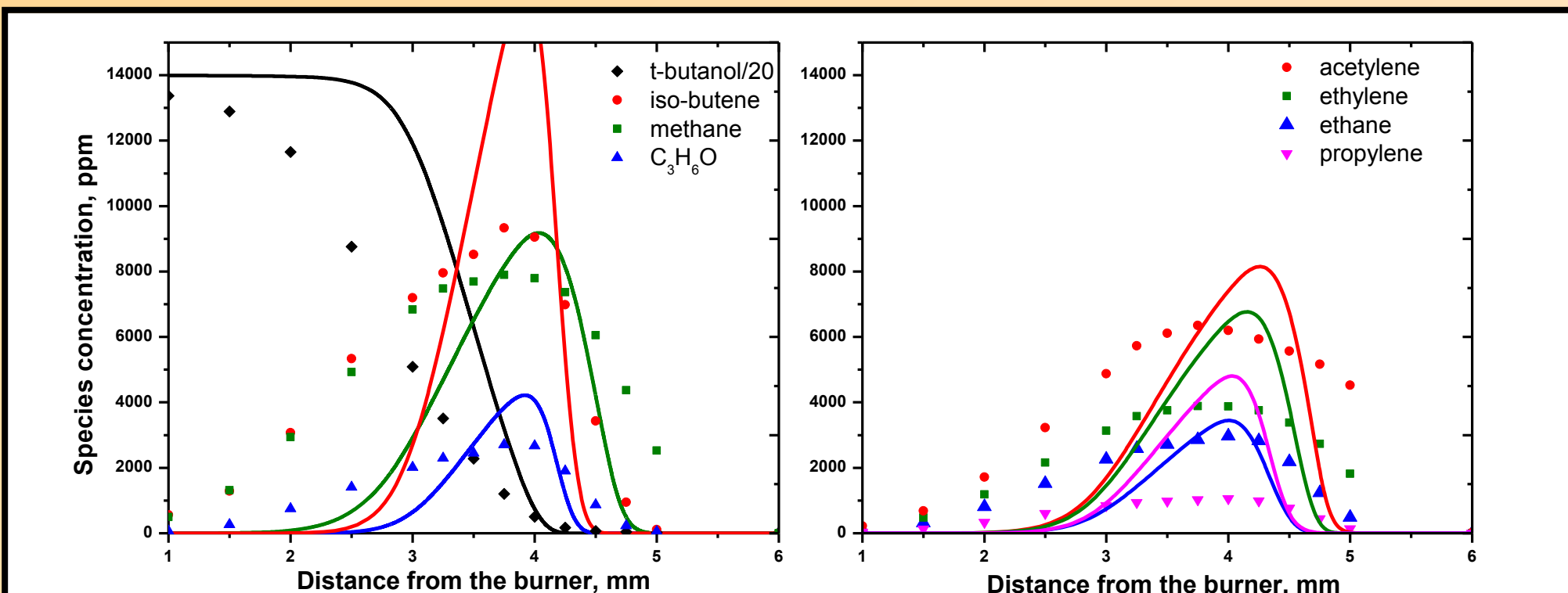


Figure 6. Speciation profile of the *t*-butanol diffusion flame,  $X_f = 0.28$ ,  $a = 100\text{s}^{-1}$ , compared with the Grana et al. model [3].

- *iso*-Butene is found to be the most abundant intermediate species, indicates that dehydration reactions dominate *t*-butanol decomposition at high temperatures.
- Model predicts experiments well in terms of overall species peak locations. However, *iso*-butene is over-predicted and all profiles are narrower than the measurements.

## Counterflow Results: Extinction

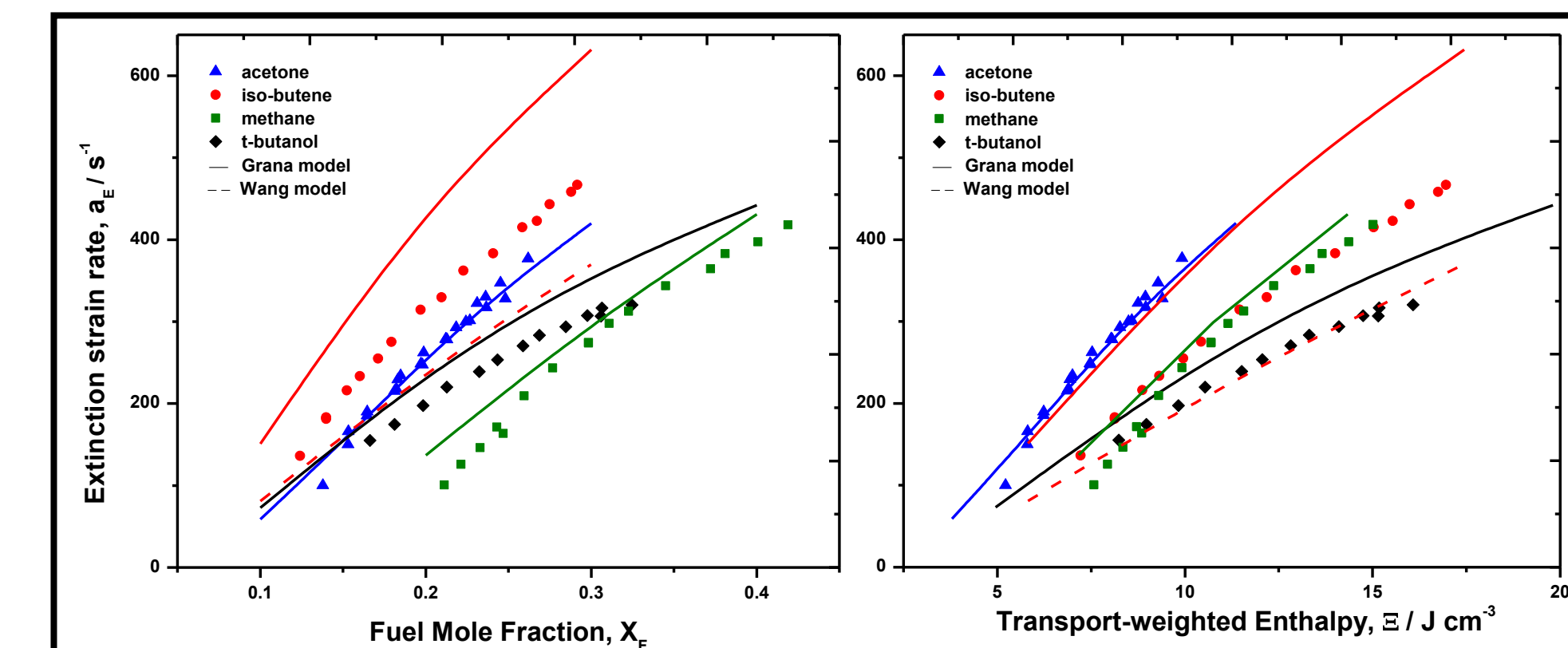


Figure 7. Extinction strain rate measurements of *t*-butanol, *iso*-butene, acetone, and methane compared with the Grana et al. model [3].

- *t*-butanol is found to be less reactive than its primary intermediates, *iso*-butene and acetone.
- Reasons are the large production of water early in the decomposition process, the endothermicity of all the initial decomposition reactions, and the large concentration of methyl radicals (which react slower than other radicals).
- Model predicts acetone and methane well, but over-predicts *t*-butanol and *iso*-butene. *t*-Butanol over-prediction is likely due to problems with the *iso*-butene sub-mechanism.

## References

- [1] J. T. Moss, A. M. Berkowitz, M. A. Oehlschlaeger, J. Biet, V. [4] J. Lefkowitz, J. Heyne, S.H. Won, S. Dooley, H.H. Kim, Warth, P. Glaude, and F. Battin-Leclerc, *J. Phys. Chem. A* 112 (2008) 10843-10855.
- [2] F. M. Haas, M. Chaos, and F. L. Dryer, *Combustion and* [5] J.K. Lefkowitz, J.S. Heyne, S.H. Won, S. Dooley, H.H. Kim, *Flame 156* (2009) 2346-2350.
- [3] R. Grana, A. Frassoldati, T. Faravelli, U. Niemann, E. Ranzi, R. Seiser, R. Cattolica, and K. Seshadri, *Combustion and* [6] J.S. Heyne, J.K. Lefkowitz, S. Dooley, S.H. Won, H.H. Kim, F.M. Haas, S. Jahangirian, Y. Ju, F.L. Dryer, 7<sup>th</sup> US National Technical Meeting of the Combustion Institute (2011).

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