University of Connecticut

Chemical Kinetics Studies of Alternative Fuels

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Accomplishments – Year 1

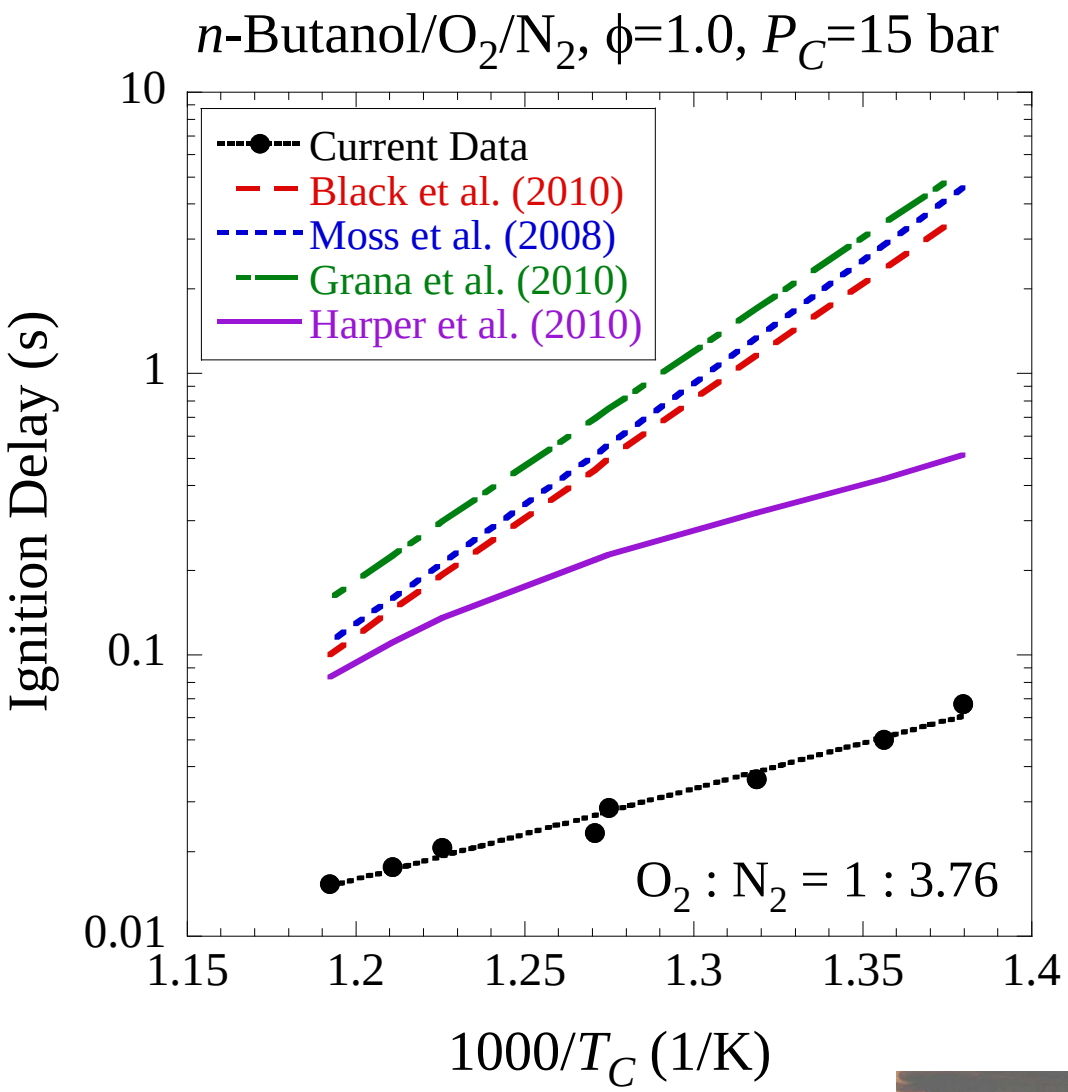
- **Autoignition of *n*-Butanol at Low to Intermediate Temperatures and Elevated Pressures***
  - **P_C = 15 – 30 bar; T_C = 675 – 925 K**
- Autoignition of Methanol: Experiments and Computations
  - P_C = 7 – 30 bar; T_C = 850 – 1100 K
- Nanoparticle-Enhanced Combustion of Liquid Fuels
  - P_C = 15 – 28 bar; T_C = 772 – 825 K
- Laminar Flame Speeds of Moist Syngas Mixtures

**** Bryan Weber, Kamal Kumar, Yu Zhang***

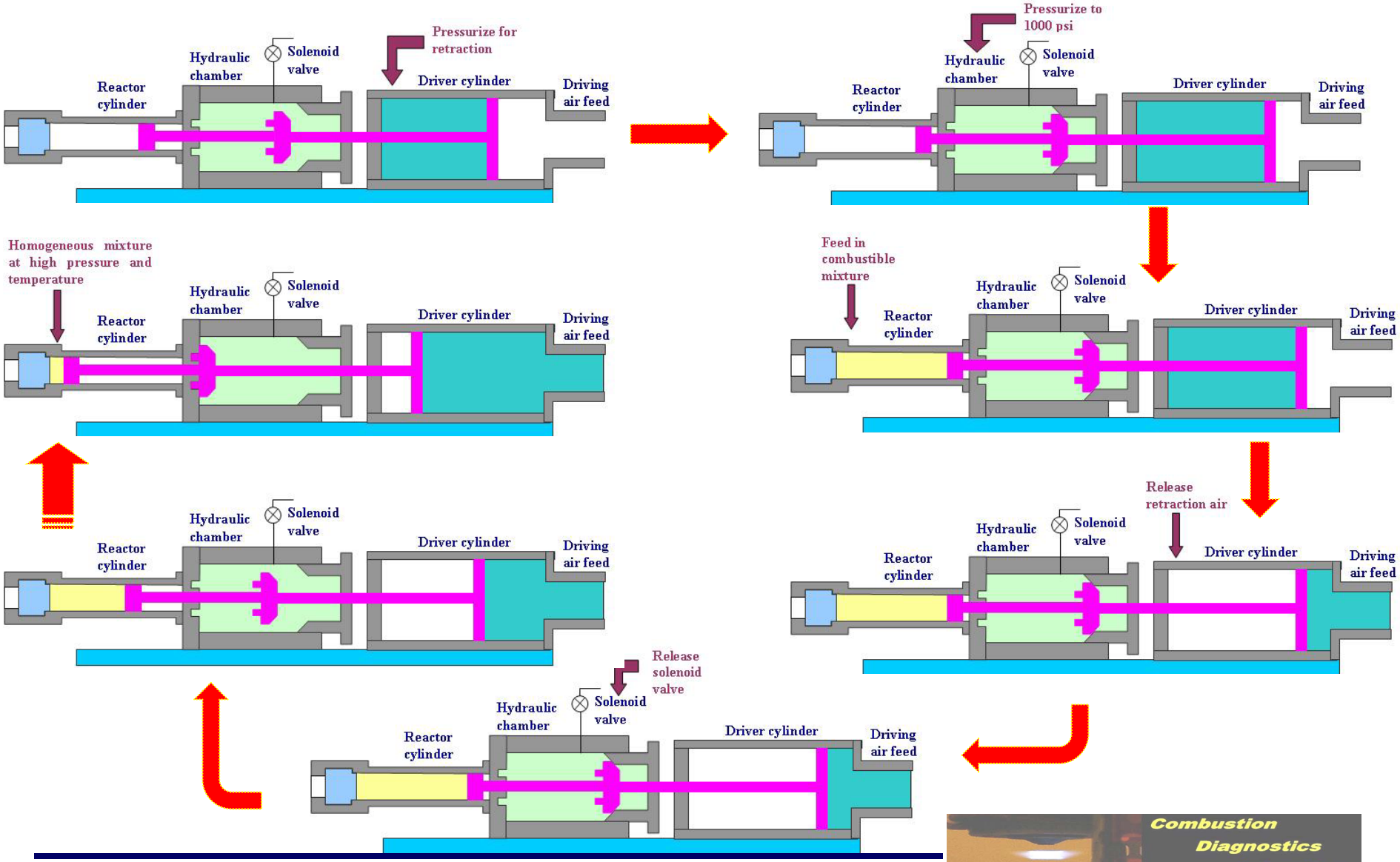
Summary: *n*-Butanol Autoignition

- Simulated ignition delays computed using four reaction mechanisms available in the literature are much longer than experimental ignition delays.
- Although the reaction mechanisms have not been validated in the temperature and pressure range studied here, the degree of difference is still rather surprising.
- Sensitivity analysis at low temperatures shows the impotence of hydrogen abstraction reaction from *n*-butanol by HO_2 to form α-hydroxybutyl radical.
- Reaction path analysis on the mechanism of Black et al. (2010) reveals several pathways which may need to have their rates adjusted and at least two pathways which are missing entirely.
  - Propanal formation and tautomerization of but-1-en-1-ol to butanal.

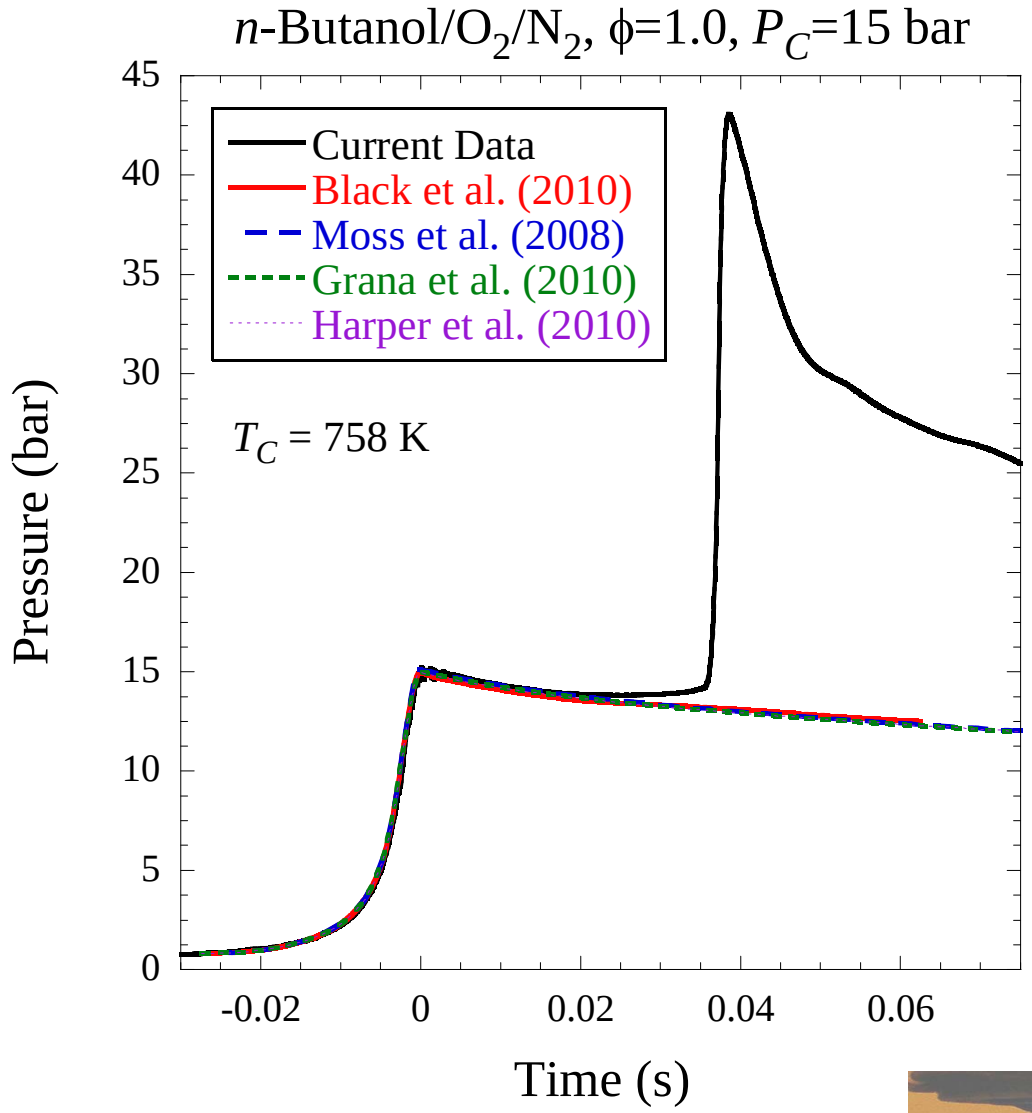
Autoignition of *n*-Butanol: Experiments vs. Simulations



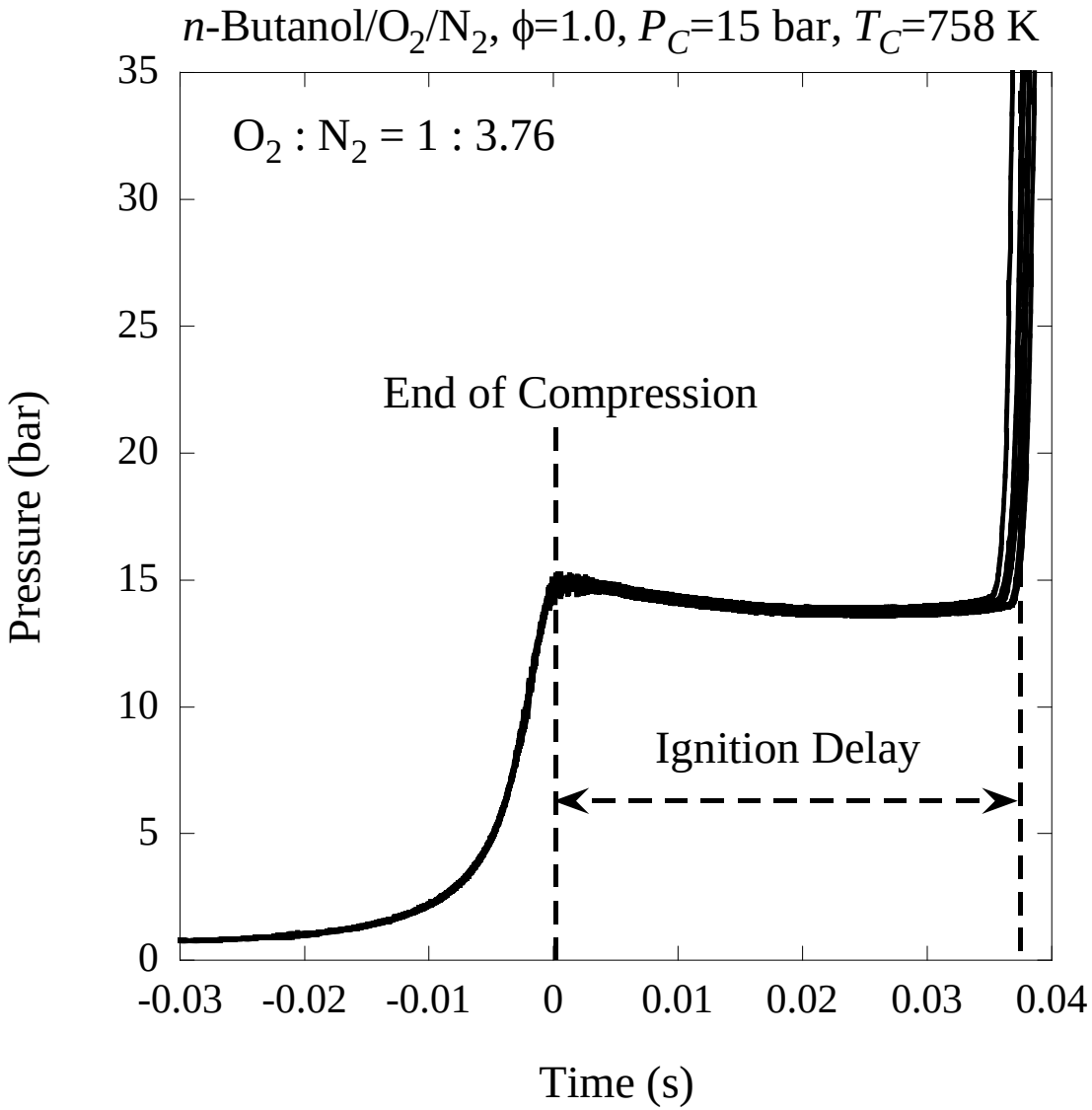
Rapid Compression Machine Operation



Autoignition of *n*-Butanol: RCM Simulations

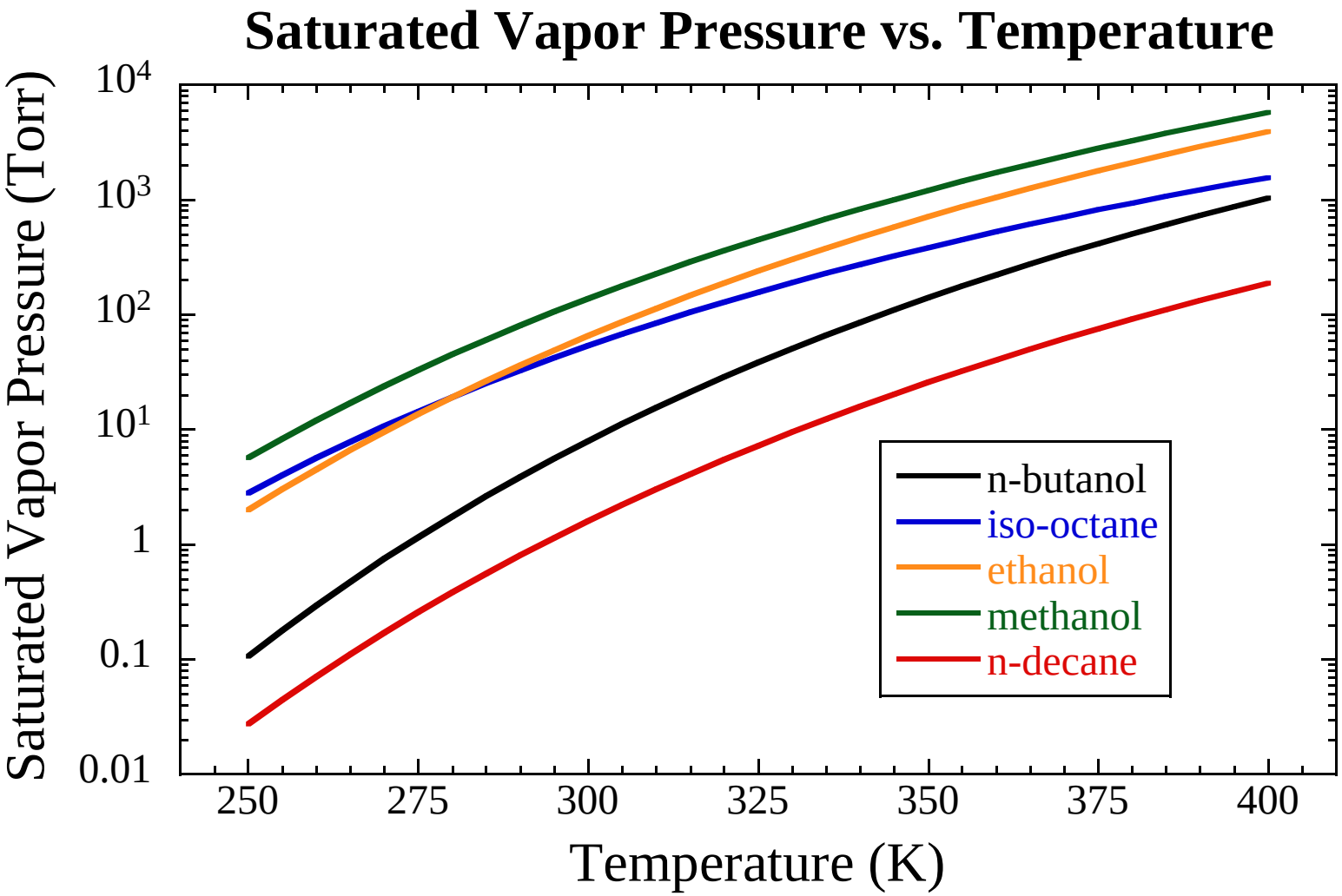


Experimental Reproducibility



- Each compressed pressure and temperature condition is repeated at least 6 times to ensure reproducibility.

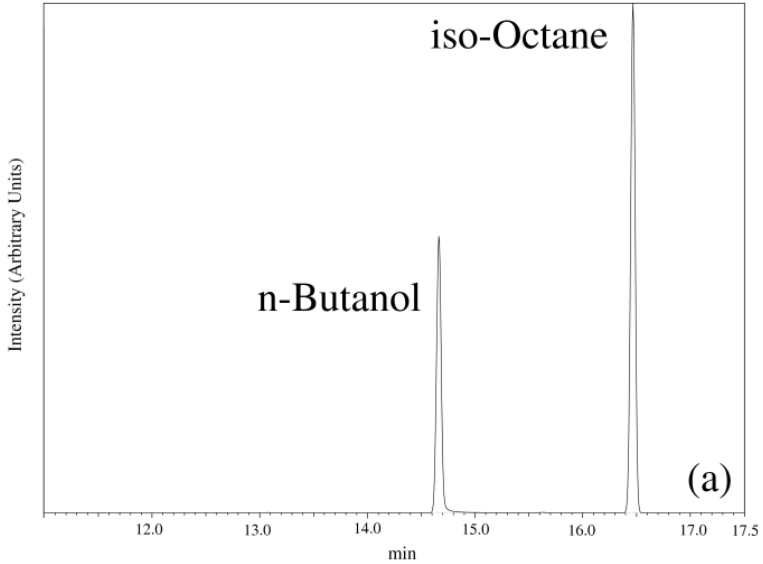
Mixture Preparation (1)



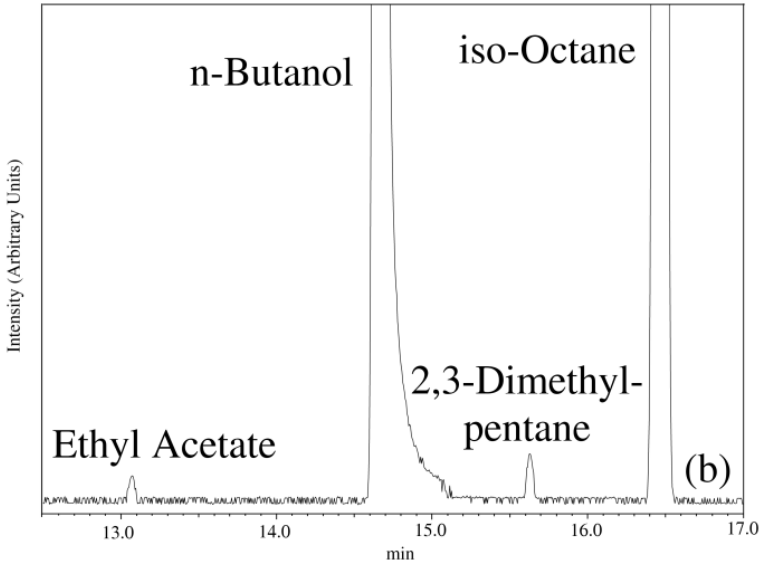
Mixture Preparation (2)

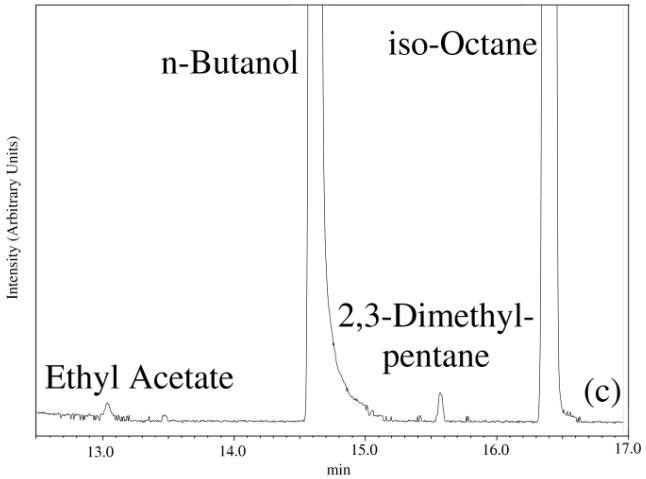
- Homogeneous test mixture prepared in a *stirred*, *heated* stainless steel tank of known volume
  - Gaseous components in the test mixture are determined manometrically
  - Liquid fuel components are added on a gravimetric basis
- Add air/fuel under ambient temperature conditions
- Preheat temperature (below the boiling points of the liquid fuel components)
  - Continuous magnetic stirring
  - Soak time ~ 1.5 hours for complete vaporization of the liquid components

Composition Confirmation

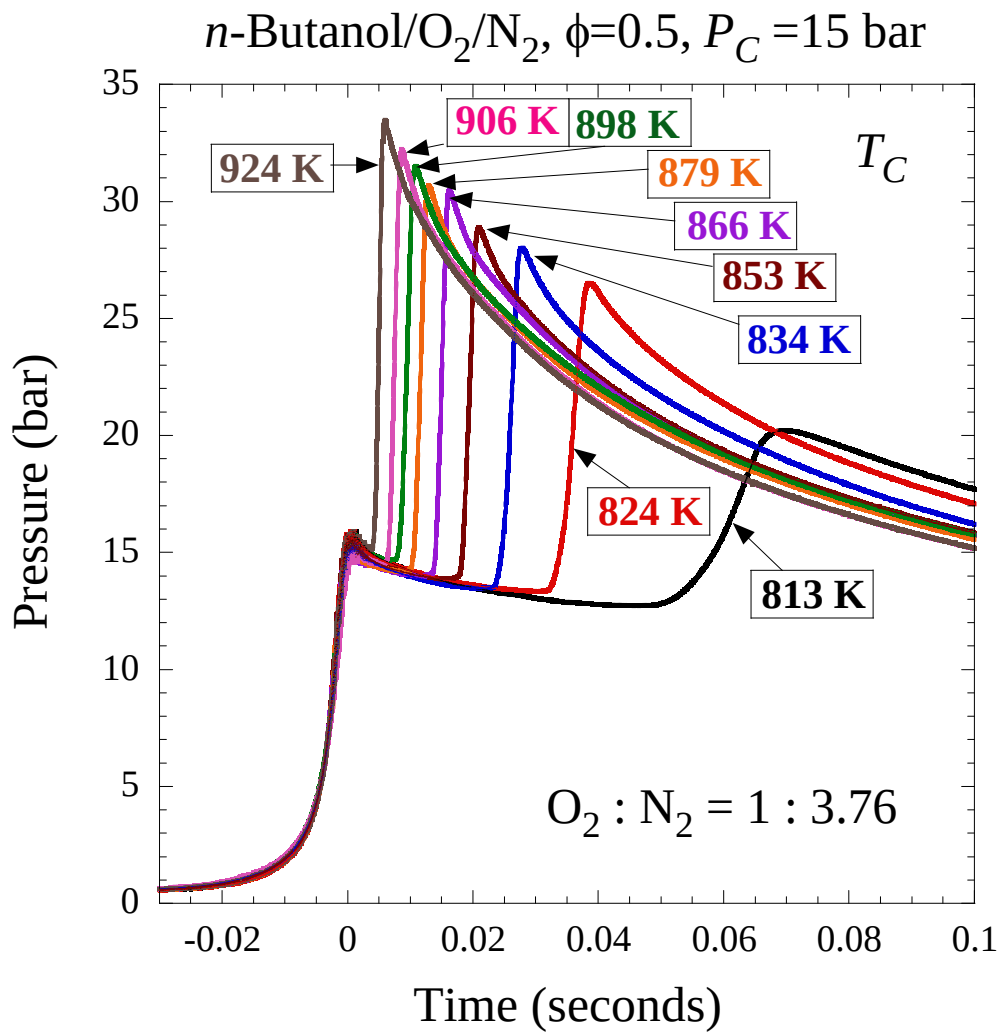


- Liquid calibration standards and gas samples withdrawn from the mixing tank are analyzed using GCMS
- There is no decomposition for initial mixing tank temperature of 87˚C
- *iso*-Octane is used as an internal standard for checking the concentration of *n*-butanol
- Composition checks show actual concentration is within 4% of expected concentration



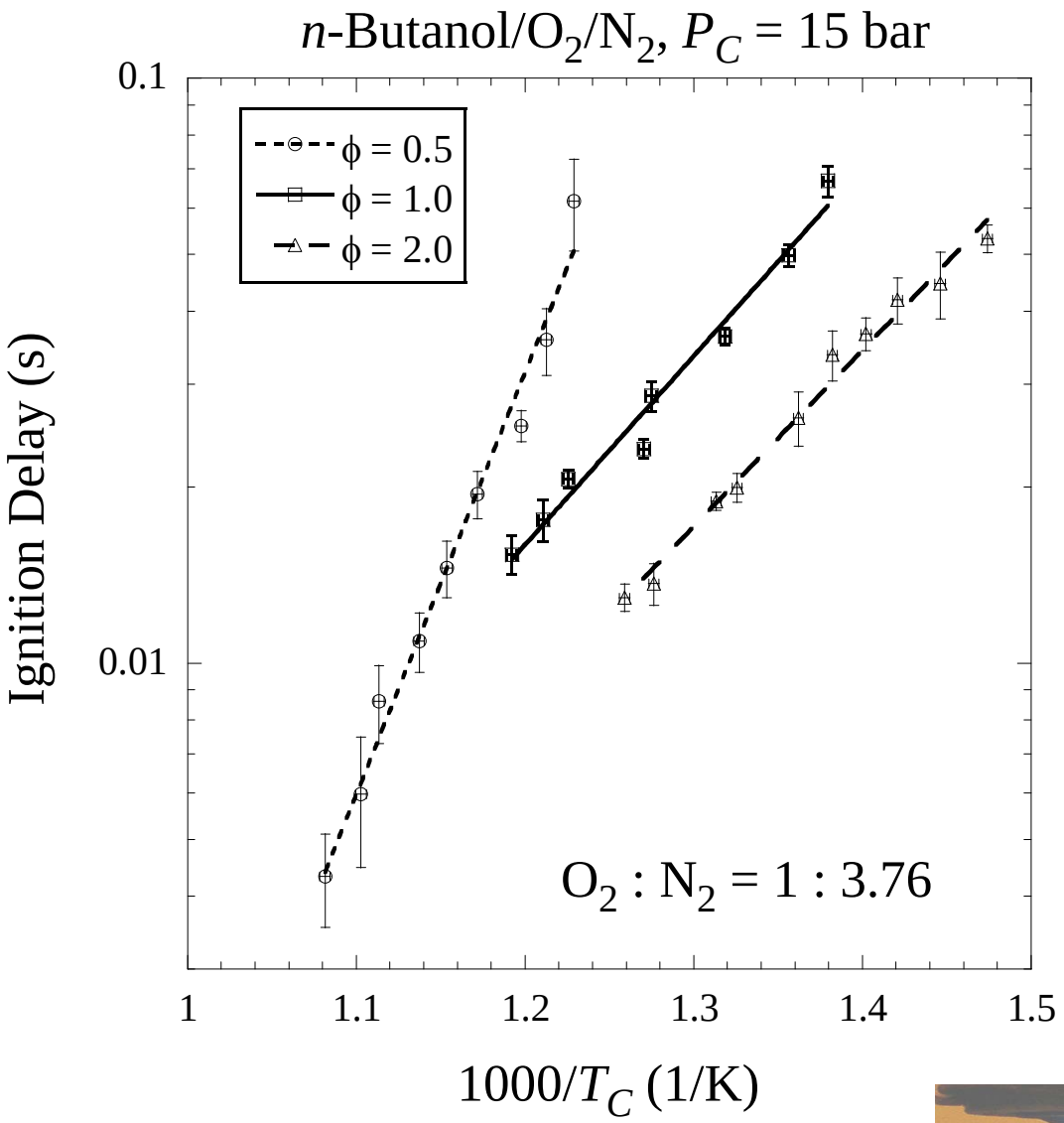


Autoignition of *n*-Butanol (1)

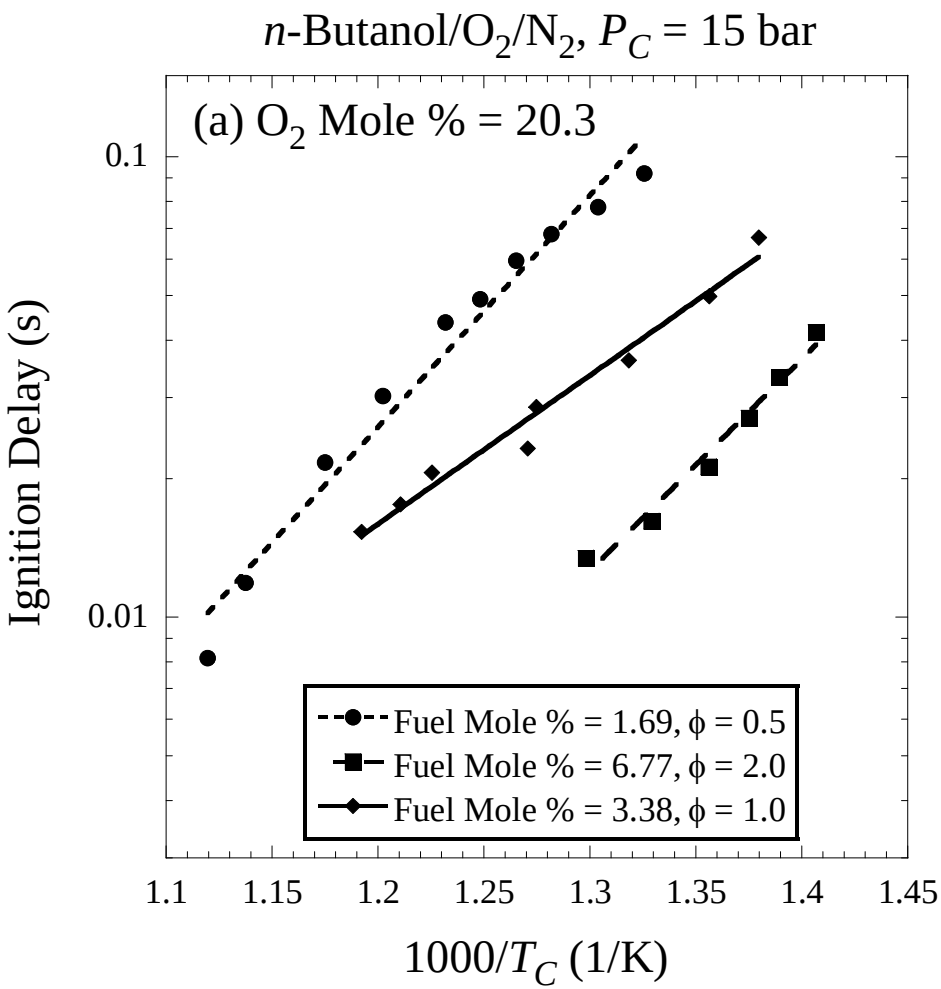


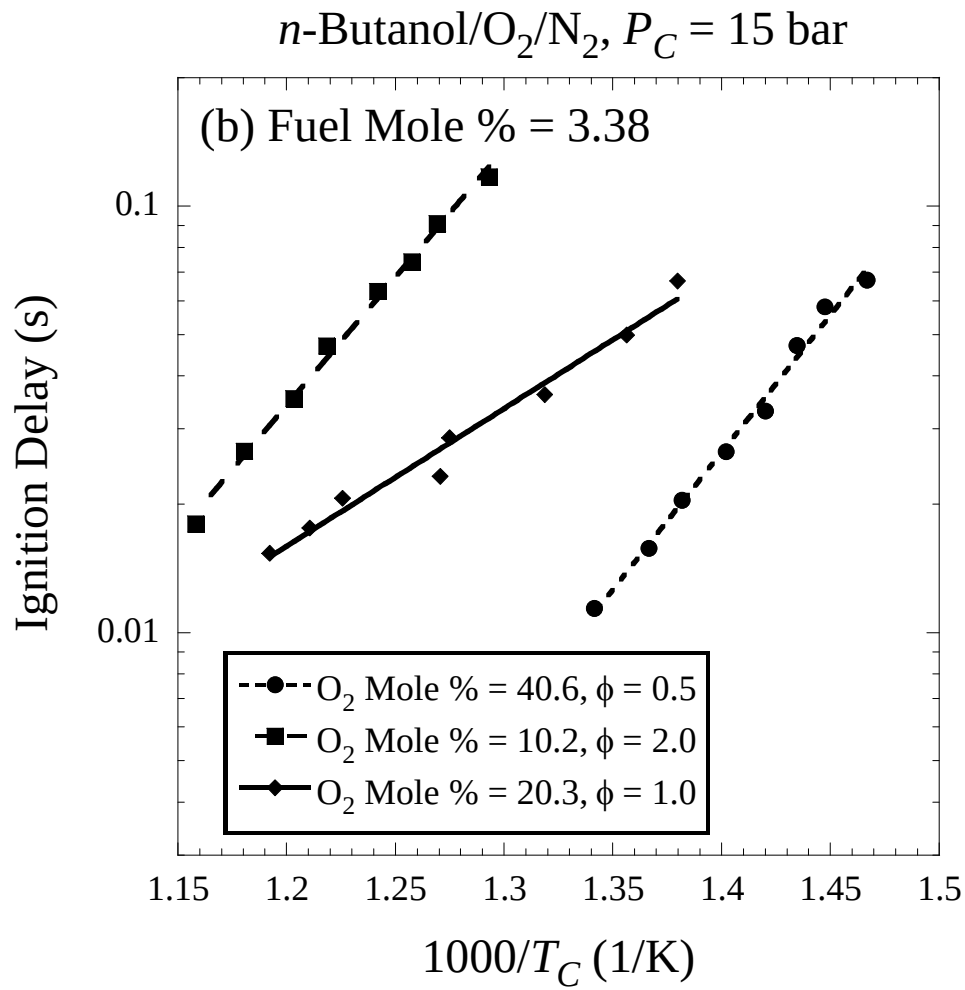
- Increasing compressed temperature reduces ignition delay monotonically.
- No two-stage ignition and no NTC behavior found for the conditions tested.

Autoignition of *n*-Butanol (2)

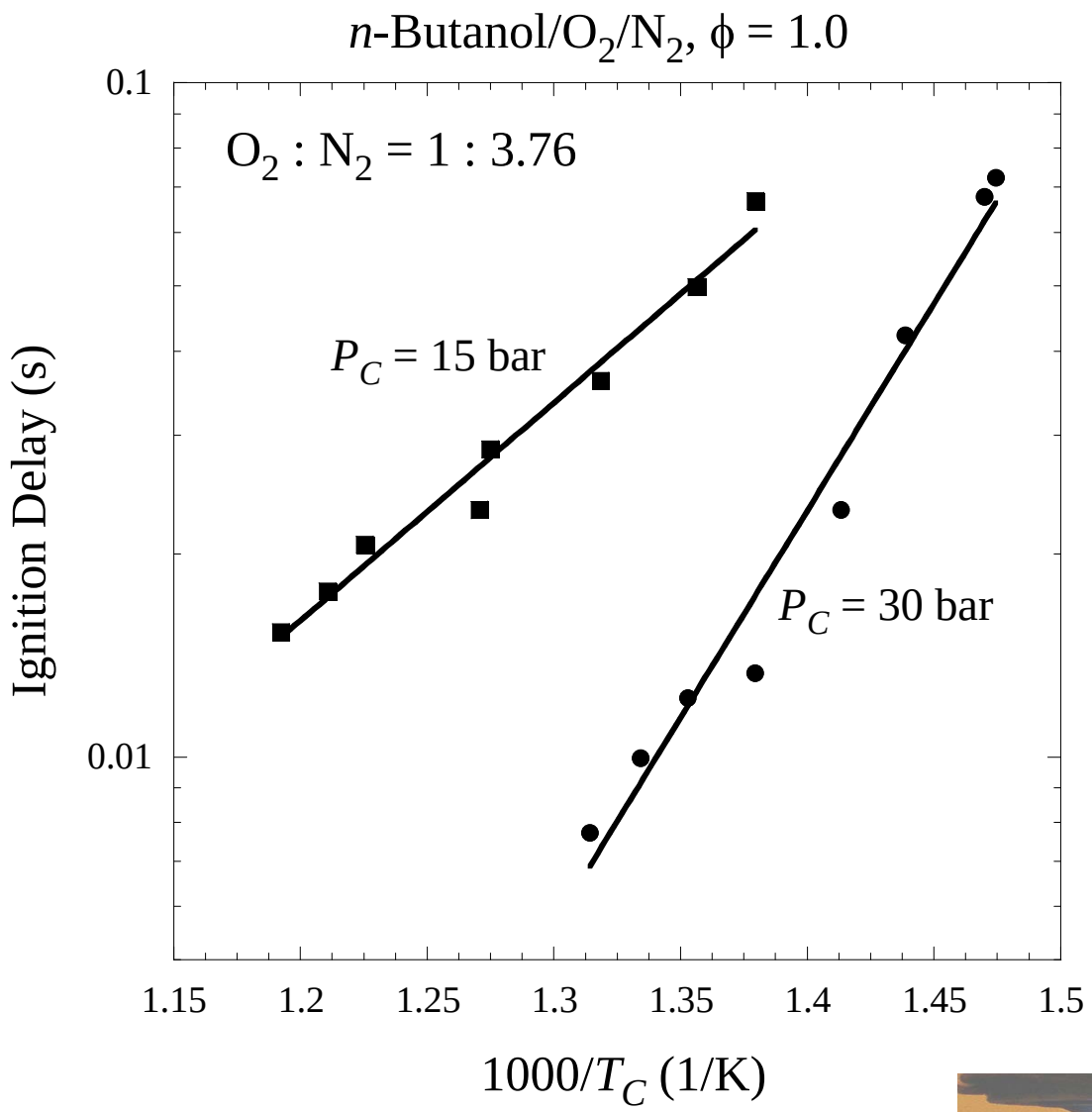


Autoignition of *n*-Butanol (3)

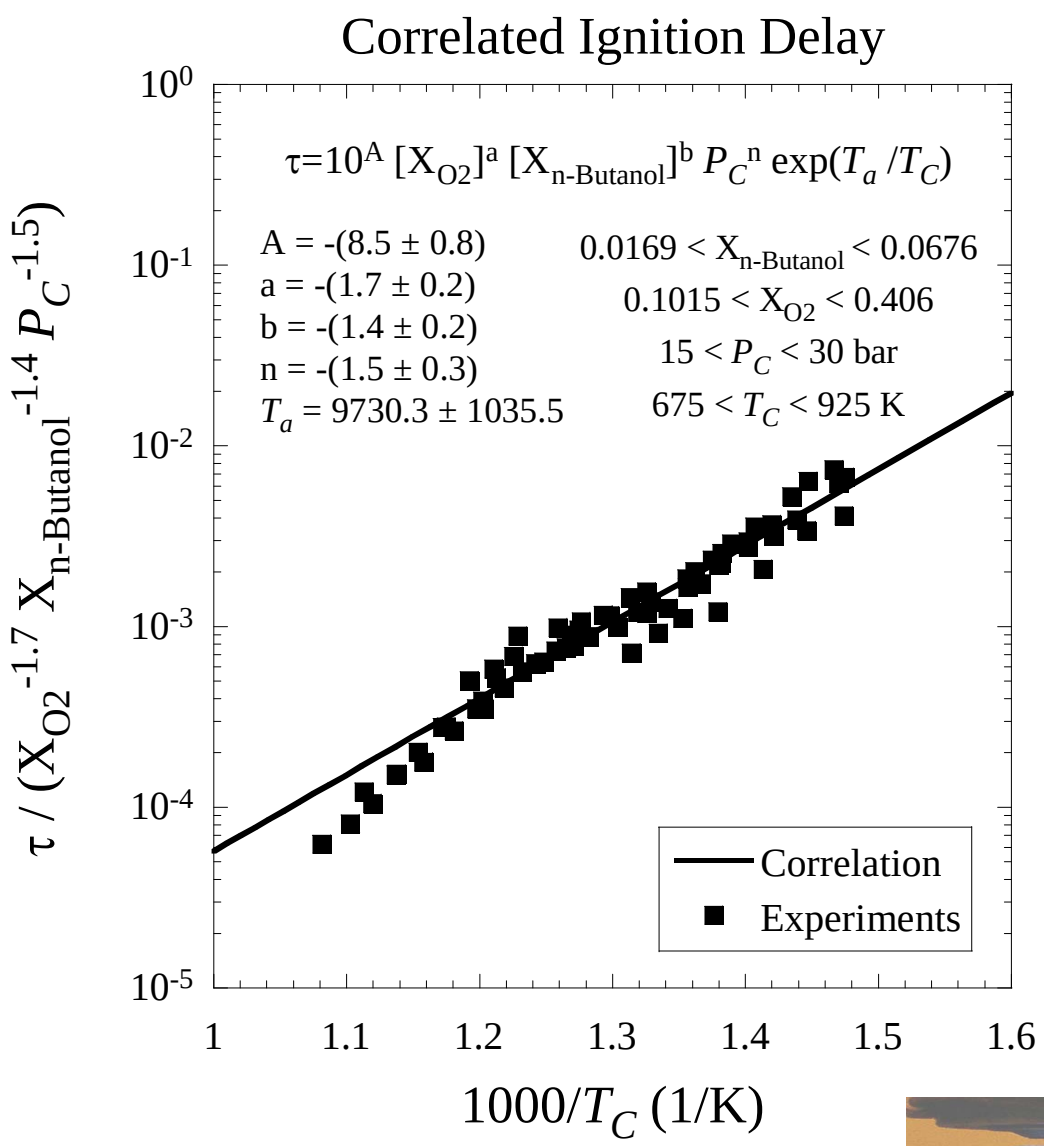




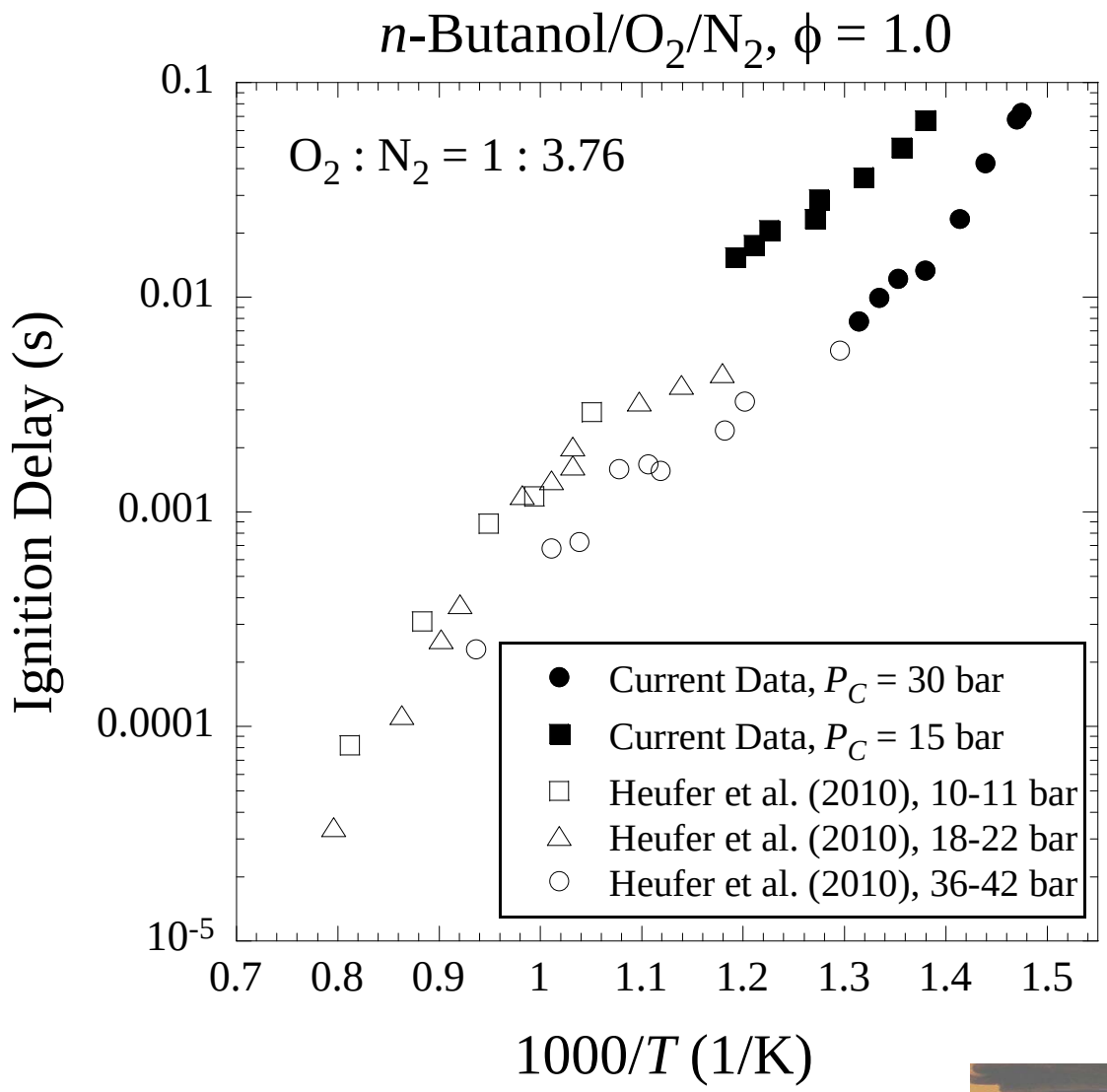
Autoignition of *n*-Butanol (4)



Autoignition of *n*-Butanol (5)



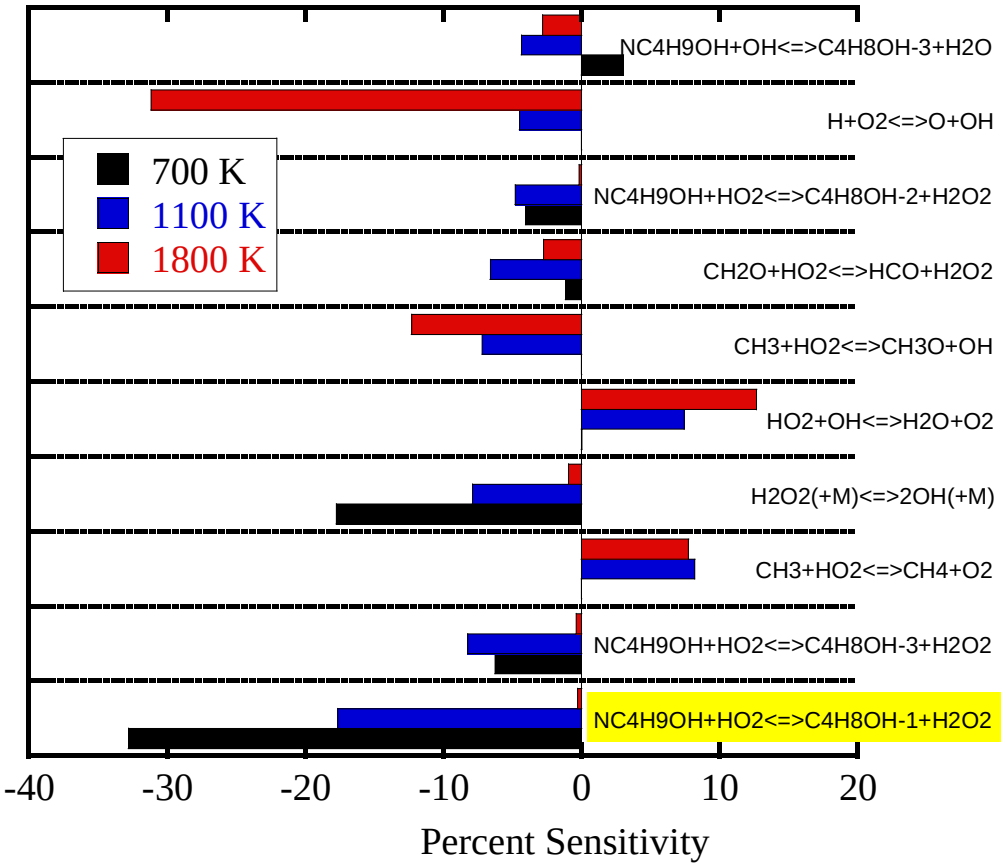
Ignition Delay Comparison



Sensitivity Analysis

$$\% \text{ sensitivity} = \frac{\tau(2k_i) - \tau(k_i)}{\tau(k_i)} \times 100\%$$

n-Butanol/O_2/N_2, ϕ=1.0, P_C =15 atm, O_2 : N_2 = 1 : 3.76



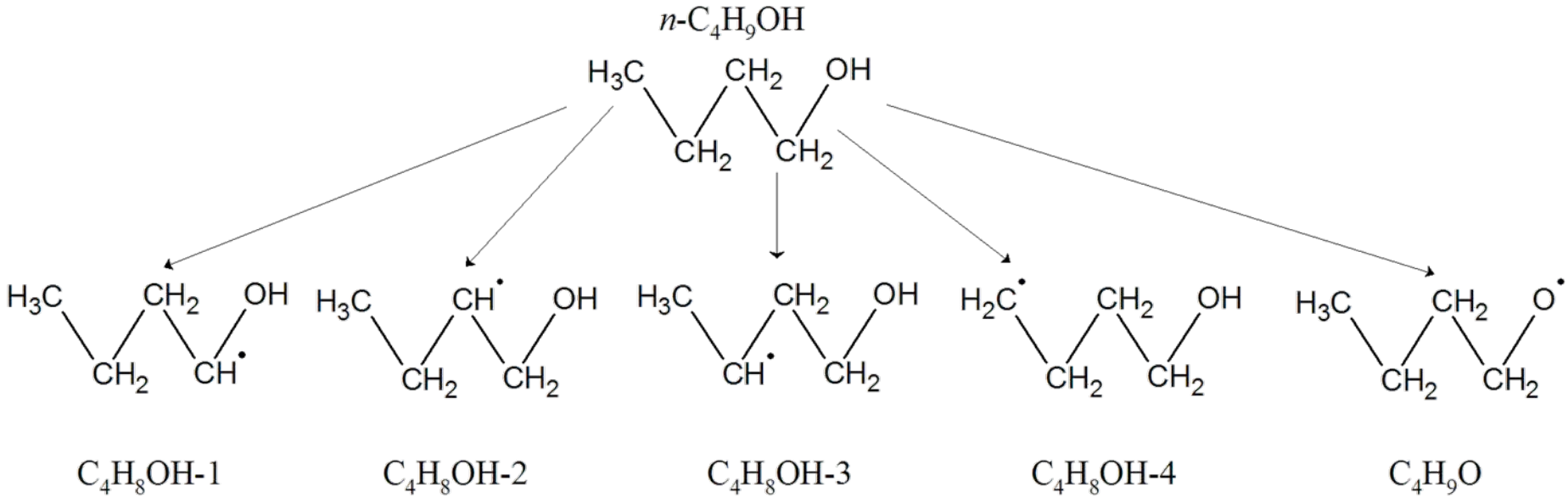
- NUI mechanism is most sensitive to the reaction of *n*-butanol+HO_2 to form α-hydroxybutyl.
- The sensitivity is significantly reduced at higher temperatures.

Reaction Path Analysis (1)

- A Reaction Path Diagram shows the percent of the reactant destroyed to form the product indicated by the arrow.
- The percent destruction represents the cumulative destruction of each reactant up to the point in time where the mole fraction of fuel has been reduced 20% compared to the initial value.

Reaction Path Analysis (2)

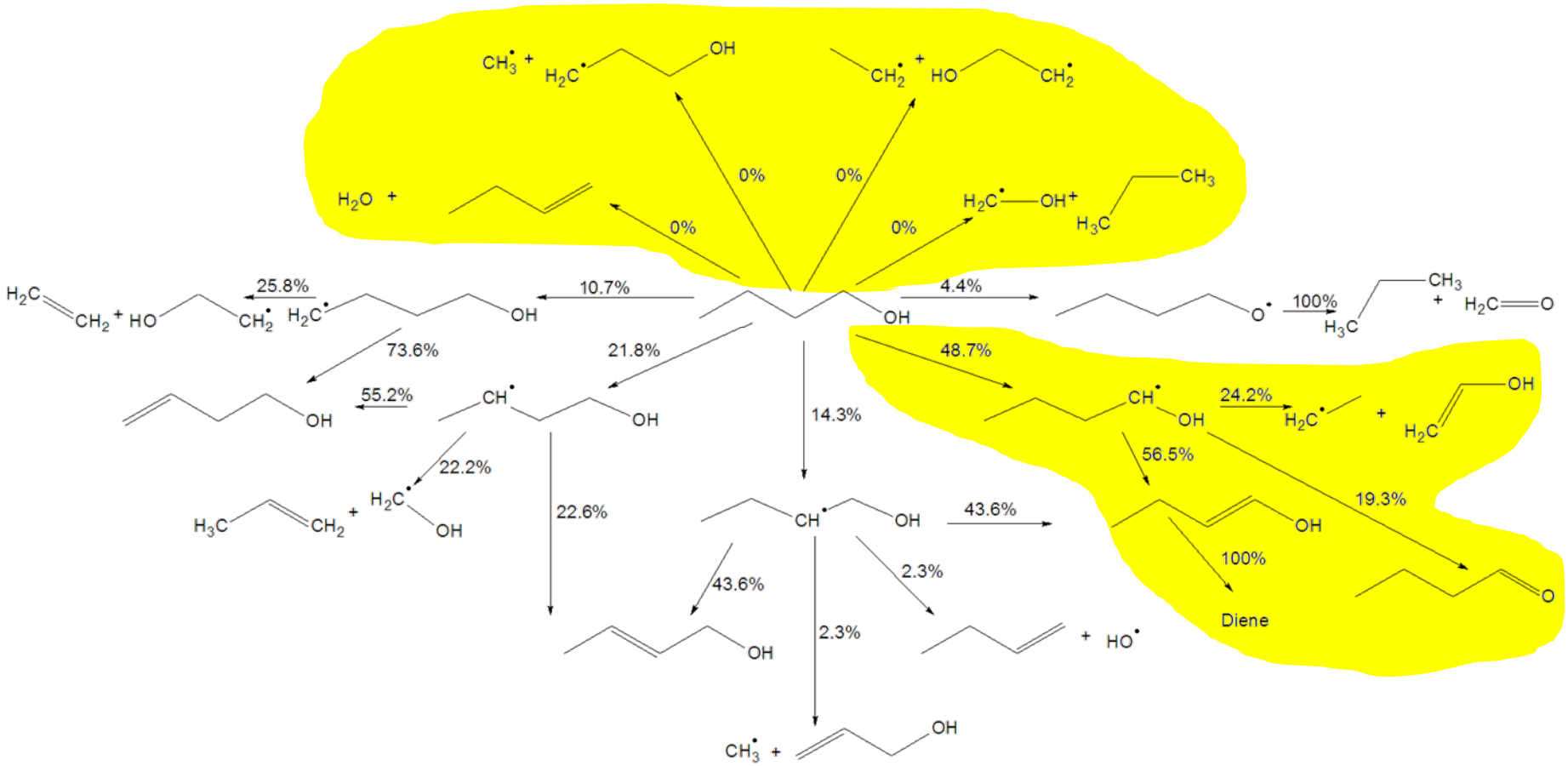
- *n*-Butanol (C_4H_9OH) is destroyed by H-atom abstraction producing 5 radicals.



- These radicals are not equally produced.

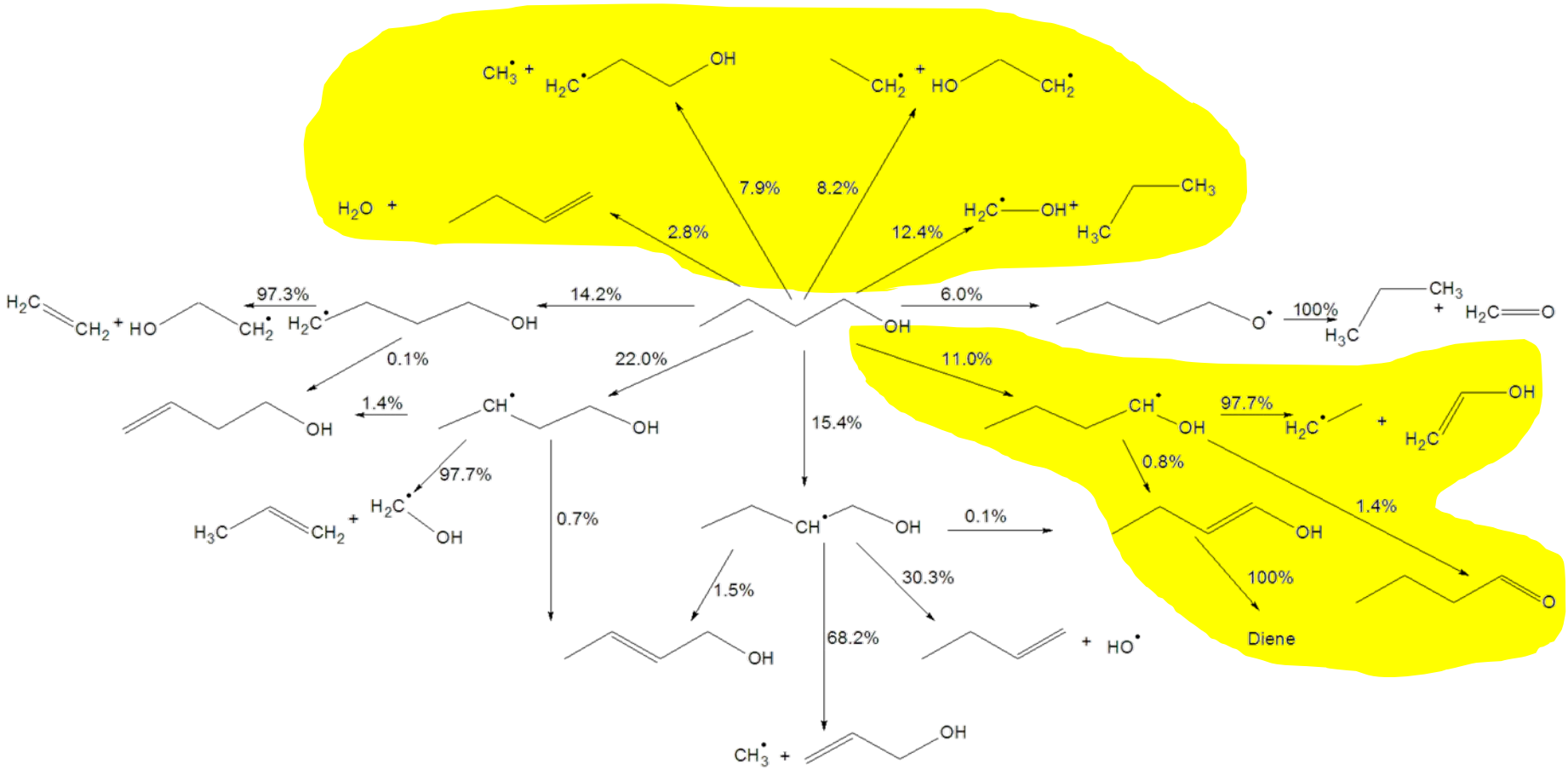
Reaction Path Analysis (3)

800K, 15 atm, ϕ=1.0



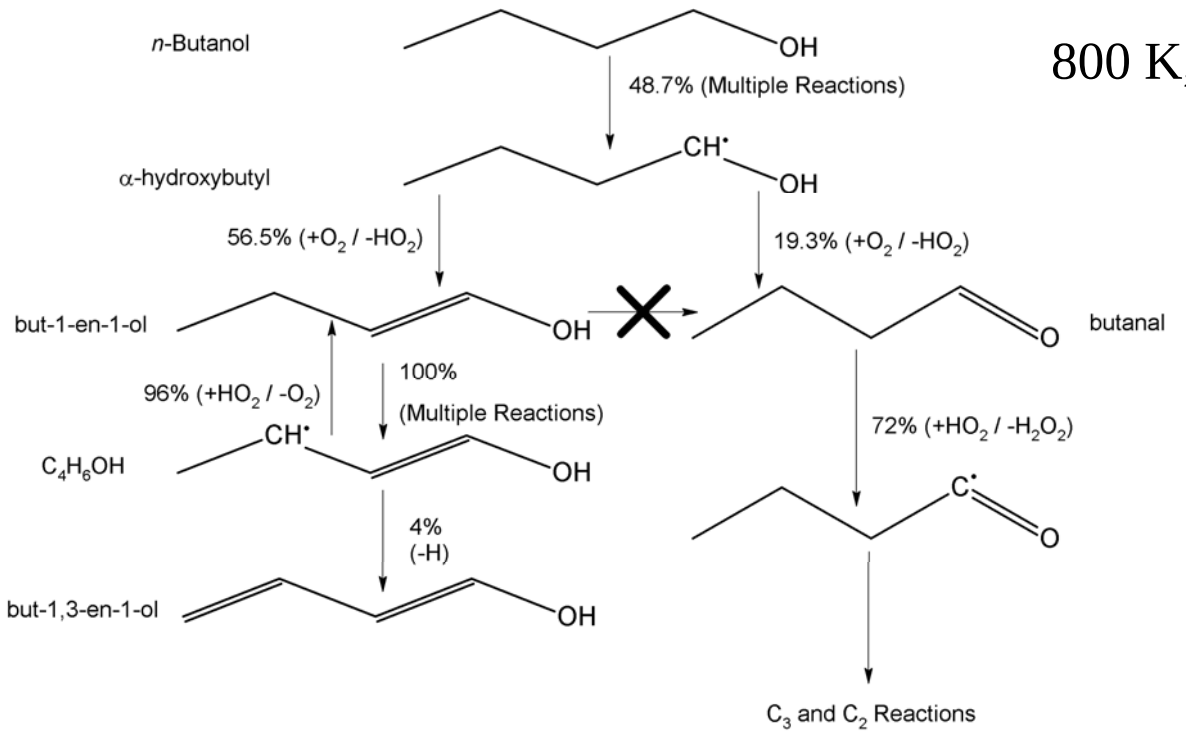
Reaction Path Analysis (4)

1600K, 15 atm, ϕ=1.0



Reaction Path Analysis (5)

800 K, 15 atm, and ϕ=1.0



- Several fuel decomposition pathways have been reported in the literature, but are missing from the mechanism by Black et al. (2010).
- These missing pathways, or other pathways with questionable reaction rates, may be causing the discrepancy between experimental results and simulations.
- Quantum calculations on fuel decomposition reaction rates and speciation measurements during the ignition process are needed.

Future Work

- Autoignition of Butanol Isomers
- Autoignition of other Emerging Biofuels (e.g. *iso*-pentanol, 2-buten-1-ol)
- Autoignition of Gasoline/Bio-Alcohol Blends
- *In situ* Absorption Spectroscopy in Rapid Compression Machine