An Autoignition Study of *iso*-Butanol: Experiments and Modeling

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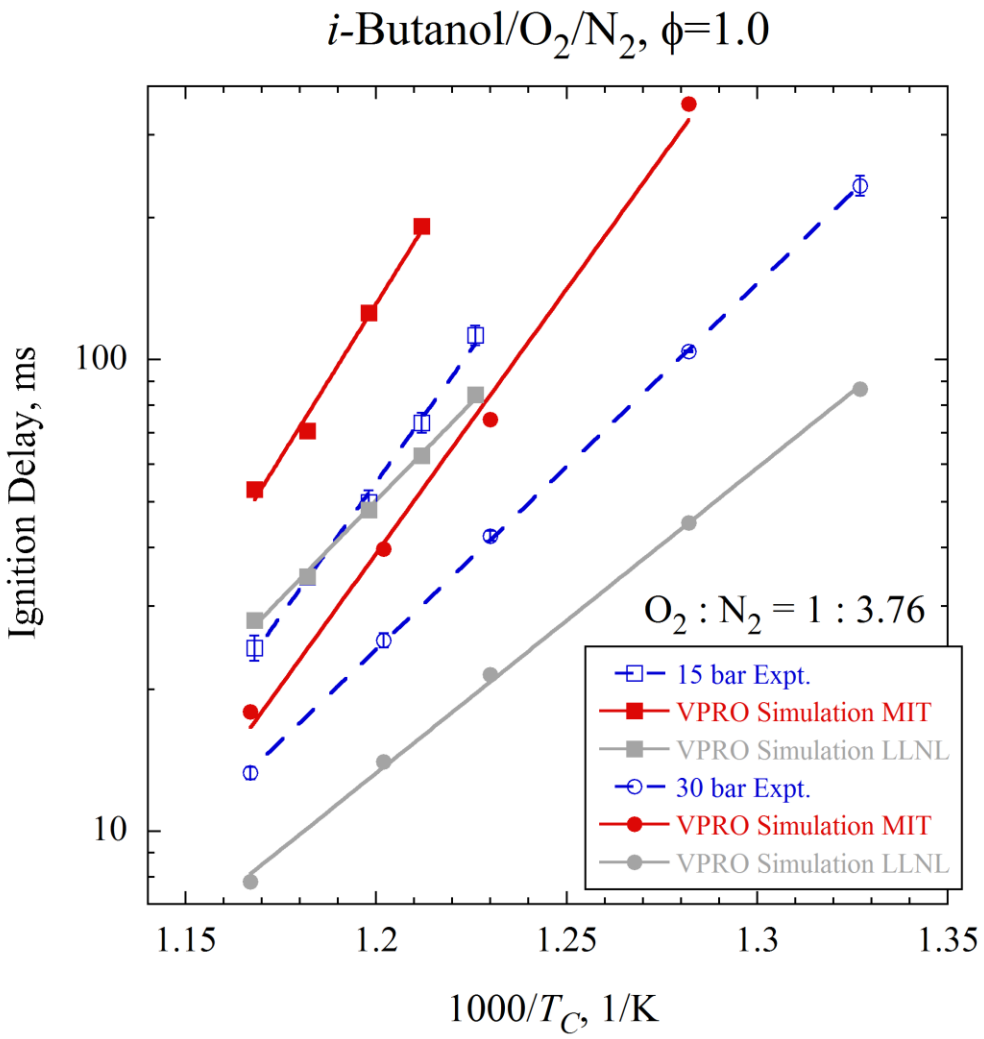
Introduction

- *iso*-Butanol has been suggested as a potent second-generation biofuel
- It has a higher RON and MON than *n*-butanol, while simultaneously being easier to produce biologically
- Several companies have started to commercialize butanol production technologies
- Nevertheless, the combustion properties of *iso*-butanol have not been investigated thoroughly, particularly for off-stoichiometric conditions at high pressure and low temperature

Motivation

- Previous work for stoichiometric ignition delays of *iso*-butanol found diverging predictions of low temperature ignition delays using different models
- Our objectives are to develop a comprehensive, predictive, kinetic model for *iso*-butanol combustion and use the model and new experiments to explore the behavior of the autoignition



Experimental Conditions

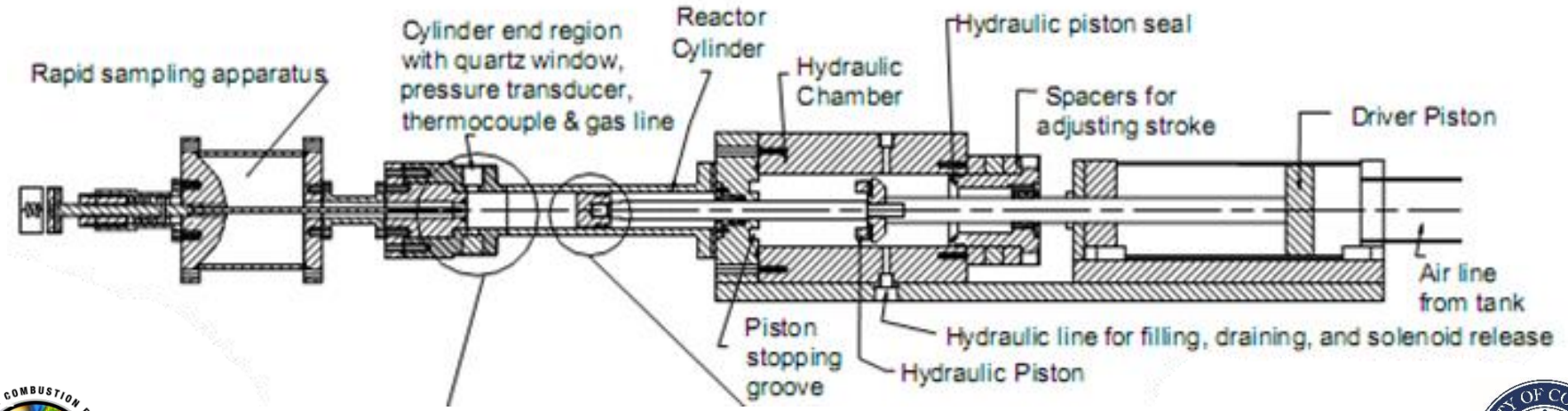
- Most previous work on *iso*-butanol ignition focused on lean to stoichiometric mixtures, and at relatively high temperature and high dilution
- We include high pressure, low-to-intermediate temperature (770-950 K), high fuel loading, and rich conditions

ϕ	P_C (bar)	Fuel Mole Fraction	O_2 Mole Fraction	N_2 Mole Fraction	Oxidizer
1.0	15 & 30	0.0338	0.2030	0.7632	O_2/N_2 Air
0.5	15 & 30	0.0172	0.2065	0.7763	O_2/N_2 Air
0.5	15 & 30	0.0338	0.4060	0.5602	Oxygen Rich
2.0	15 & 30	0.0338	0.1015	0.8647	Oxygen Lean

Weber and Sung, Energy and Fuels, **2013**, *27* (3), pp 1688–1698

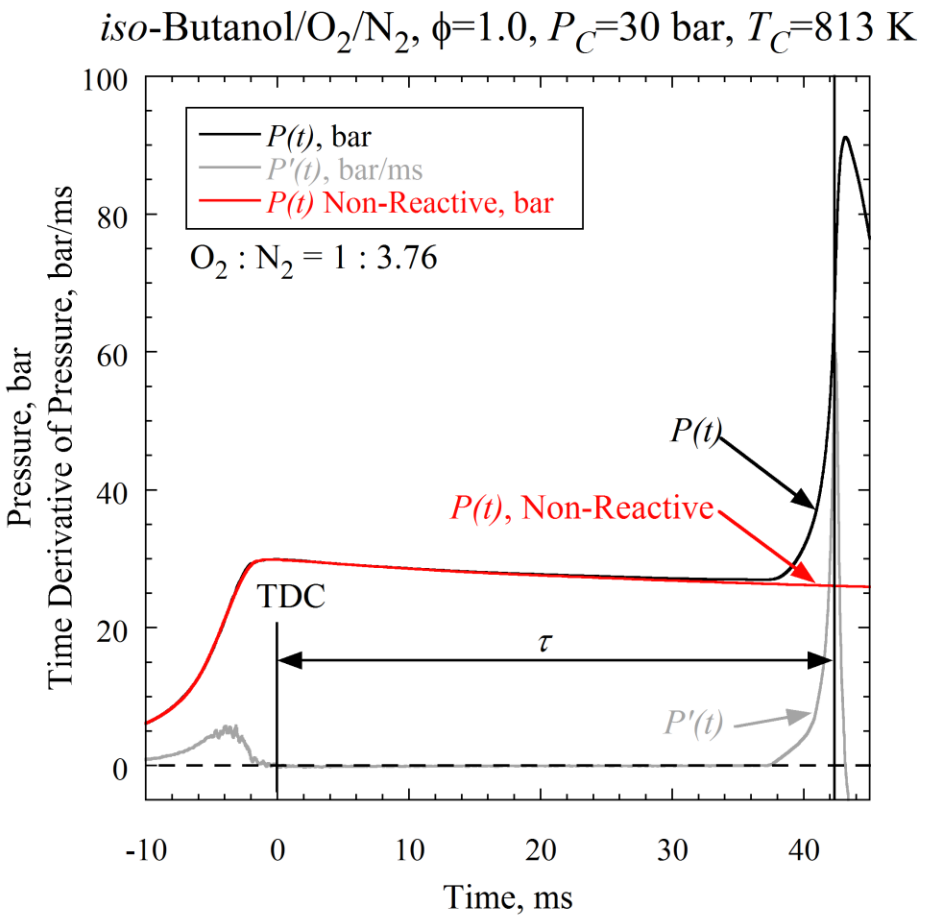
Experimental Methods

- Experiments to measure the ignition delay of *iso*-butanol are performed in a heated Rapid Compression Machine (RCM)
- Homogeneous gas-phase mixtures of fuel and oxidizer are compressed and the piston is held in place at Top Dead Center (TDC), creating a constant volume reactor
- The compression ratio of the RCM, and the initial pressure and initial temperature of the mixture are varied to vary the pressure and temperature at TDC
- The pressure and temperature at TDC are referred to by subscript "C" – i.e. P_C & T_C respectively

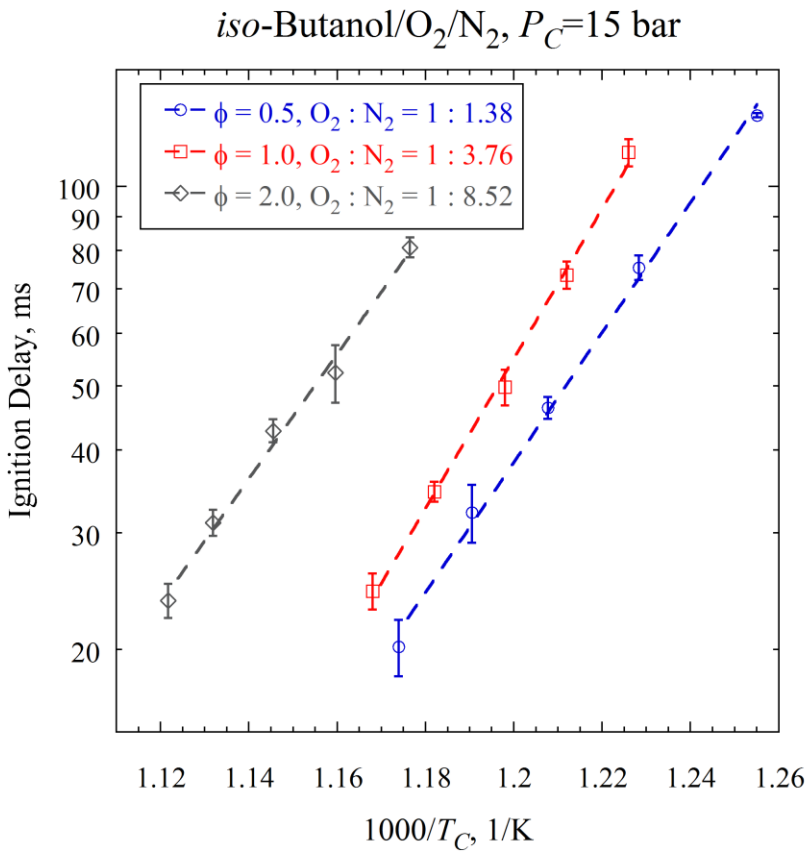


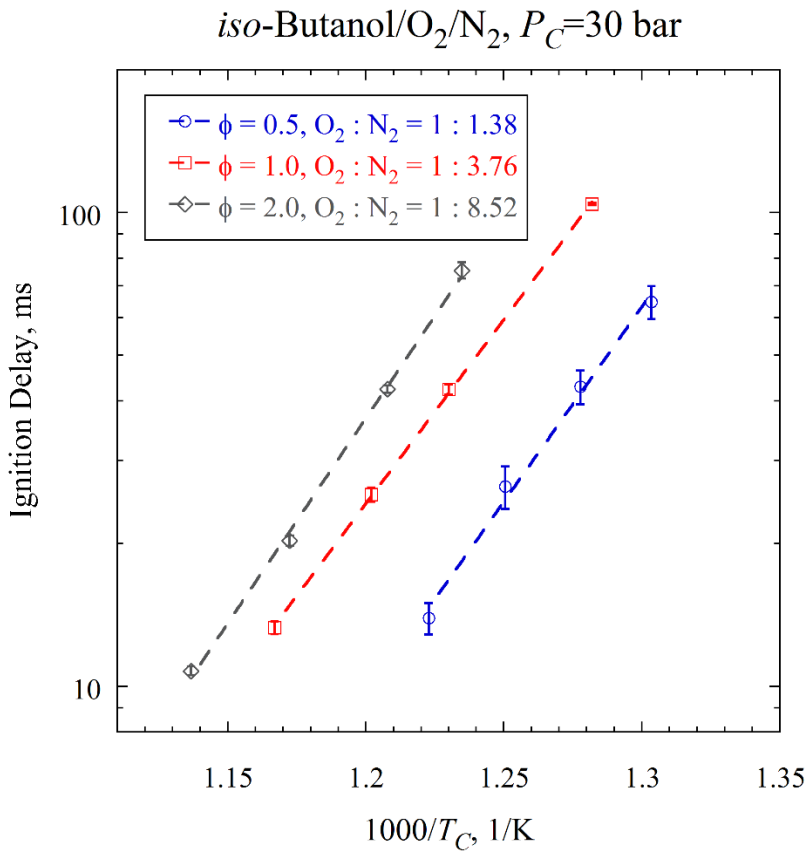
Experimental Methods

- The ignition delay is the time from TDC to the maximum of the time derivative of the pressure
- During the ignition delay, the reactants are losing energy by heat transfer to the relatively colder reactor walls
- Because we have a constant volume, closed reactor, the heat loss produces pressure drop
- We characterize this pressure drop by replacing oxygen with nitrogen in the mixture to eliminate the explosion but retain a similar heat loss profile to the reactive experiments
- T_C is taken as the temperature at TDC of a non-reactive simulation



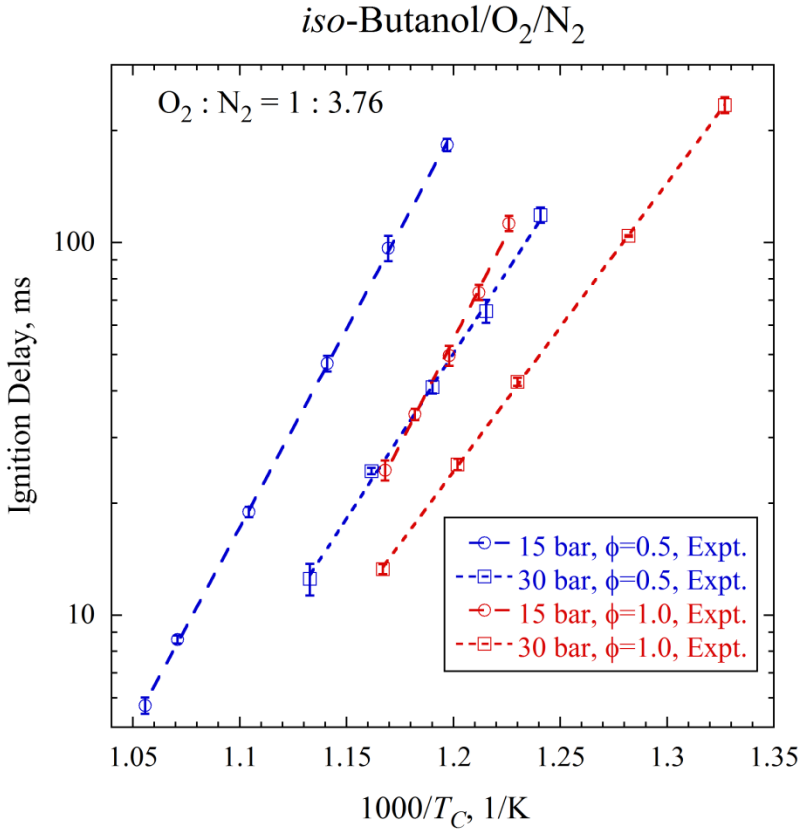
Experimental Results





- For the experiments with changing oxidizer ratio, $\phi = 0.5$ is the most reactive and $\phi = 2.0$ is the least reactive
- The same effect has been shown for *n*-butanol in our previous work

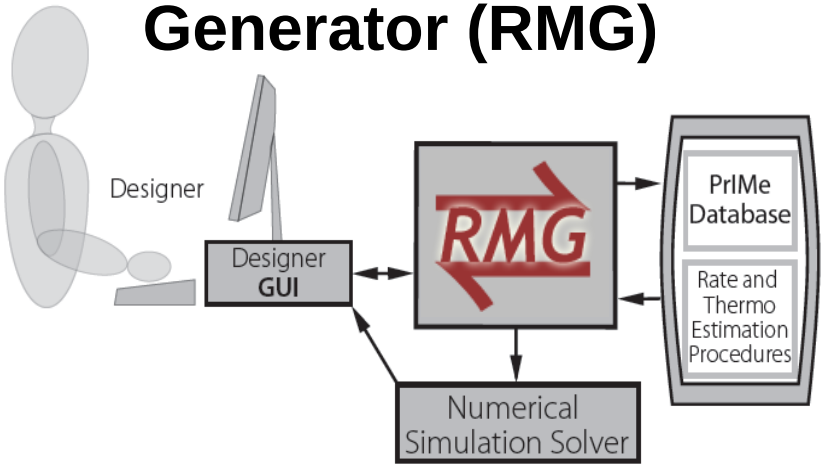
Experimental Results



- For the experiments in air, $\phi = 0.5$ is less reactive than $\phi = 1.0$ for the same compressed pressure because of the reduced fuel concentration
- Reactivity increases as pressure increases for constant ϕ

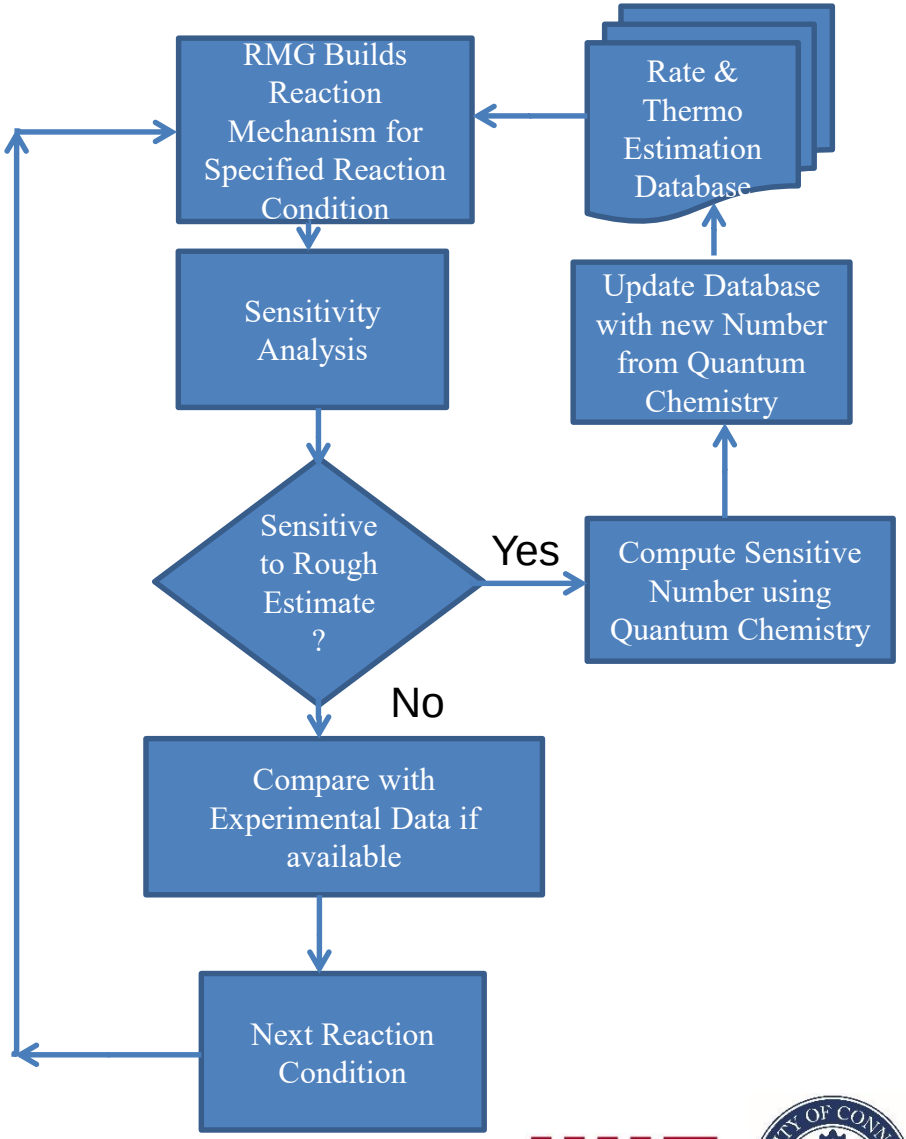
Model Development Paradigm

Reaction Mechanism Generator (RMG)



Free and open source software:

http://rmg.mit.edu/



Iso-Butanol Low Temperature Model

Seed Mechanism
Validated under high temperature combustion and pyrolysis (P 30 torr – 30 bar)

372 species,
8723 reactions:

Hansen *et al., Combust and Flame.* **2013**, *accepted*

Extend to T < 850 K
T = 750 – 1000 K
P = 15 - 30 bar

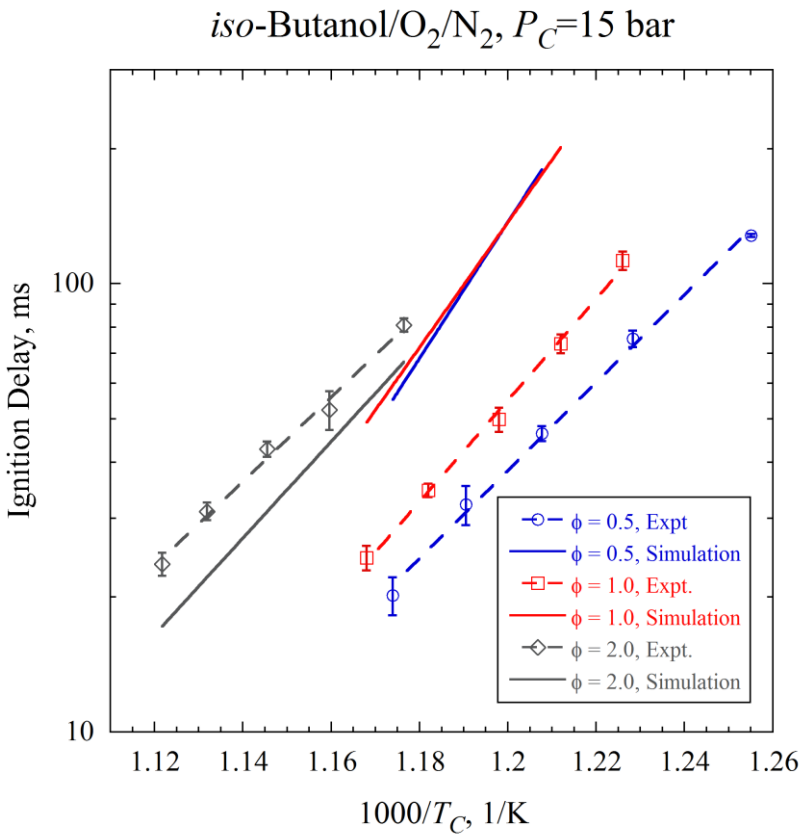
Supplied rate library for peroxy chemistry based on quantum calculations for n-butanol
Welz *et al.* 2013 (submitted to C&F)

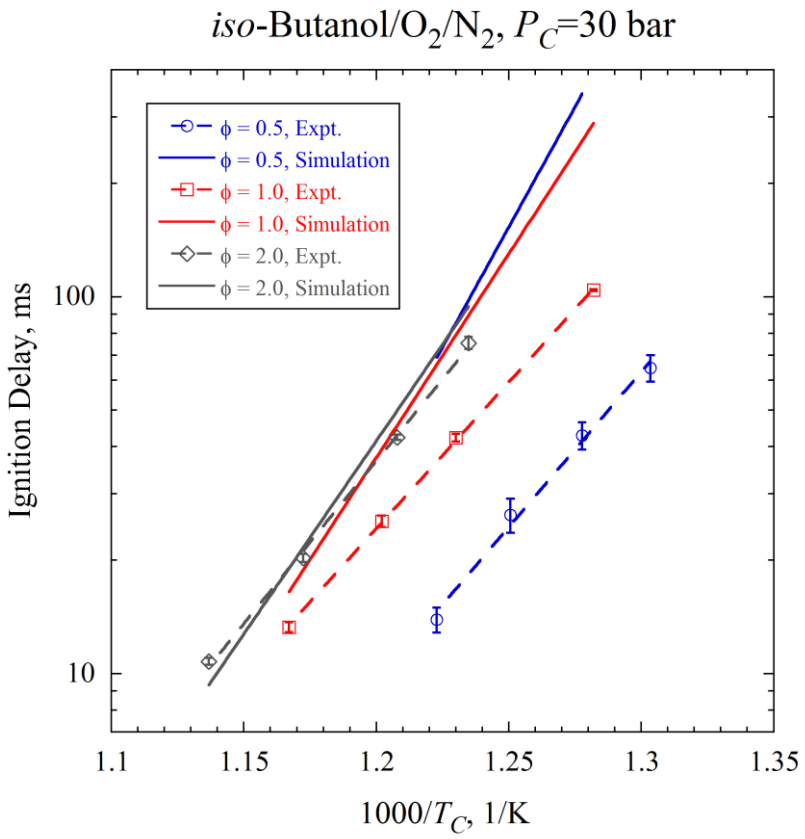
Computer considered:
>1,000 species and
>10,000 reactions

Weber *et al.,* 8th U.S. National Combustion Meeting. **2013**

418 species,
10413 reactions:

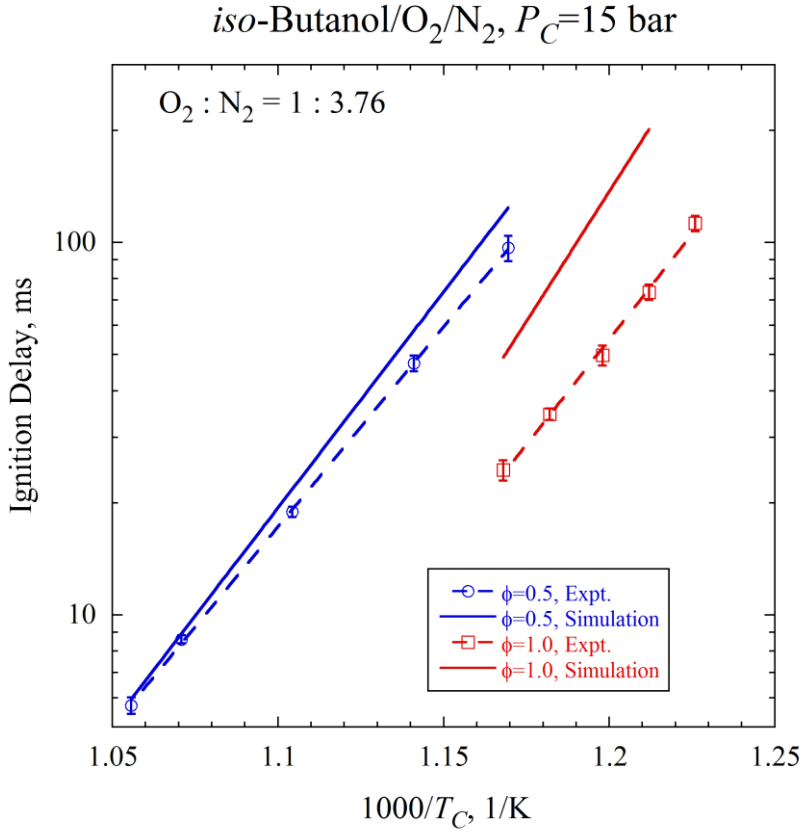
The model doesn't predict the correct [O_2] dependence

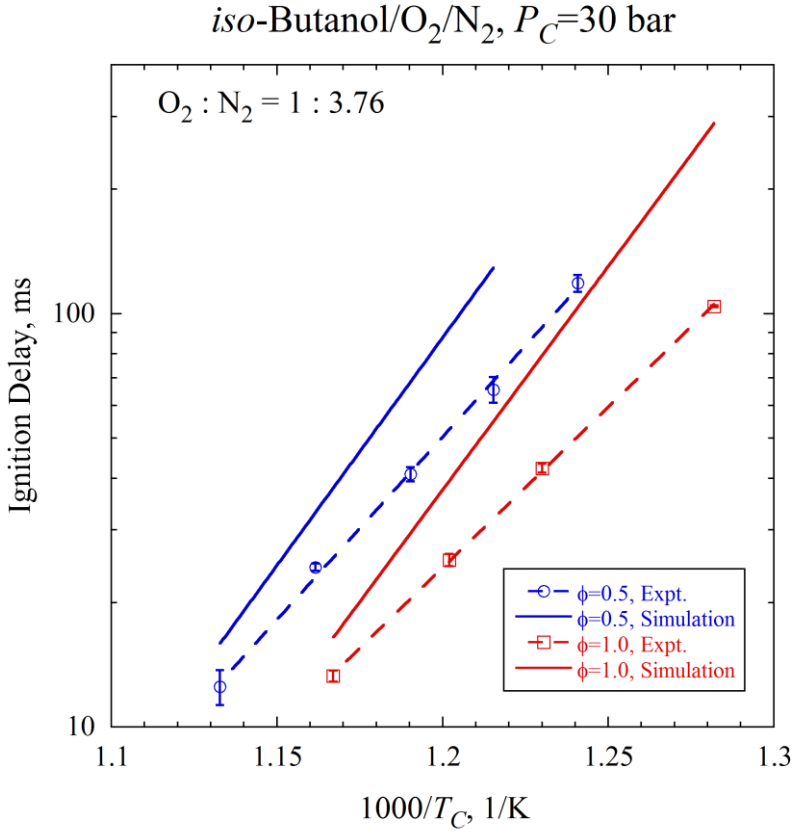




- The model can predict $\phi = 2.0$ ignition delays reasonably well but does not predict the proper [O_2] sensitivity
- Previous models built with RMG are also unable to predict the [O_2] dependence of *n*-butanol ignition delay

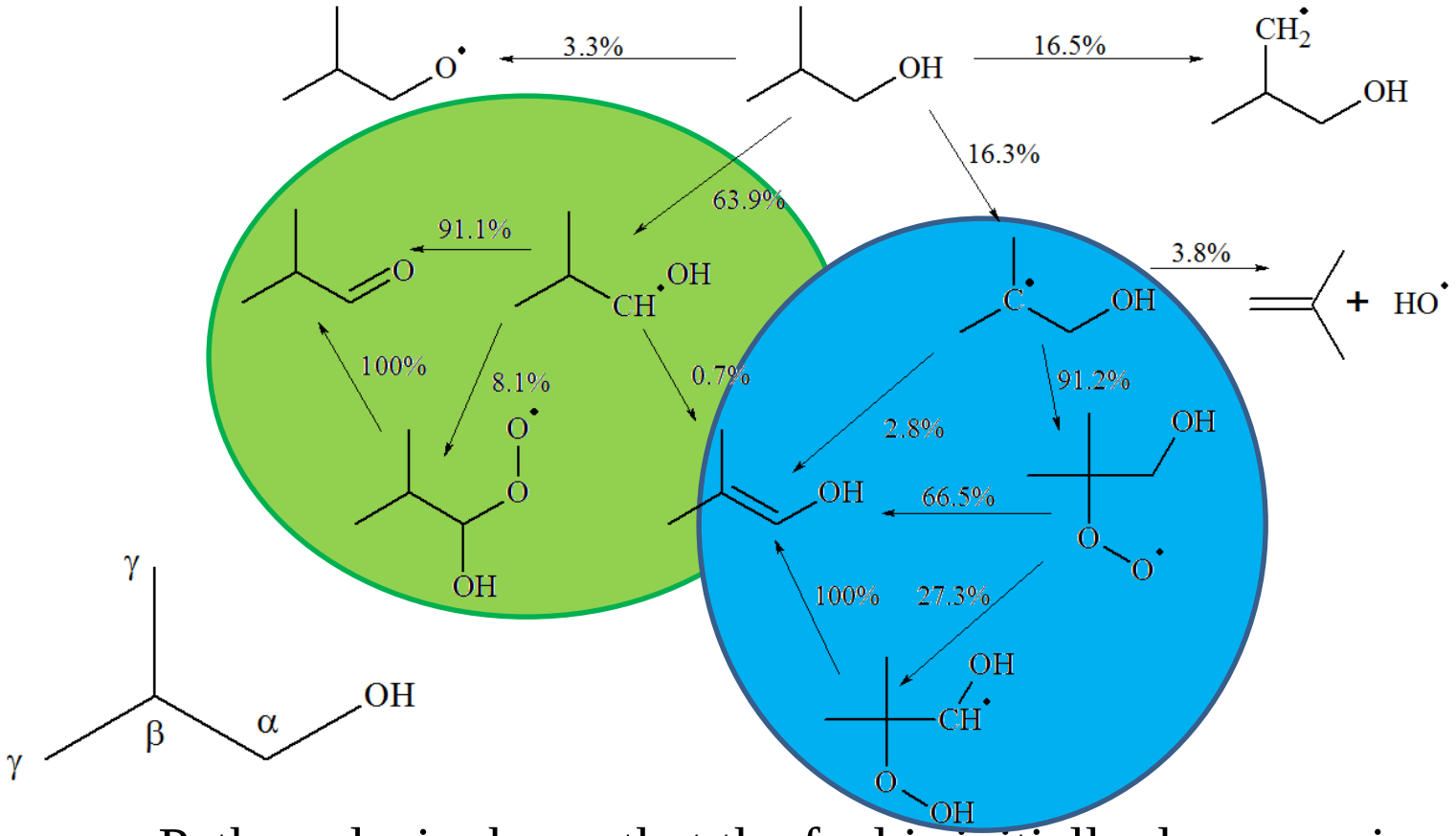
The model predicts ignition delays in air pretty well





- The model is able to predict lean ignition delays in air at the lower pressure very well, but still over-predicts the ignition delay for all of the conditions
- The experiments are predicted to within a factor of 2-3 for the other conditions

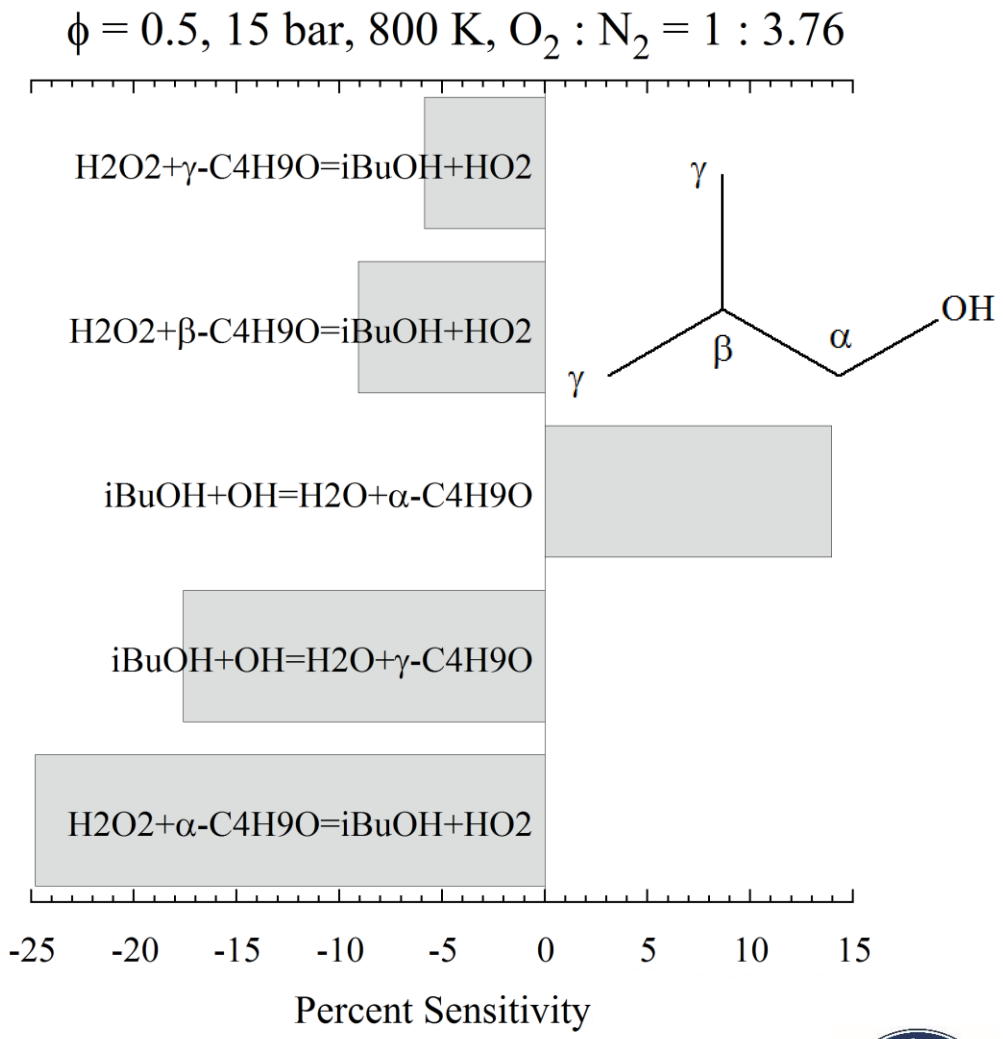
Path Analysis - $\phi = 1.0$, 800 K, 30 bar



- Path analysis shows that the fuel is initially decomposing through the expected channels
- The β-hydroxybutylperoxy radical does not undergo the Waddington reaction although it is included in the mechanism

Sensitivity Analysis of Fuel Reactions

- Sensitivity analysis shows the importance of the initiation reactions with the fuel
- Fuel + OH => α has positive sensitivity because this is an effective OH terminating pathway
- Fuel + HO_2 => α has negative sensitivity because this is an OH branching pathway (through H_2O_2 reactions)



Conclusions

- New experimental ignition delays for *iso*-butanol have been measured in a heated RCM
- A new chemical kinetic model has been built using low-temperature reaction pathways and validated with the new experiments
- For lean and stoichiometric conditions in air, the model is able to predict the ignition delay to within a factor of 2-3
- For lean, stoichiometric, and rich conditions at constant initial fuel mole fraction, the model is unable to predict the dependence of the ignition delay on the initial oxygen concentration
- Path and sensitivity analysis provide clues to improve the mechanism

Thank you! Questions?