

# Validation of Kinetic Models of the Butanol Isomers at High Pressure using a Rapid Compression Machine

## Introduction and Objectives:

- Energy security and climate change are driving development of fuels from many new sources, particularly renewable bio-sources
- Accurate kinetic models are required to enable design of new engine technologies to optimize operation towards emerging non-petroleum derived fuels
- The butanol system is the smallest system with primary, secondary, and tertiary alcohols groups
- Goal is to provide validation data using a heated rapid compression machine (RCM) at high pressures and low to intermediate temperatures

## Rapid Compression Machine:

- Single, retractable, piston
- Piston is pneumatically driven and hydraulically stopped
- Piston is machined with crevices to control the roll-up vortex effect
- Pressure and temperature from TDC reported as compressed conditions
- The RCM has the ability to vary compressed temperature and compressed pressure independently

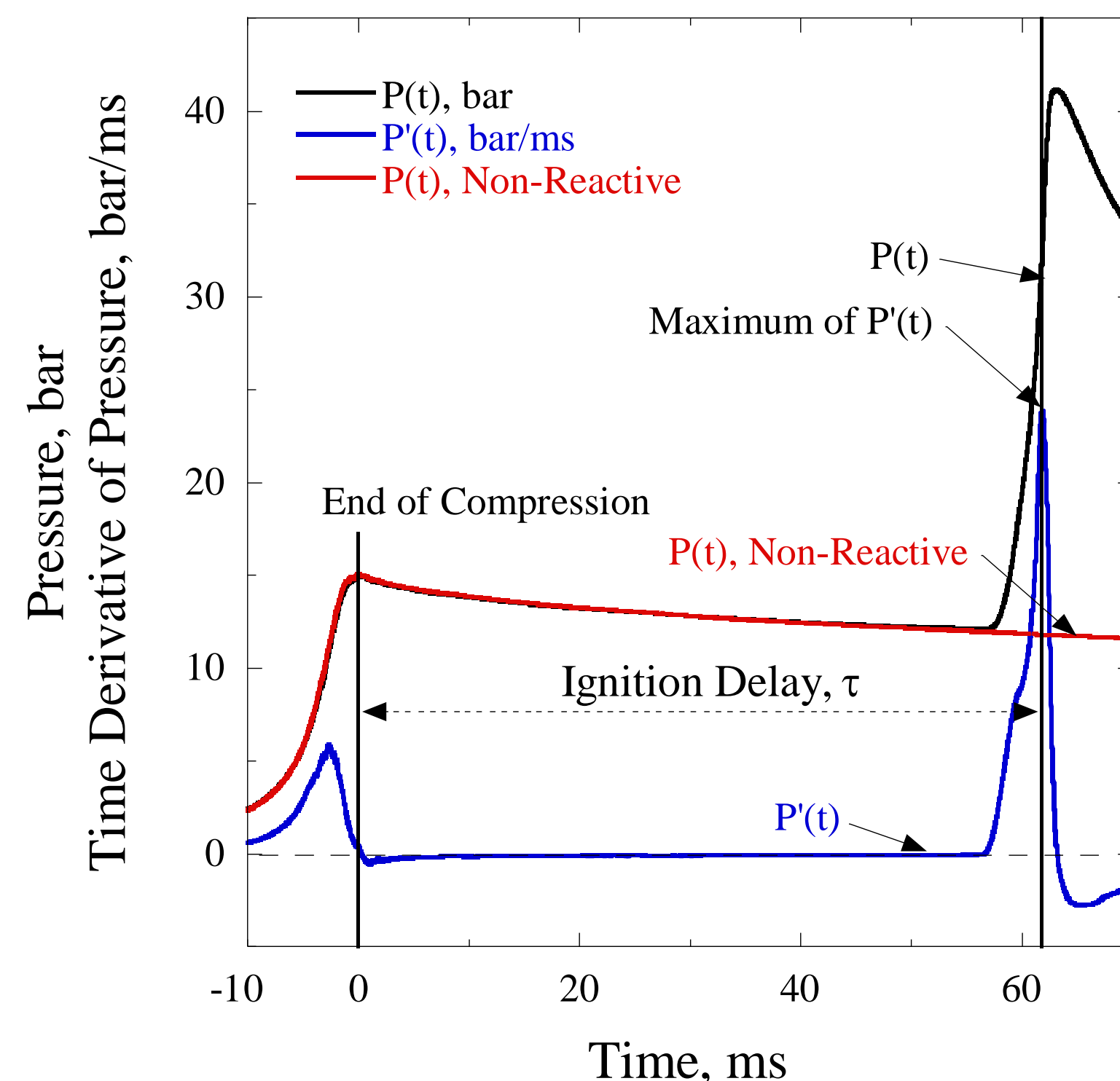
## Experimental Conditions:

- Compressed Temperature Range: 680-860 K
- Compressed Pressure Range: 15 and 30 bar
- Equivalence Ratio:  $\phi = 1.0$ ,  $O_2:N_2 = 1:3.76$

## Experimental Analysis:

- Ignition is defined by the local maximum of the time derivative of the post-compression pressure
- Compressed temperature is computed using a non-reactive run, where oxygen in the mixture is replaced by nitrogen to eliminate reactions while maintaining a similar specific heat ratio

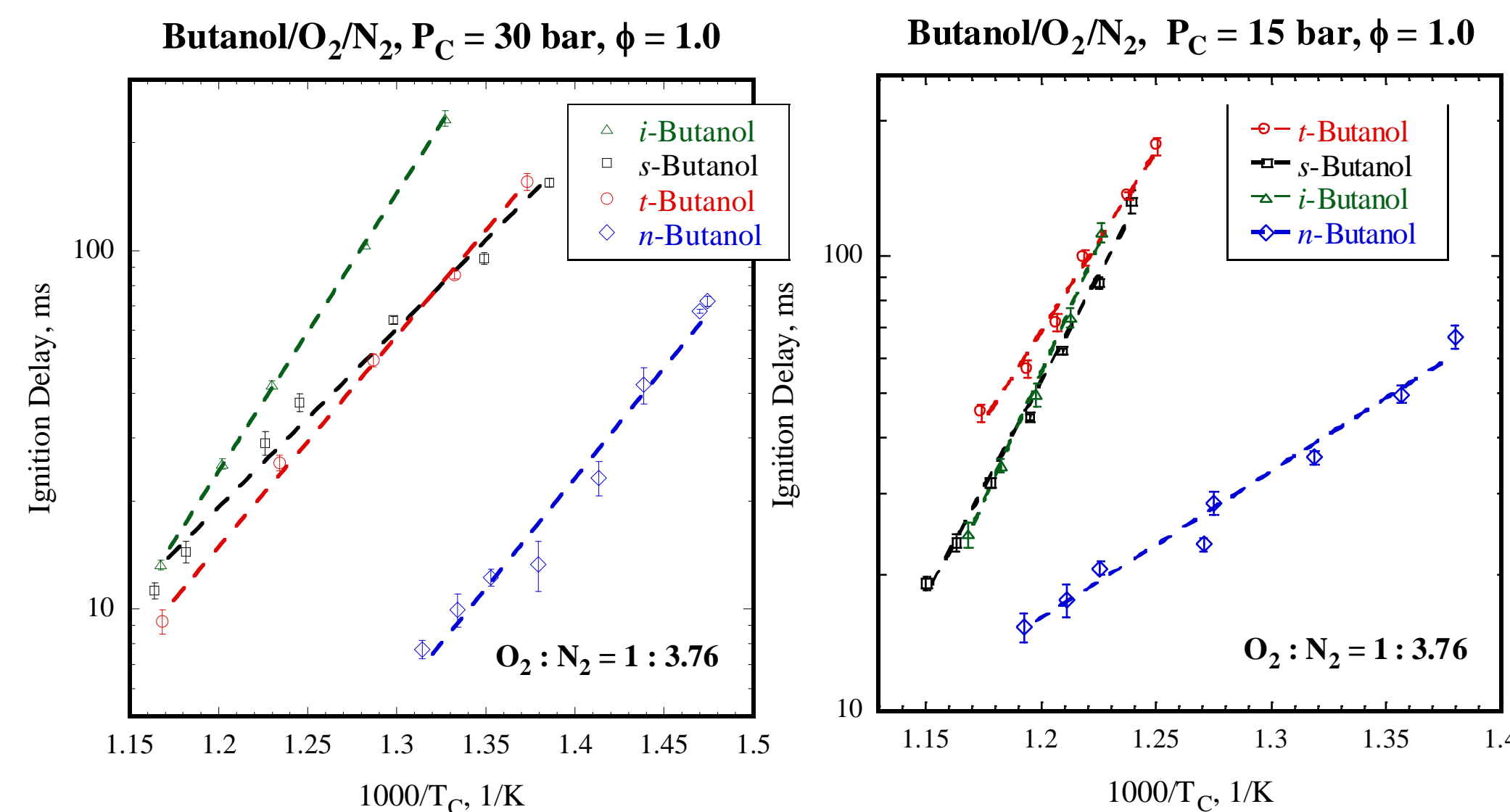
***s*-Butanol/ $O_2/N_2$ ,  $\phi=1.0$ ,  $P_C=15$  bar,  $T_C=827$  K**



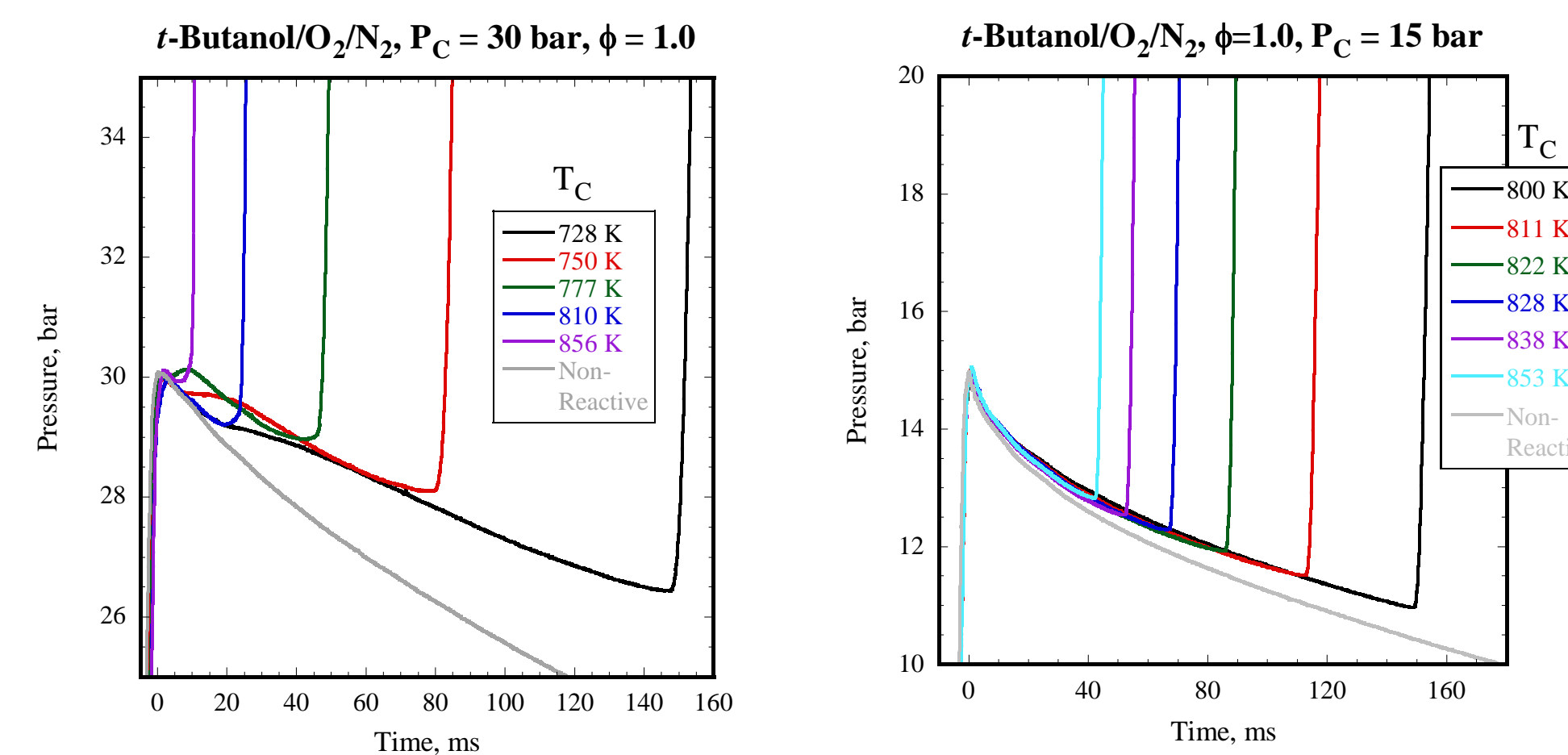
Bryan W. Weber\*, Chih-Jen Sung  
Department of Mechanical Engineering  
University of Connecticut  
Storrs, CT, 06269, USA

## Experimental Results:

- Arrhenius plots of the ignition delay show a clear dependence on compressed pressure
- The order of reactivity of the isomers changes at higher pressure, from  $n\text{-BuOH} > s\text{-BuOH} \approx i\text{-BuOH} > t\text{-BuOH}$  at 15 bar to  $n\text{-BuOH} > t\text{-BuOH} > s\text{-BuOH} > i\text{-BuOH}$  at 30 bar
- There does not appear to be a negative temperature dependence region in these data



- Pressure traces from the RCM do not show two-stage ignition for any of the isomers, in either pressure range
- However, there is significant pre-ignition heat release for *t*-butanol and *n*-butanol, but not as much for the other isomers



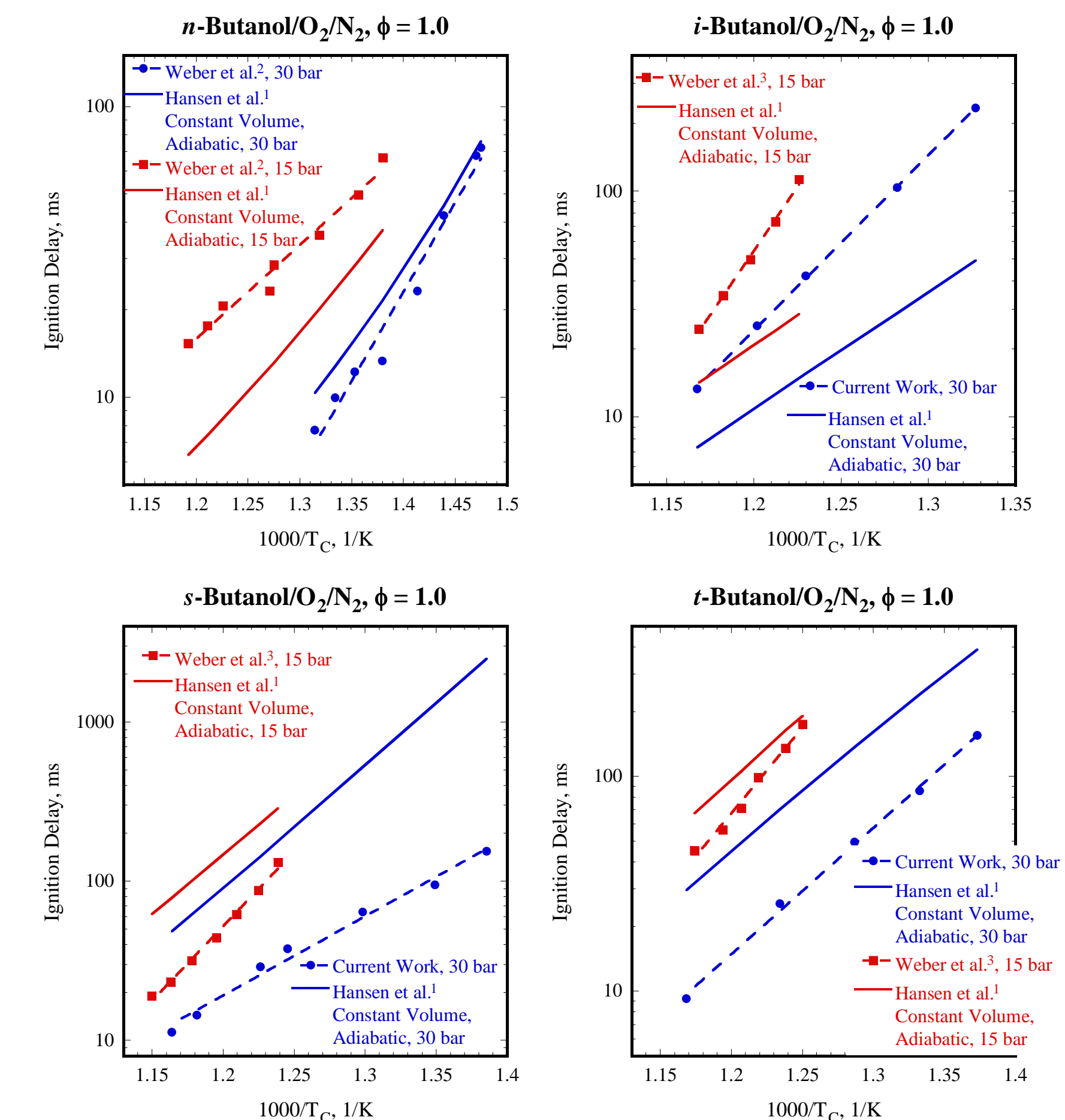
### Acknowledgements:

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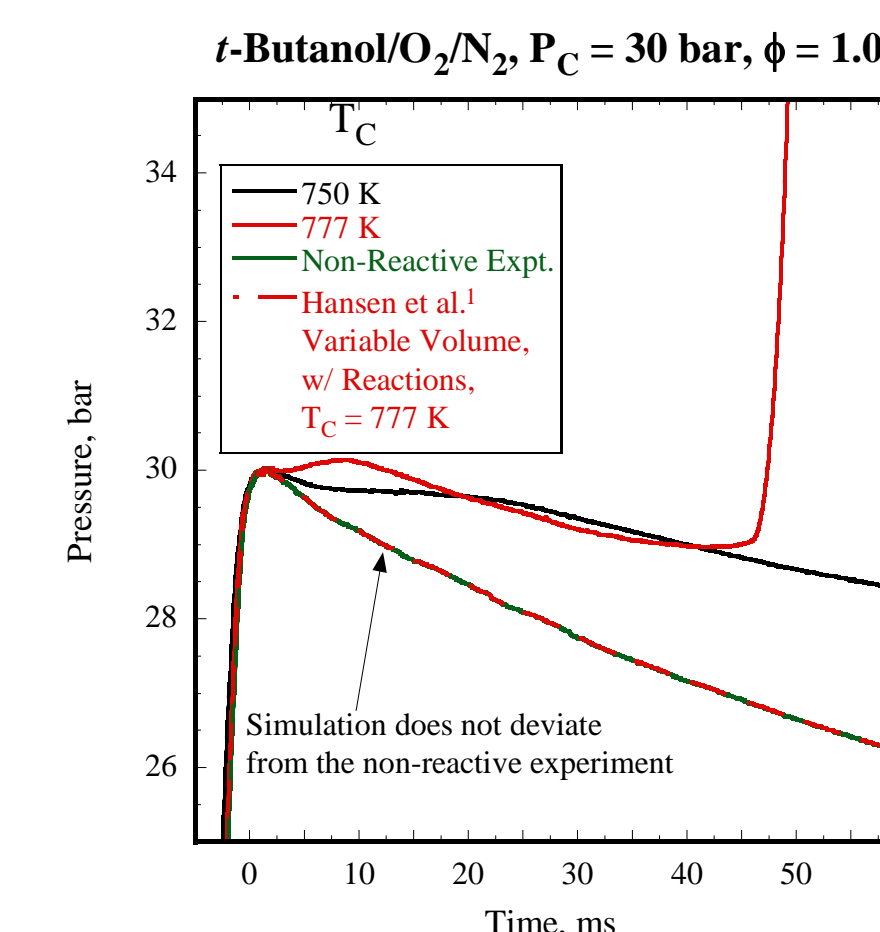


## Modeling Results:

- Constant volume, adiabatic simulations were performed using one recent mechanism from Hansen et al.<sup>1</sup>
- Simulations do not capture the pressure dependence of *n*-butanol ignition delays, under predicting at lower pressure and over predicting at higher pressure
- The deviations from experiments for *i*- and *s*-butanol are similar in both pressure ranges
- The discrepancy for *t*-butanol becomes worse at higher pressure – this may have to do with the effect of pre-ignition heat release



- The mechanism from Hansen et al.<sup>1</sup> is unable to reproduce the pre-ignition heat release behavior of *t*-butanol



### References:

- [1] Hansen, N., Harper, M.R., and Green, W.H., 7<sup>th</sup> US National Combustion Meeting, Georgia Institute of Technology, Atlanta, GA, March 20-23, 2011, paper 1B09
- [2] Weber, B.W., Kumar, K., Zhang, Y., and Sung, C.J., Combustion and Flame, Volume 158, Issue 5, Pages 809-819 doi:10.1016/j.combustflame.2011.02.005
- [3] Weber, B.W. and Sung, C.J., 7<sup>th</sup> US National Combustion Meeting, Georgia Institute of Technology, Atlanta, GA, March 20-23, 2011, paper RK13

\* bryan.weber@uconn.edu

