

Comparative Investigation of the High Pressure Autoignition of the Butanol Isomers

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Presenting: Bryan Weber

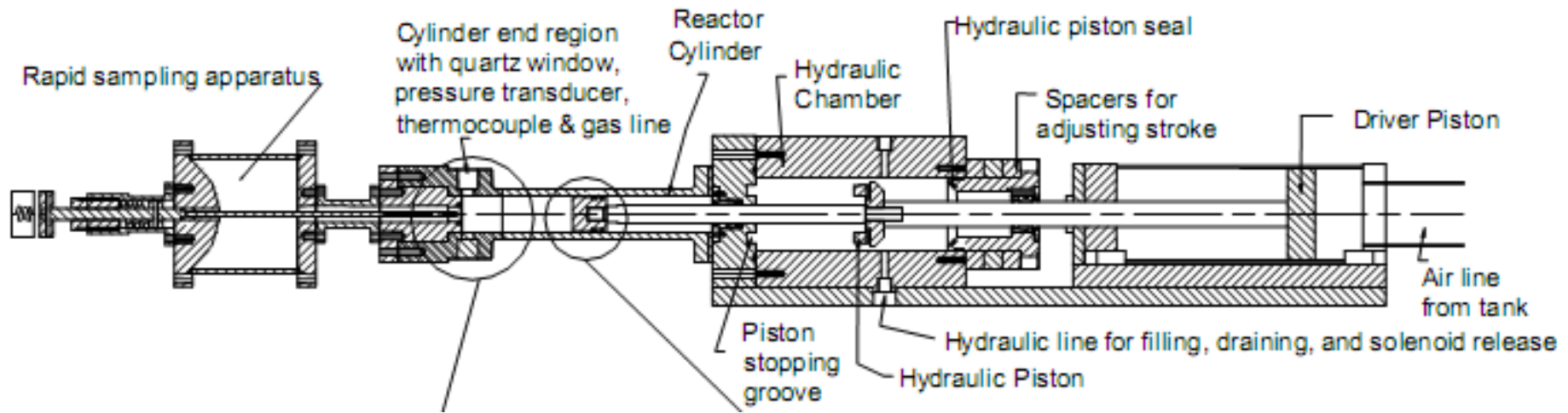
A Short PR Digression



- Butanols – 4 carbon alcohol with 4 isomers
- Motivation – Why Butanol?
 - *n*-Butanol is a second generation biofuel with the potential to replace ethanol and gasoline
 - The isomers of butanol have potential as high-octane gasoline additives
 - The butanol system is the smallest alcohol system with primary, secondary and tertiary alcohol groups

Objectives

- Investigate the butanol isomers to help determine their suitability for replacing traditional fuels in transportation applications
- Low-temperature ignition delays provide a key measure of performance related to compression or spark ignition engines
- Provide ignition delay data for all four butanol isomers at engine relevant conditions
- Evaluate the ability of chemical kinetic models to predict the ignition delays



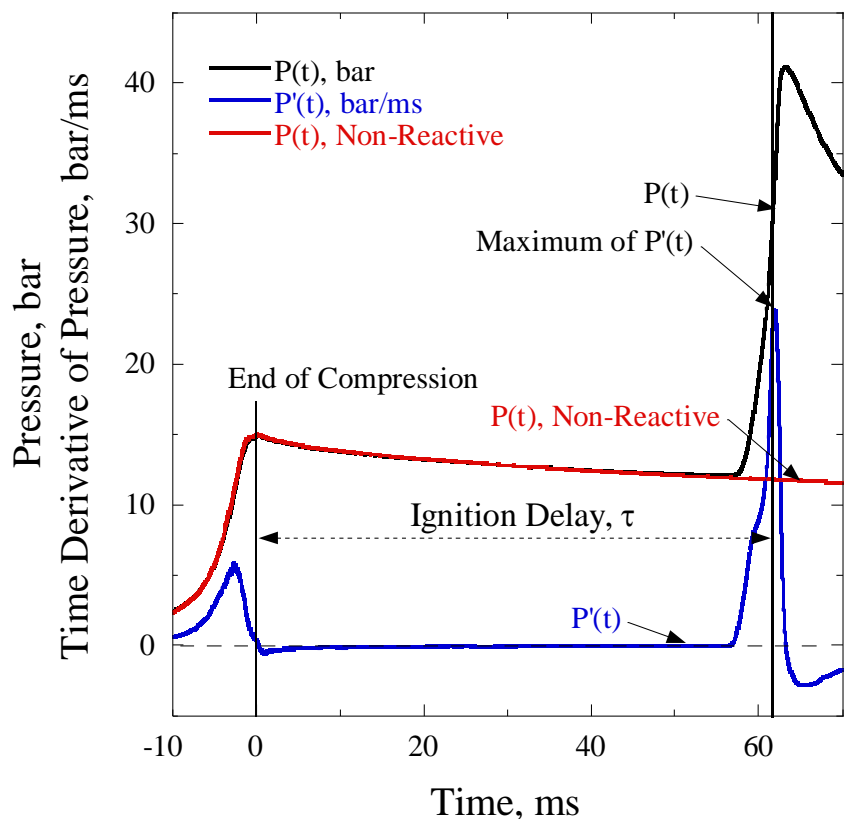
- Single, retractable piston
- Piston is pneumatically driven and hydraulically stopped, with compression time around 30 ms
- Piston is machined with crevices to contain roll-up vortex created by piston motion

- Pressure and Temperature from Top Dead Center (TDC) are reported as “compressed conditions”, P_C and T_C
- Ability to vary P_C and T_C independently
 - P_C up to 45 bar
 - T_C between 660-1100 K (CR:7-15)
- Fuel and oxidizer are preheated (60°C – 140°C) and mixed by magnetic stirrer in a 15 L mixing tank to ensure homogeneity

- Overall Compressed Temperature Range:
680 K to 860 K
- Overall Compressed Pressure Range:
15 and 30 bar
- Overall Equivalence Ratio Range:
 $\phi = 0.5, 1.0, 2.0$
- Not all fuels have been studied at all
conditions (yet)

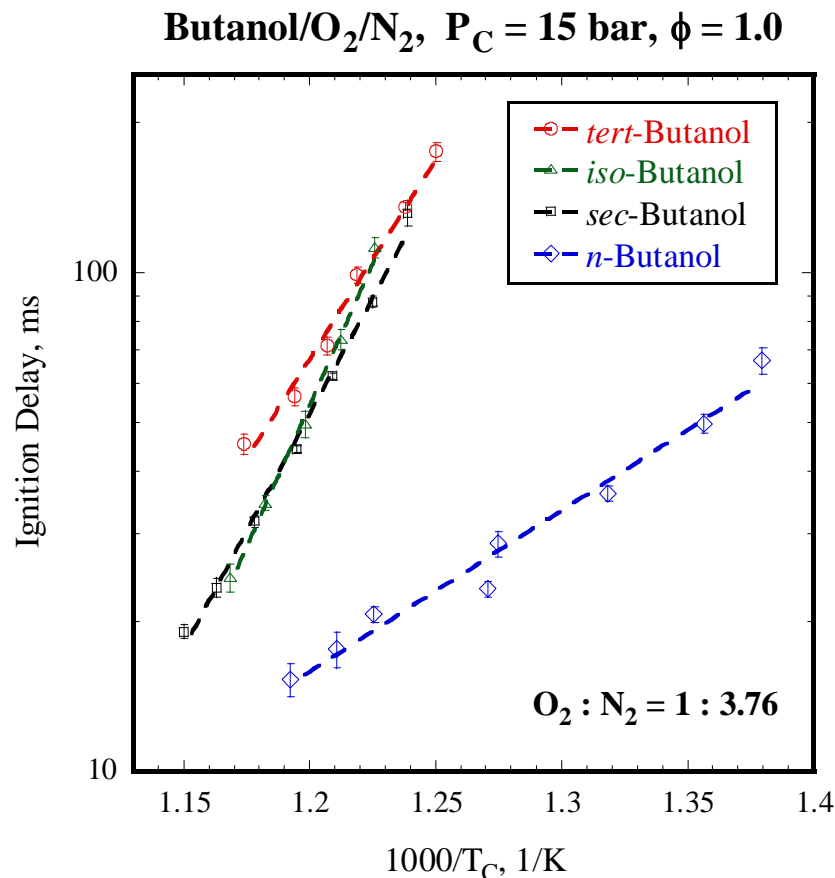
Definition of Ignition Delay

sec-Butanol/O₂/N₂, $\phi=1.0$, $P_C=15$ bar, $T_C=827$ K



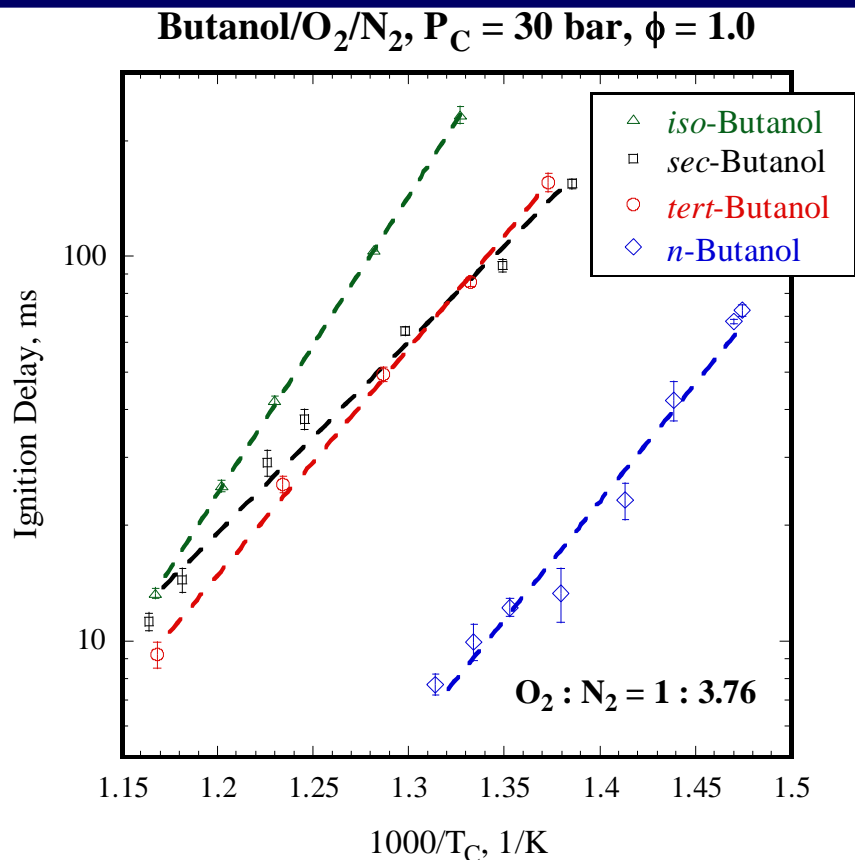
- Ignition criteria is the maximum rate of pressure rise
- Ignition delay is the time difference from the end of compression to ignition point
- Each condition is repeated at least 5 times to ensure repeatability
- Non-reactive case replaces O₂ with inert to quantify effect of heat loss to the reactor walls

Experimental Results (1)



- Reactivity at 15 bar: $n\text{-butanol} > \text{sec-butanol} \approx \text{iso-butanol} > \text{tert-butanol}$

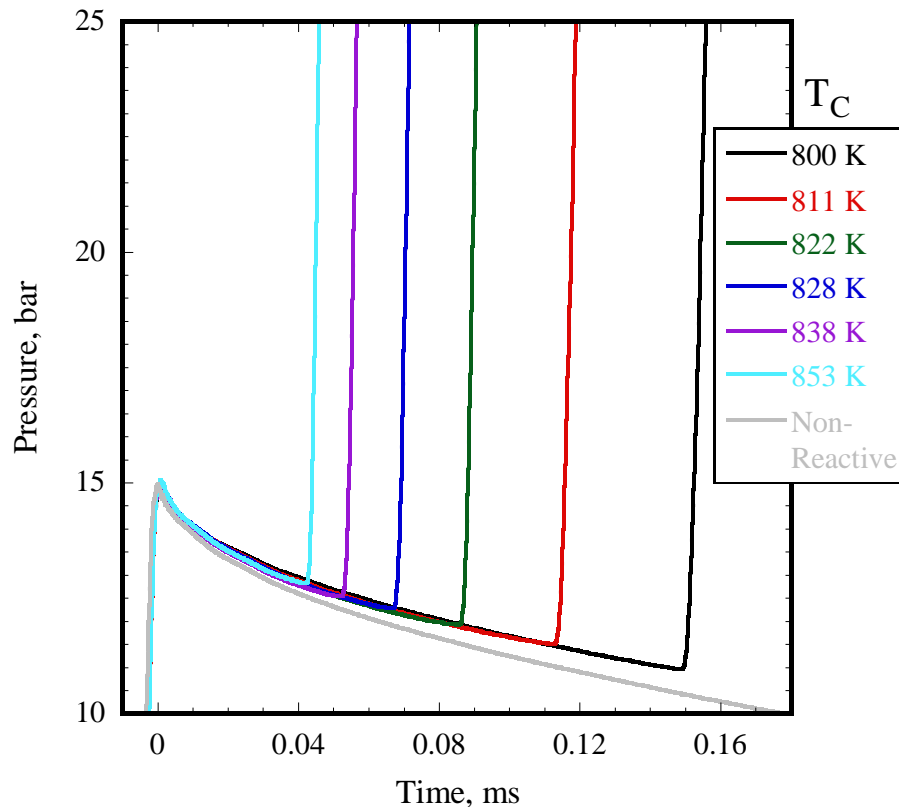
Experimental Results (2)



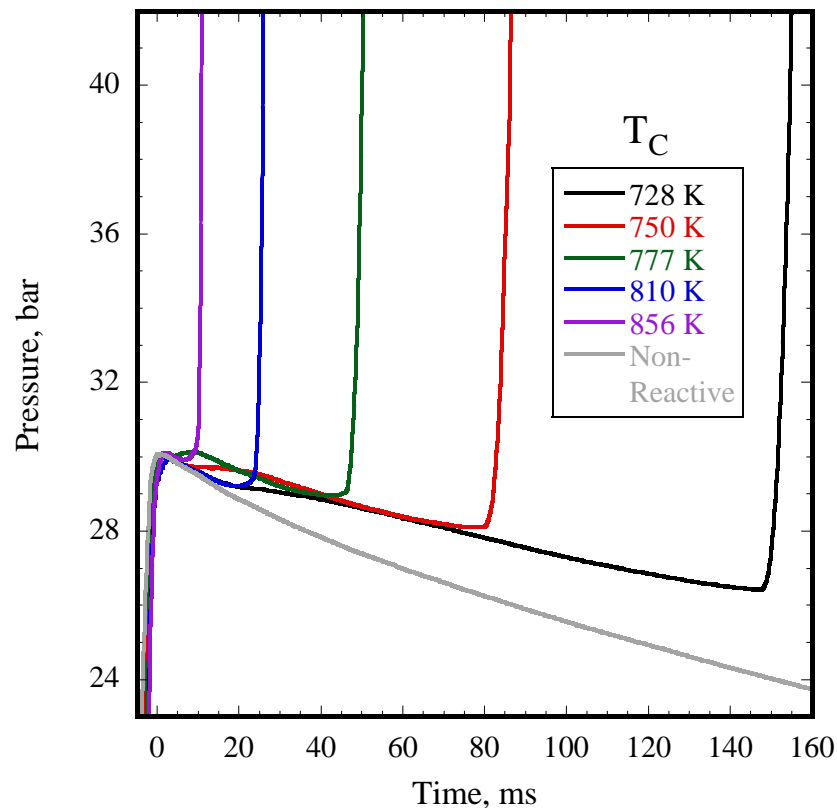
- Reactivity at 30 bar: *n*-butanol > *tert*-butanol > *sec*-butanol > *iso*-butanol
- Why does *tert*-butanol become relatively more reactive at higher pressures?

Experimental Results (3)

tert-Butanol/O₂/N₂, $\phi=1.0$, $P_C = 15$ bar



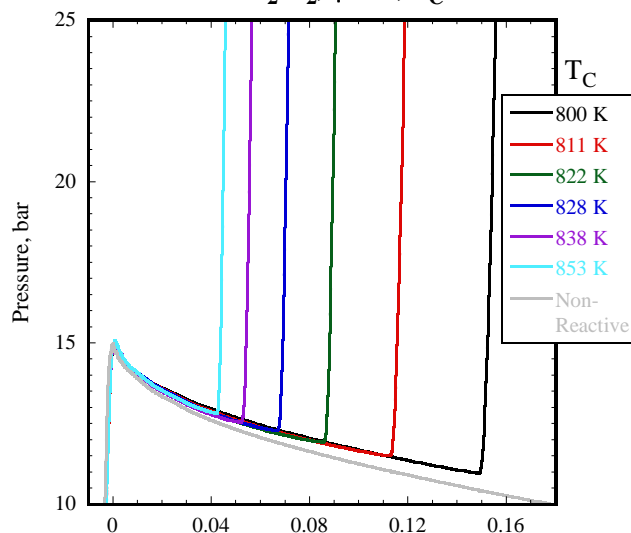
tert-Butanol/O₂/N₂, $\phi = 1.0$, $P_C = 30$ bar



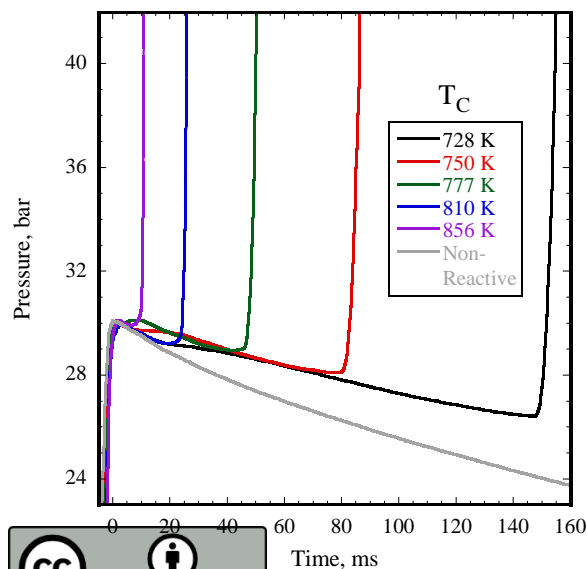
- Pressure traces from the RCM show clearly that there is pre-ignition heat release

Experimental Results (4)

tert-Butanol/O₂/N₂, $\phi=1.0$, $P_C = 15$ bar



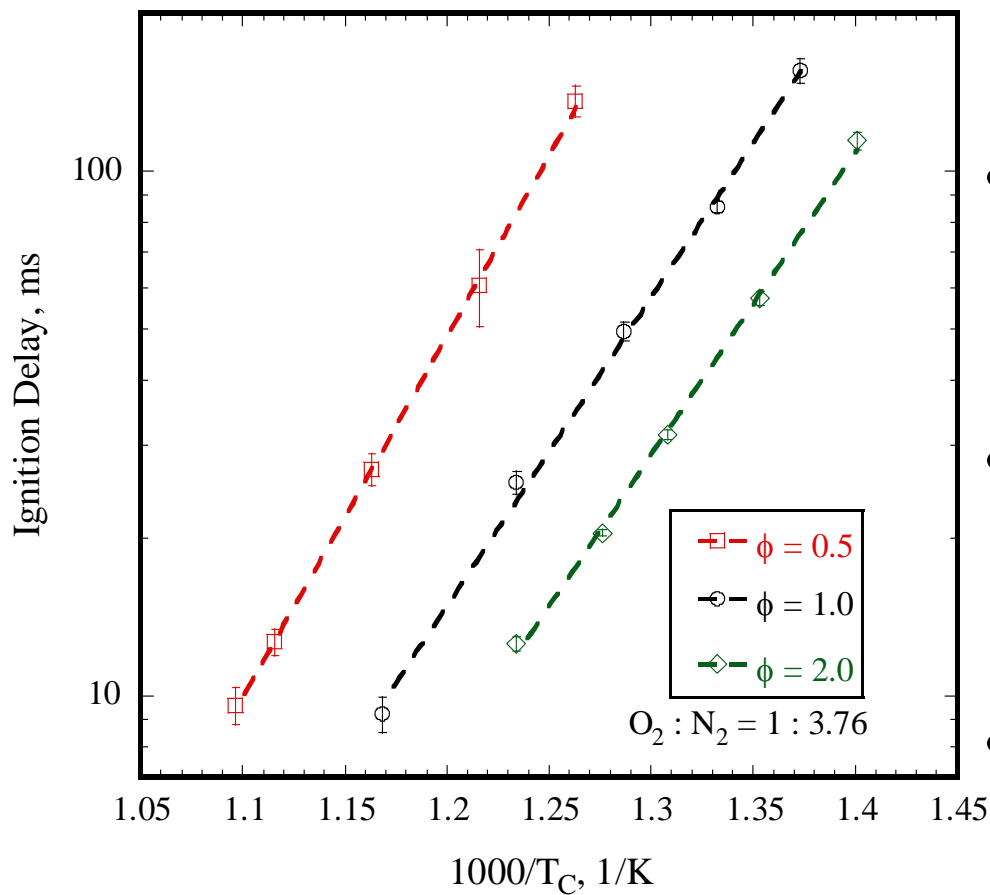
tert-Butanol/O₂/N₂, $\phi = 1.0$, $P_C = 30$ bar



- No other isomers show this extreme behavior (*n*-butanol deviates slightly from its non-reactive traces)
- To help answer what is causing this heat release, we need data at different conditions
- How dependent on fuel concentration is the heat release?

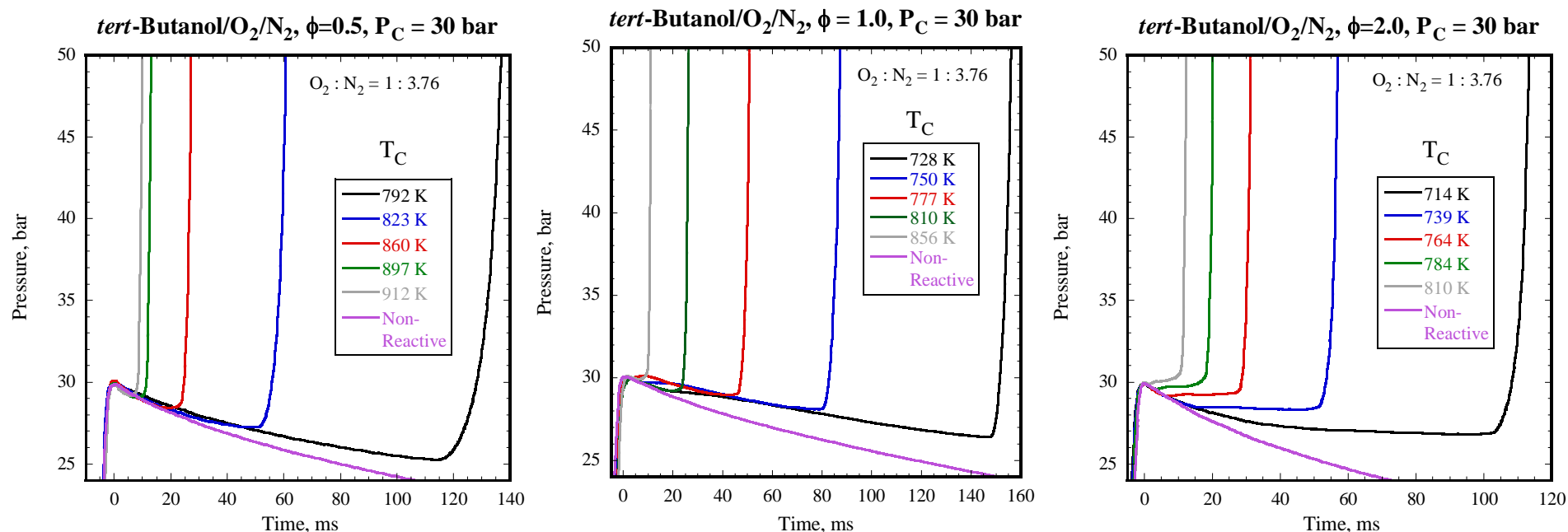
Experimental Results (5)

tert-Butanol/O₂/N₂, P_C = 30 bar



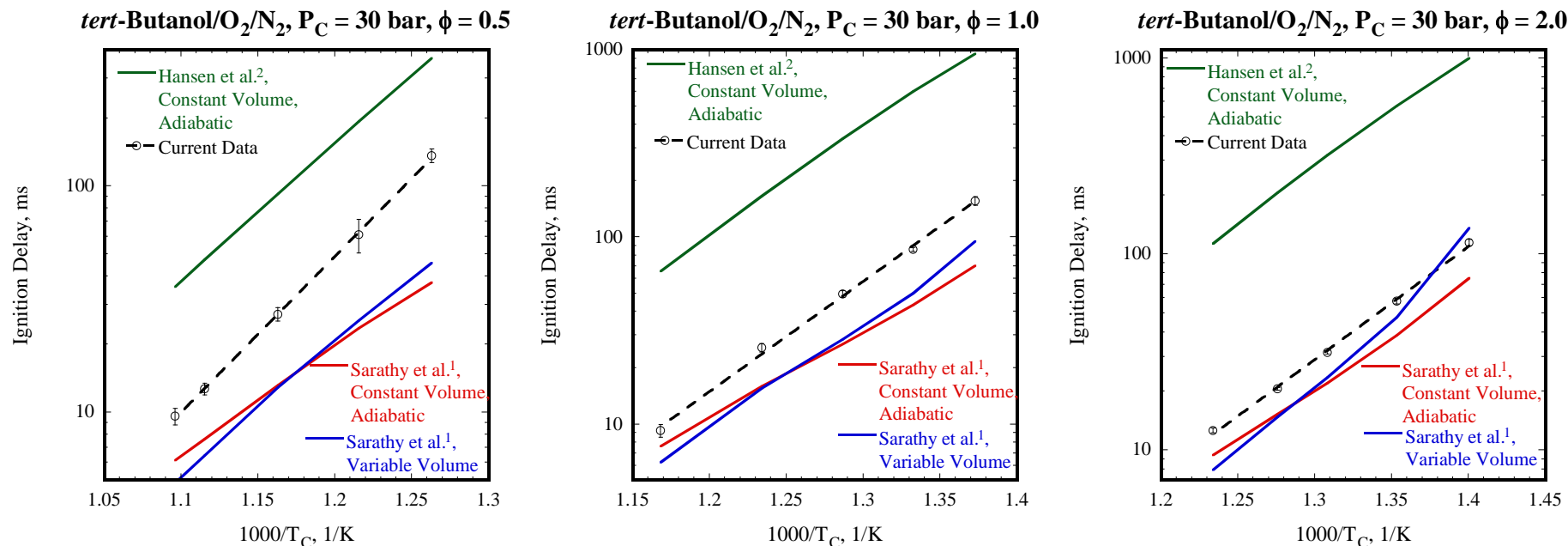
- Ignition delays at two other equivalence ratios ($\phi = 0.5$ and 2.0) in air are measured at 30 bar
- Fuel Mole Fractions:
 $\phi = 0.5 : X = 0.0172$
 $\phi = 1.0 : X = 0.0338$
 $\phi = 2.0 : X = 0.0654$
- Slopes of Arrhenius plots are similar, indicating a similar overall activation energy
- Overall reactivity is in the expected order ($2.0 > 1.0 > 0.5$)

Experimental Results (6)



- At lower and higher fuel concentrations, pre-ignition heat release is still evident
- Results for different equivalence ratios are qualitatively different

Comparison with Simulations (1)



- Simulations show that the mechanism from MIT (Hansen et al.²) consistently over-predicts the *tert*-butanol data, while the mechanism from LLNL (Sarathy et al.¹) under-predicts the data
- Neither mechanism is validated for these experiments

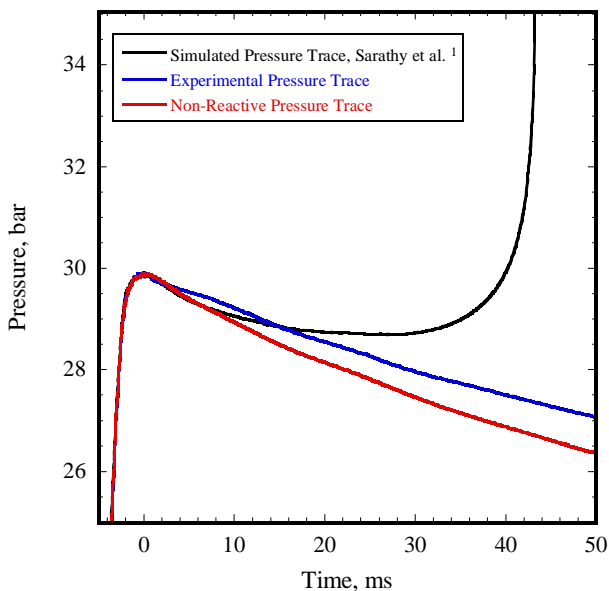
1. Sarathy, S.M., Vranckx, S., Yasunaga, K., Mehl, M., Obwald, P., Westbrook, C. K., Pitz, W.J., Kohse-Hoinghaus, K., Fernandes, R.X., and Curran, H.J. Submitted to *Combustion and Flame*, Sept. 2011

2. Hansen, N., Harper, M.R., and Green, W.H. Submitted to *Physical Chemistry Chemical Physics*, Aug. 2011

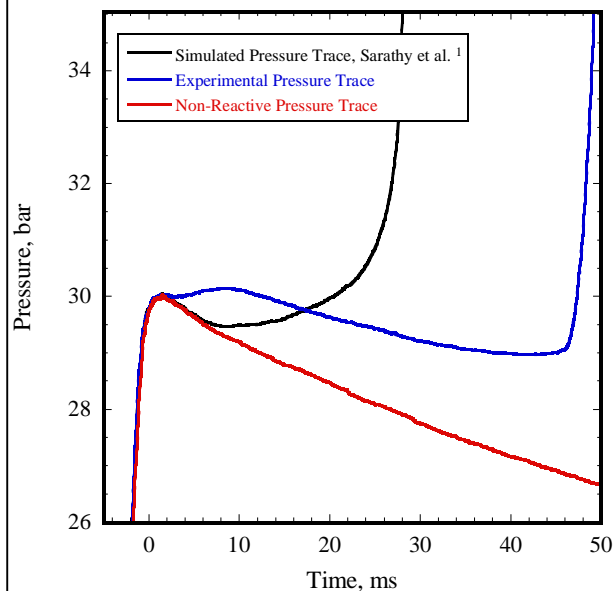


Comparison with Simulations (2)

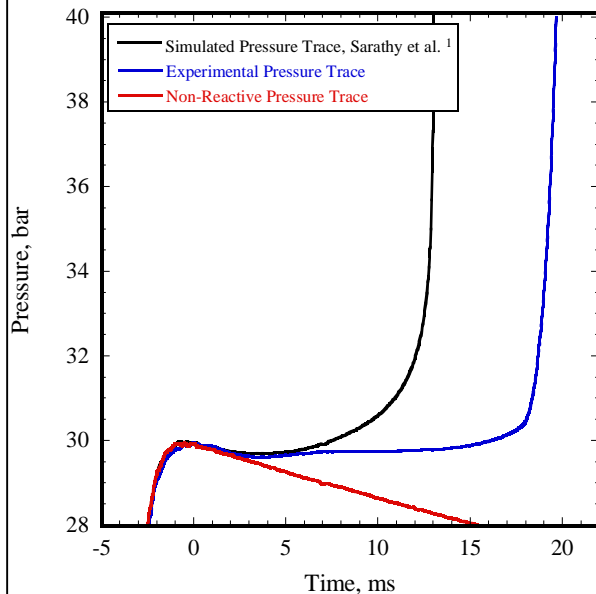
tert-Butanol/O₂/N₂, $\phi=0.5$, $P_C=30$ bar, $T_C=792$ K



tert-Butanol/O₂/N₂, $\phi=1.0$, $P_C=30$ bar, $T_C=777$ K



tert-Butanol/O₂/N₂, $\phi=2.0$, $P_C=30$ bar, $T_C=784$ K



- Despite reasonable agreement in overall ignition delay, the pressure traces are not well reproduced by the mechanism from LLNL

Summary (1)

- Autoignition delays of the isomers of butanol show unexpected behavior over the currently studied temperature and pressure ranges
- Pre-ignition heat release during *tert*–butanol autoignition delays were unable to be reproduced by mechanisms, so the chemistry causing this is unclear
- New autoignition delays for off-stoichiometric conditions of *tert*–butanol in air have been collected to help determine the cause of the pre-ignition heat release

Summary (2)

- Although the overall activation energy of three equivalence ratios of *tert*-butanol ($\phi = 0.5, 1.0, 2.0$) are quite similar, they show markedly different pressure profiles
- One recent mechanism was able to reproduce the ignition delays within a factor of ~ 2 -3, despite not being validated for these conditions
- Despite this relatively good agreement, the pressure profile is still unable to be reproduced

- This material is based upon work supported as part of the Combustion Energy Frontier Research Center, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Award Number DE-SC0001198
- Dr. Mani Sarathy for providing his mechanism prior to publication, and for helpful discussions
- Dr. Bill Green for providing his mechanism prior to publication, and for helpful discussions

Thank you!

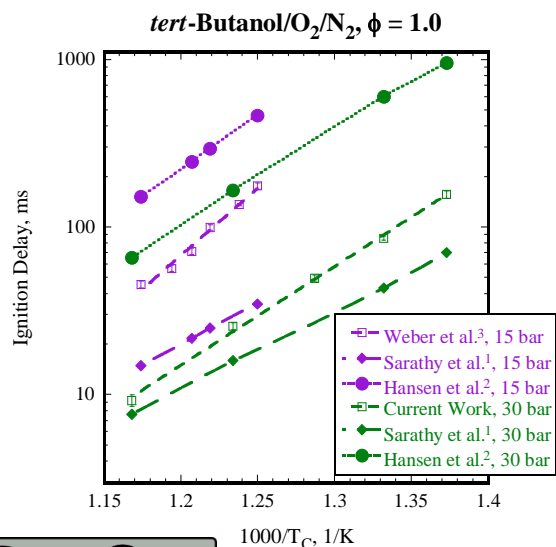
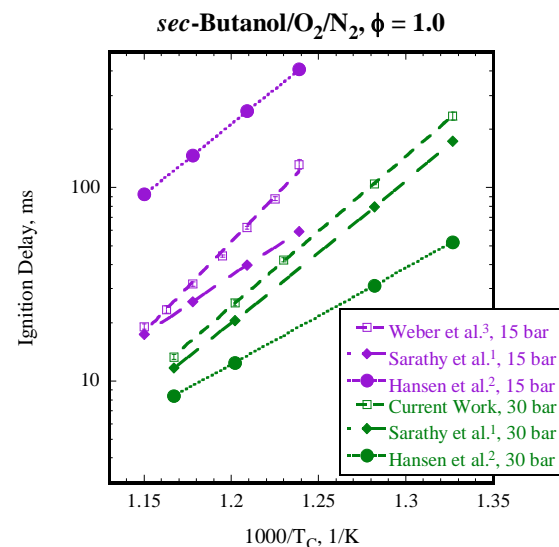
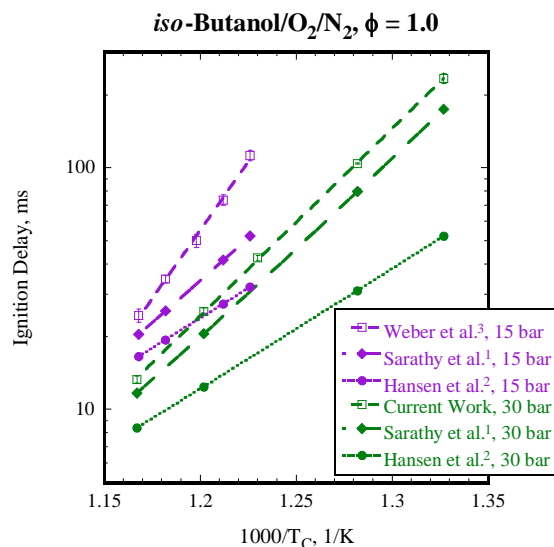
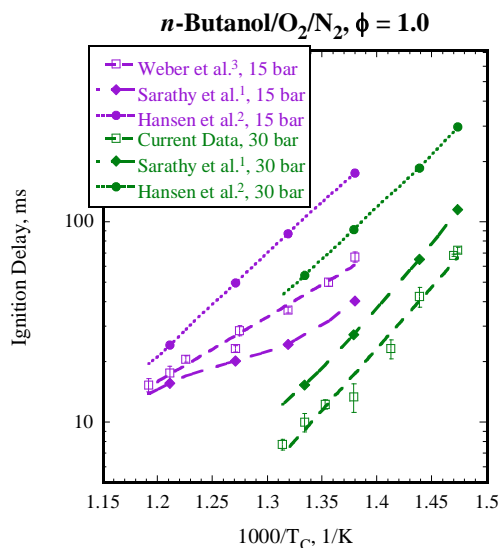
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Comparison with Simulations



- Constant Volume, Adiabatic Simulations
- Mechanisms are NOT validated for 30 bar cases
- Agreement for 15 bar cases is reasonable – agreement for 30 bar cases is luck of the draw

1. Sarathy, S.M., Vranckx, S., Yasunaga, K., Mehl, M., Oßwald, P., Westbrook, C. K., Pitz, W.J., Kohse-Hoinghaus, K., Fernandes, R.X., and Curran, H.J. Submitted to *Combustion and Flame*, Sept. 2011
2. Hansen, N., Harper, M.R., and Green, W.H. Submitted to *Physical Chemistry Chemical Physics*, Aug. 2011
3. Weber, B.W., and Sung, C.J. National Combustion Meeting.