

Autoignition of Butanol Isomers at Elevated Pressure and Low to Intermediate Temperature Using a Rapid Compression Machine

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- Butanols – 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

- Black et al.¹ have measured ignition delays of *n*-butanol in a shock tube at low pressure and high temperature
- Moss et al.² have measured ignition delays of all four isomers of butanol in a shock tube at low pressure and high temperature
- Grana et al.³ have measured flame speeds of the isomers of butanol
- Van Geem et al.⁴ have performed pyrolysis experiments of the four isomers of butanol
- Heufer et al.⁵ have investigated high pressure and intermediate to high temperature ignition delays of *n*-butanol in a shock tube

1. Black, G., Curran, H., Pichon, S., Simmie, J. M., and Zhukov, V., *Combustion and Flame*, Vol. 157, No. 2, 2010, pp. 363-373.

2. Moss, J. T., Berkowitz, A. M., Oehlschlaeger, M. A., Biet, J., Warth, V., Glaude, P., and Battin-Leclerc, F., *The Journal of Physical Chemistry. A*, Vol. 112, No. 43, 2008, pp. 10843-10855.

3. Grana, R., Frassoldati, A., Faravelli, T., Niemann, U., Ranzi, E., Seiser, R., Cattolica, R., and Seshadri, K., *Combustion and Flame*, Vol. 157, 2010, pp. 2137-2154.

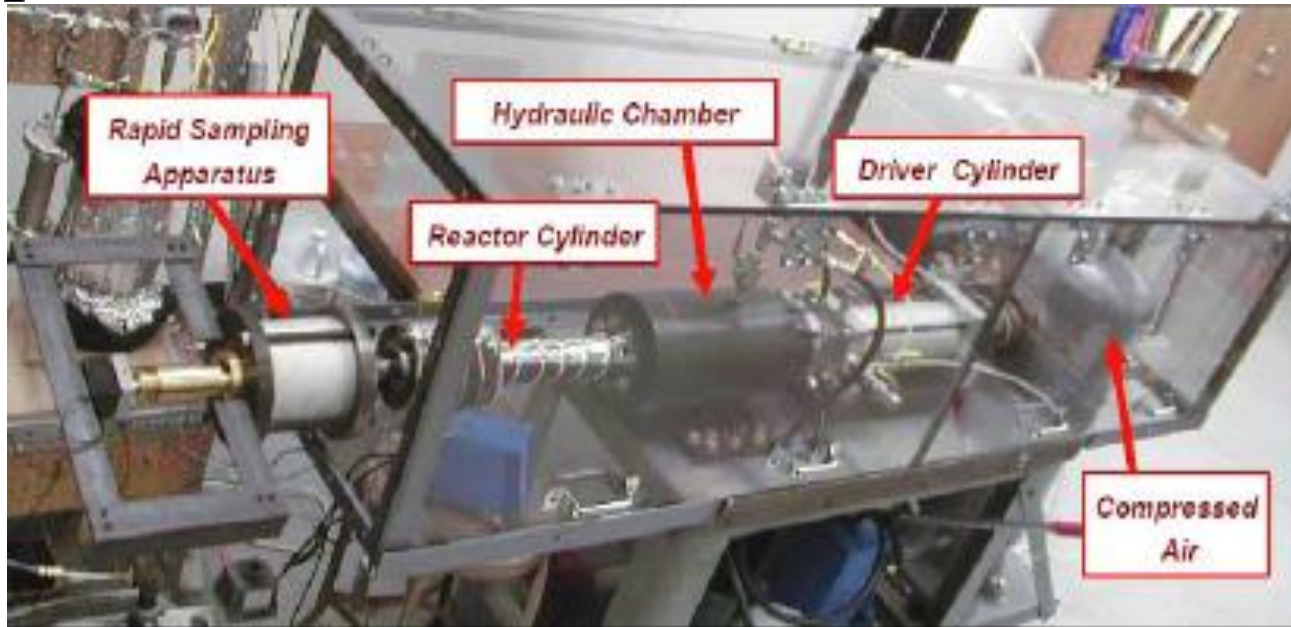
4. Van Geem, K. M., Pyl, S., Marin, G., Harper, M., and Green, W., *Industrial & Engineering Chemistry Research*, Vol. 49, No. 21, 2010, pp. 10399-10420.

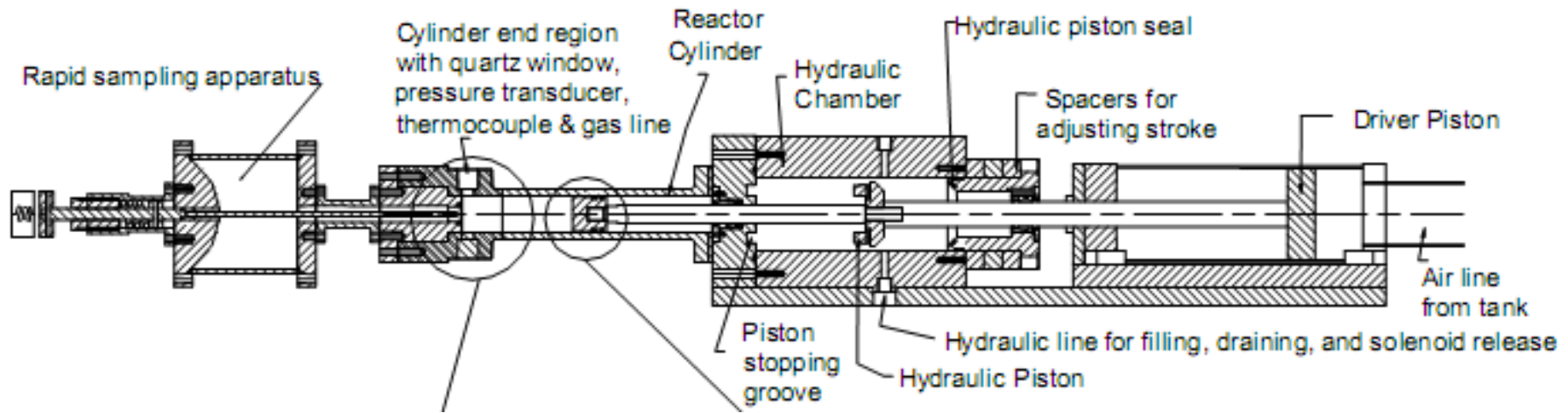
5. Heufer, K.A., Fernandes, R. X., Olivier, H., Beeckmann, J., and Peters, N., *Proceedings of the Combustion Institute*, Vol. 33, 2011, pp.359-366.

Objectives

- Provide complementary data to the previous studies using a Rapid Compression Machine
 - Focus on high pressure and low to intermediate temperature conditions
- Provide validation studies for the existing reaction mechanisms
 - Cover many pressure ranges, equivalence ratios, and fuel loading conditions
- Experimental Conditions:
 - $P_C=15, 30$ bar, $T_C=680-925$ K, $\phi=0.5, 1.0, 2.0$
 - O_2/N_2 ratio varied to independently find the effects of initial fuel and oxygen mole fractions

- Obtain experimental data for autoignition delays at elevated pressures and low-to-intermediate temperatures, using a heated rapid compression machine





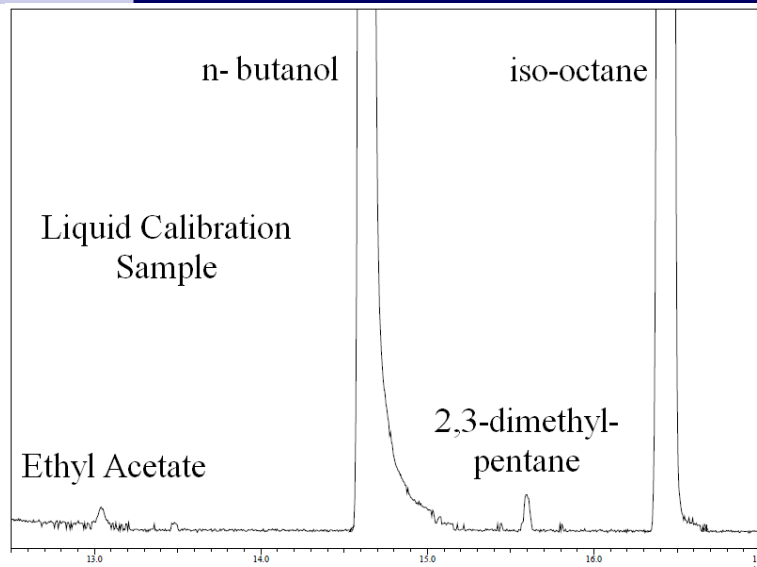
- Single, retractable piston
- Piston is pneumatically driven and hydraulically stopped, with compression time around 30 ms
- Piston is machined with crevices to contain roll-up vortex created by piston motion

- 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
- Fuel and oxidizer are preheated and mixed in a 15 L mixing tank to ensure homogeneity

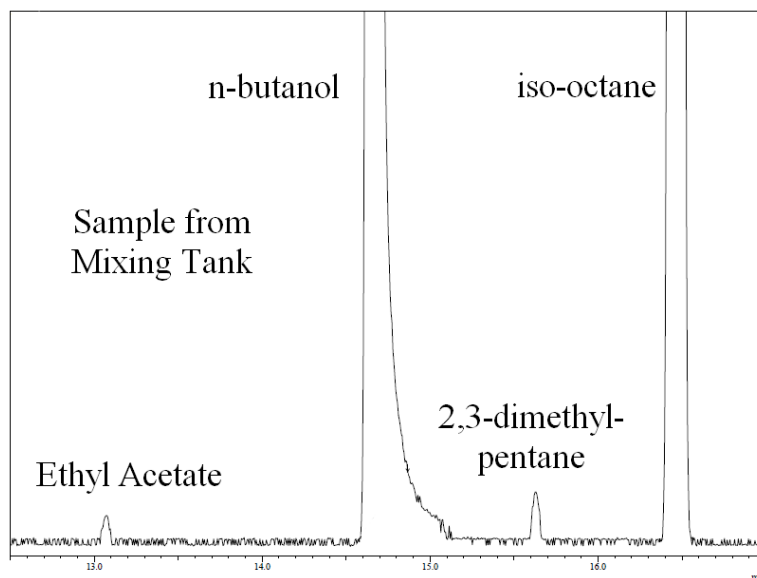
Check Mixture Composition (1)

- 2 goals:
 - Ensure fuel does not decompose while being held in the mixing tank
 - Ensure the expected composition is being created in the mixing tank
- Use GCMS to identify any decomposition products and quantify the concentration of *n*-butanol in the mixing tank
- *iso*-Octane is used as an internal standard for quantitative check of the concentration of *n*-butanol

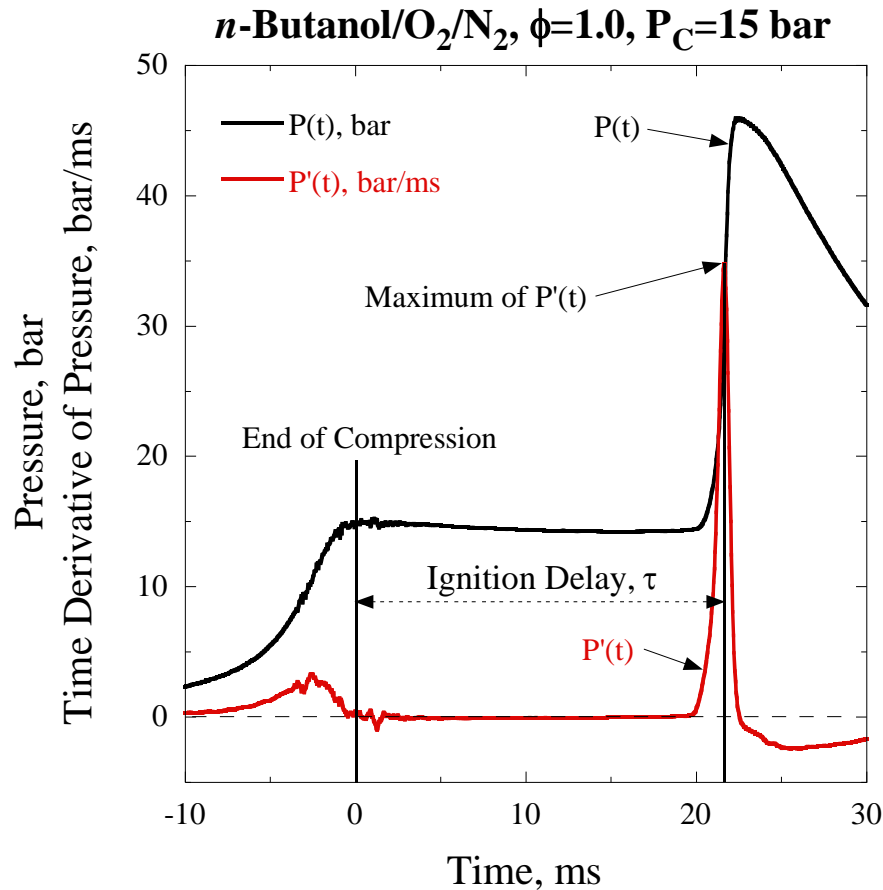
Mixture Composition Check (2)



- Liquid standard is created with known concentrations of *n*-butanol and *iso*-octane
- Small peaks are impurities from *n*-butanol and *iso*-octane
- There are no extra peaks in the chromatogram of the sample withdrawn from the mixing tank
- No decomposition!
- Concentration of *n*-butanol within 4% of expected value



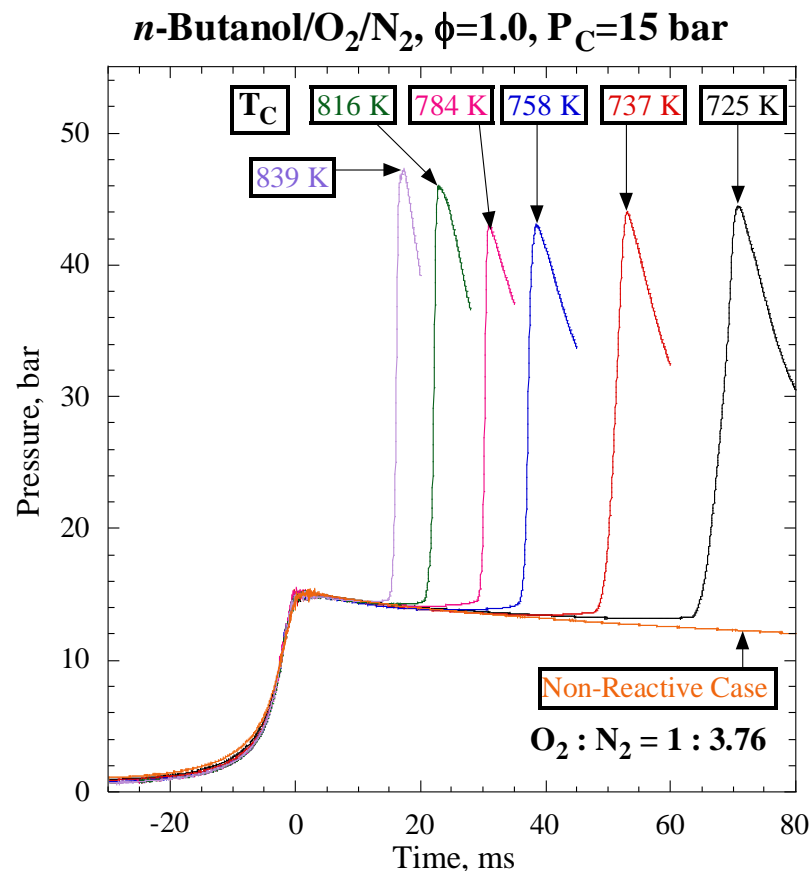
Definition of Ignition Delay



- 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 6 times to ensure repeatability

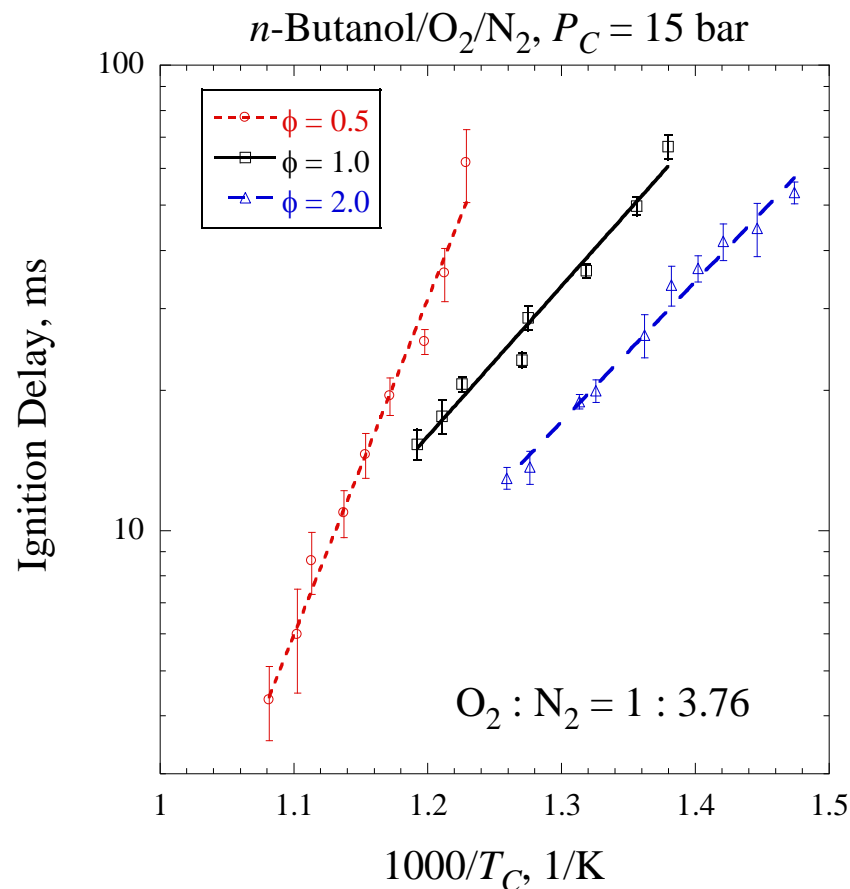
Experimental Results (1)

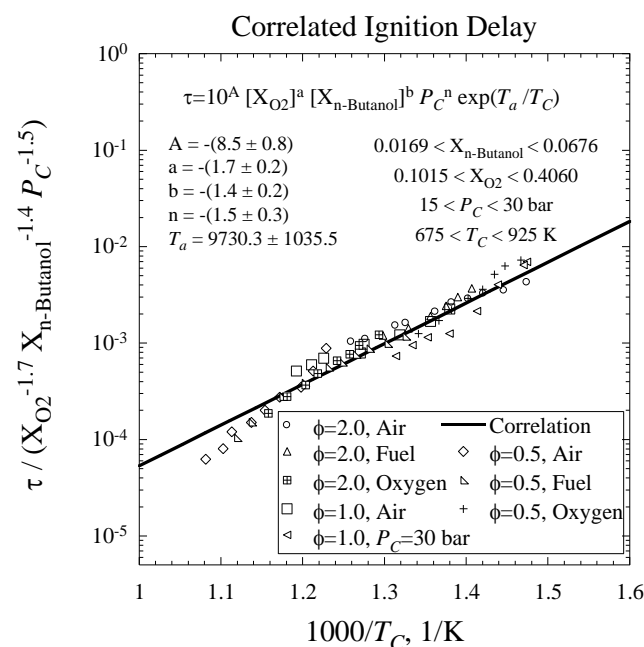
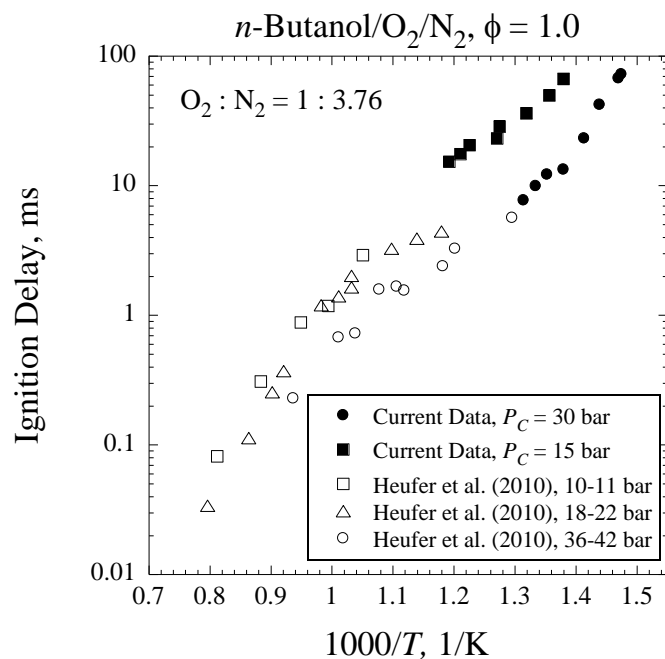
- Non-reactive case replaces oxygen with nitrogen to eliminate oxidation reactions but maintain the specific heat ratio
- Pressure traces for *n*-butanol deviate from non-reactive case
- Indicates minor pre-ignition heat release



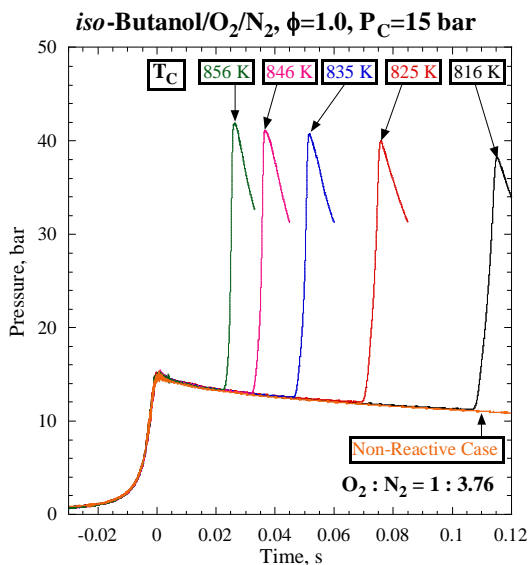
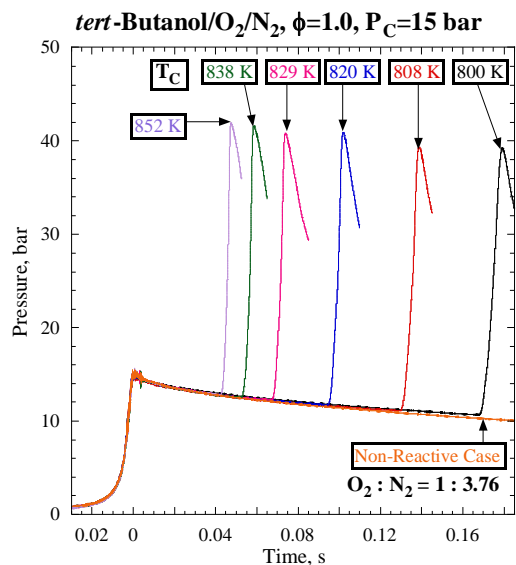
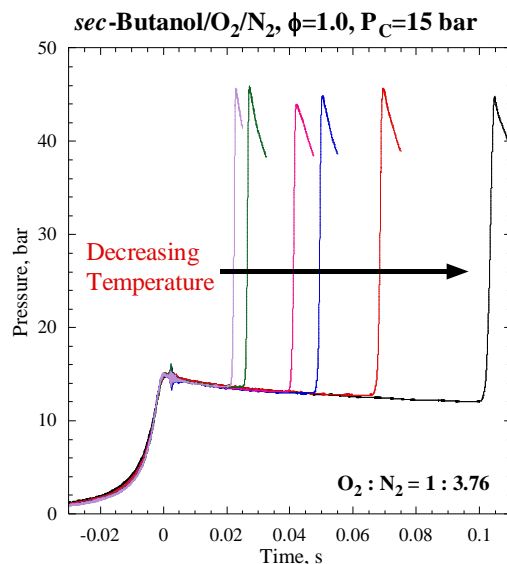
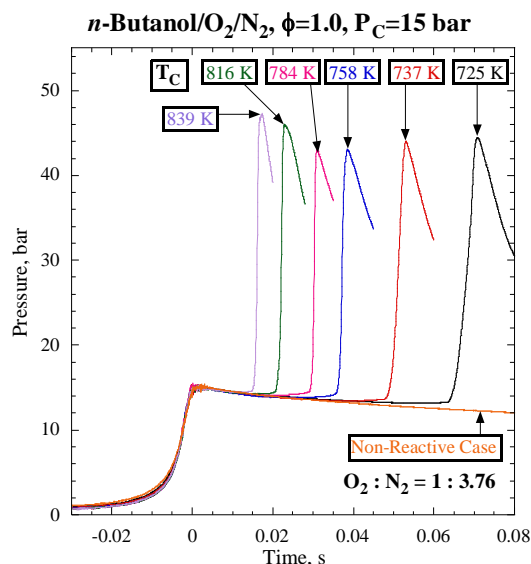
Experimental Results (2)

- Two apparent crossover points of the ignition delay for *n*-butanol
 - $\phi=0.5$ mixture becomes more reactive than the $\phi=1.0$ mixture at about 870 K
 - $\phi=0.5$ mixture becomes more reactive than the $\phi=2.0$ mixture at about 925 K
- This trend agrees with the work by Black et al.¹ and Moss et al.², who found that the lower equivalence ratios were more reactive in their high temperature shock tube studies

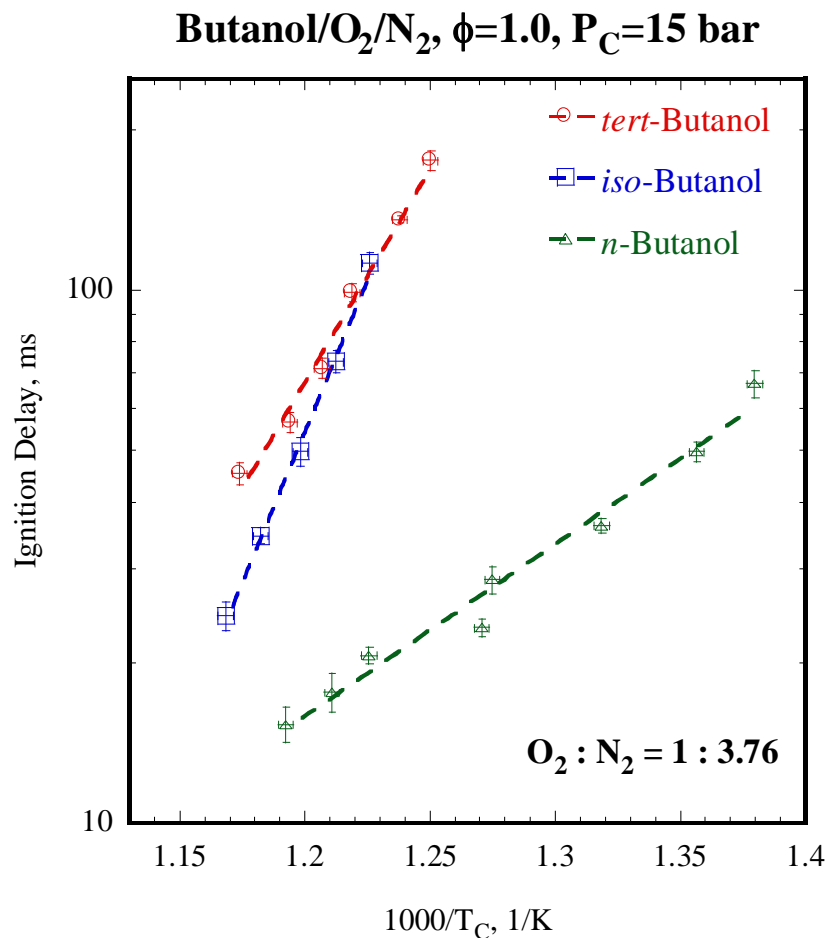




- Comparison of the data for *n*-butanol from this work and the work by Heufer et al.⁵ shows good agreement
- A correlation to the data from the current study produces a good regression for all the various fuel loading and pressure conditions considered
 - This correlation does not include data from other studies



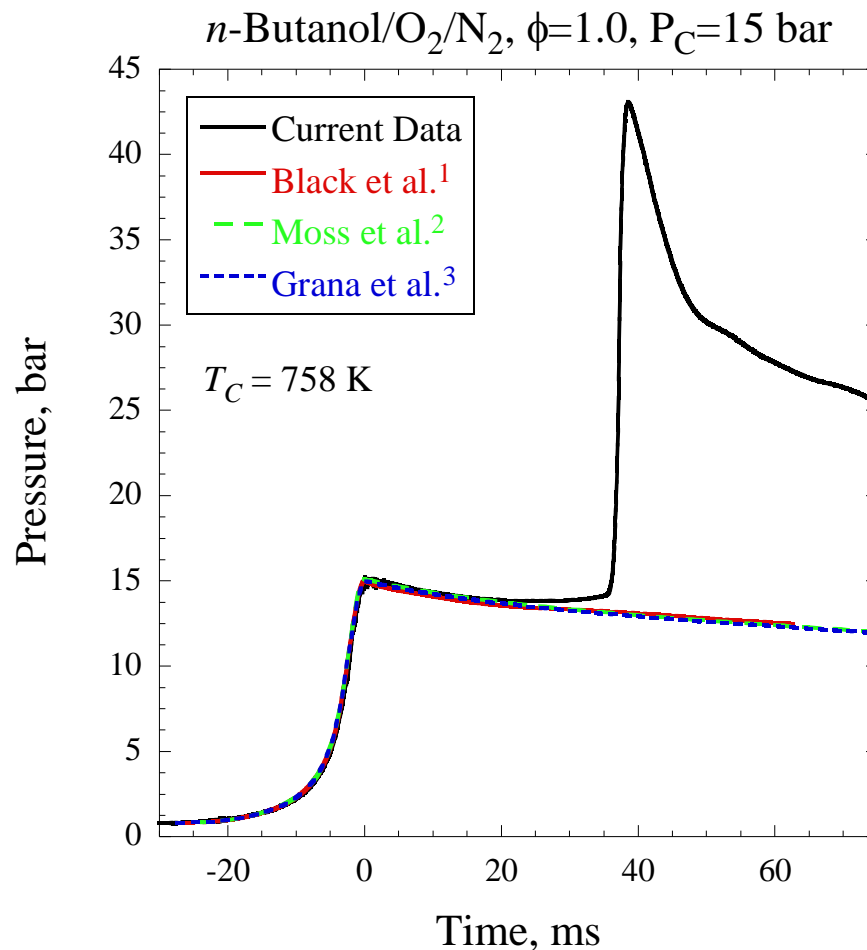
- No two-stage ignition or NTC region for any of the fuels under these conditions
- *tert*- and *iso*-butanol do not deviate significantly from the non-reactive pressure trace

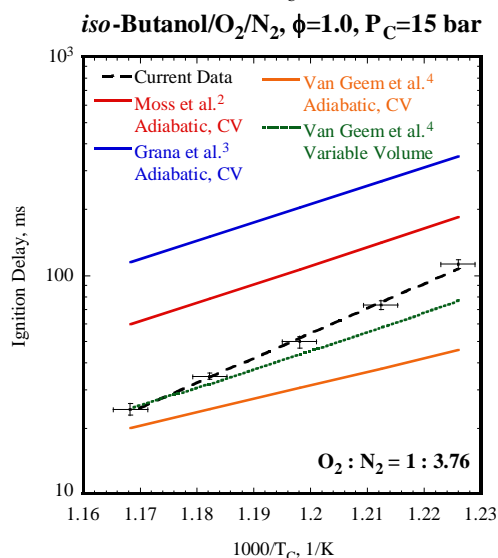
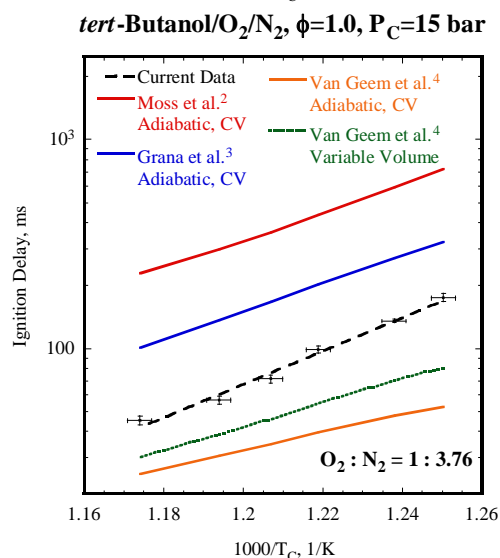
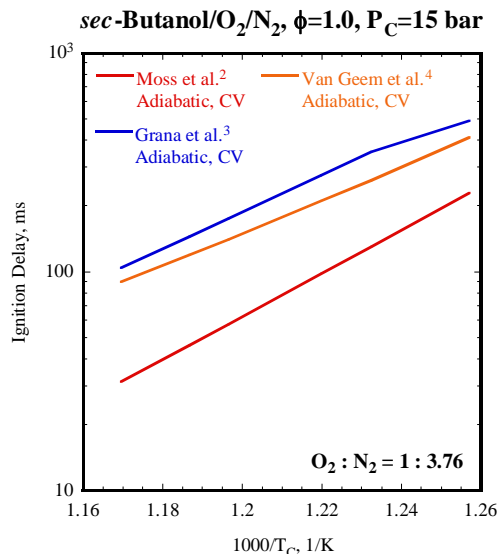
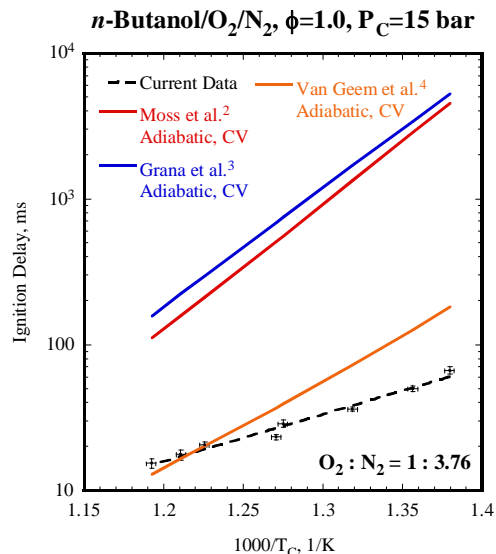


- *n*-Butanol is more reactive than *iso*-butanol, which is more reactive than *tert*-butanol
- As the temperature goes down, *tert*-butanol appears to become more reactive than *iso*-butanol

- Simulations of ignition delay are performed in CHEMKIN-PRO⁶ using four mechanisms available in the literature
- Constant Volume, Adiabatic simulations have initial conditions set to the pressure and temperature conditions at TDC, and neglect heat loss to the reactor walls
- Variable Volume simulations have the reactor volume as a controlled function of time
 - Used to compute T_C by matching the experimental pressure trace during compression
 - Include effects of heat loss after compression by including parameters deduced from non-reactive experimental cases

- For *n*-butanol, most of the reaction mechanisms do not have ignition near the experimental value despite matching the compression stroke quite well
- This is due to the fact that these do not include low temperature chemistry of *n*-butanol, which causes over-prediction of the ignition delay in this temperature range





- Most mechanisms over predict the ignition delay of all the isomers, but the mechanisms by Moss et al.² and Grana et al.³ do not include low temperature chemistry
- The mechanism by Van Geem et al.⁴ performs the best
- Variable Volume simulations improve results for *tert*- and *iso*-butanol

Summary

- New autoignition delay data has been collected for three isomers (*n*-, *tert*-, and *iso*-) of butanol at elevated pressure and low to intermediate temperature conditions
- These are, to the author's knowledge, the first data reported at these conditions for *n*-, *tert*-, and *iso*-butanol
- One reaction mechanism available in the literature predicts the ignition delay reasonably well for *n*-, *tert*- and *iso*-butanol

Acknowledgements

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