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Autoignition of *n*-Butanol at Elevated Pressure and Low- to Intermediate-Temperature Using a Rapid Compression Machine
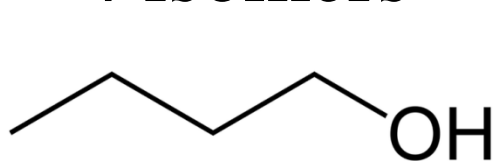
Bryan Weber

Prepared for
Master's Thesis Defense
July 21, 2010

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- Background
- Literature Review
- Experimental Apparatus
- RCM Test Matrix
- Check Mixture Composition
- RCM Results and Discussion
- Summary

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- Environmental and geopolitical concerns are driving demand for a new type of fuel

- This new fuel should be renewable and able to be produced domestically

- Biofuels, and in particular alcohols, fit these criteria very well

- Current technology requires blending biofuel with conventional fuel

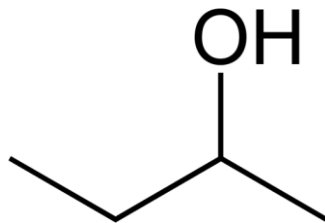- Ethanol is one of the most popular biofuels for transportation use

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- Butanol is a biofuel

  – Can be produced from bio-waste fermentation in bacteria genetically designed to increase butanol yield

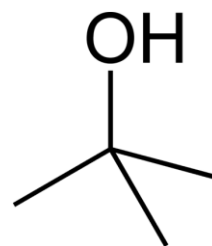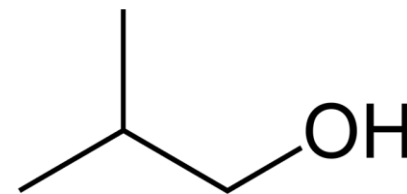- Formula – C_4H_9OH ($C_4H_{10}O$)

- 4 isomers

OH

OH

OH

OH

n-butanol
bio-butanol
1-butanol

sec-butanol

tert-butanol

iso-butanol

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- Butanol is a good test case for developing new fuels

- Butanol is the smallest alcohol with primary, secondary and tertiary alcohol groups

- The chemistry of butanol can be extended to higher alcohols

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- *n*-Butanol has several advantages over ethanol:
  - Higher specific energy
  - Less miscible with water
  - Less corrosive to engine parts and pipes
  - Lower vapor pressure
- These properties enable:
  - Using current oil and gasoline pipelines for fuel transport
  - Higher mixing ratios with gasoline
  - Improved volumetric fuel economy (mpg) over ethanol
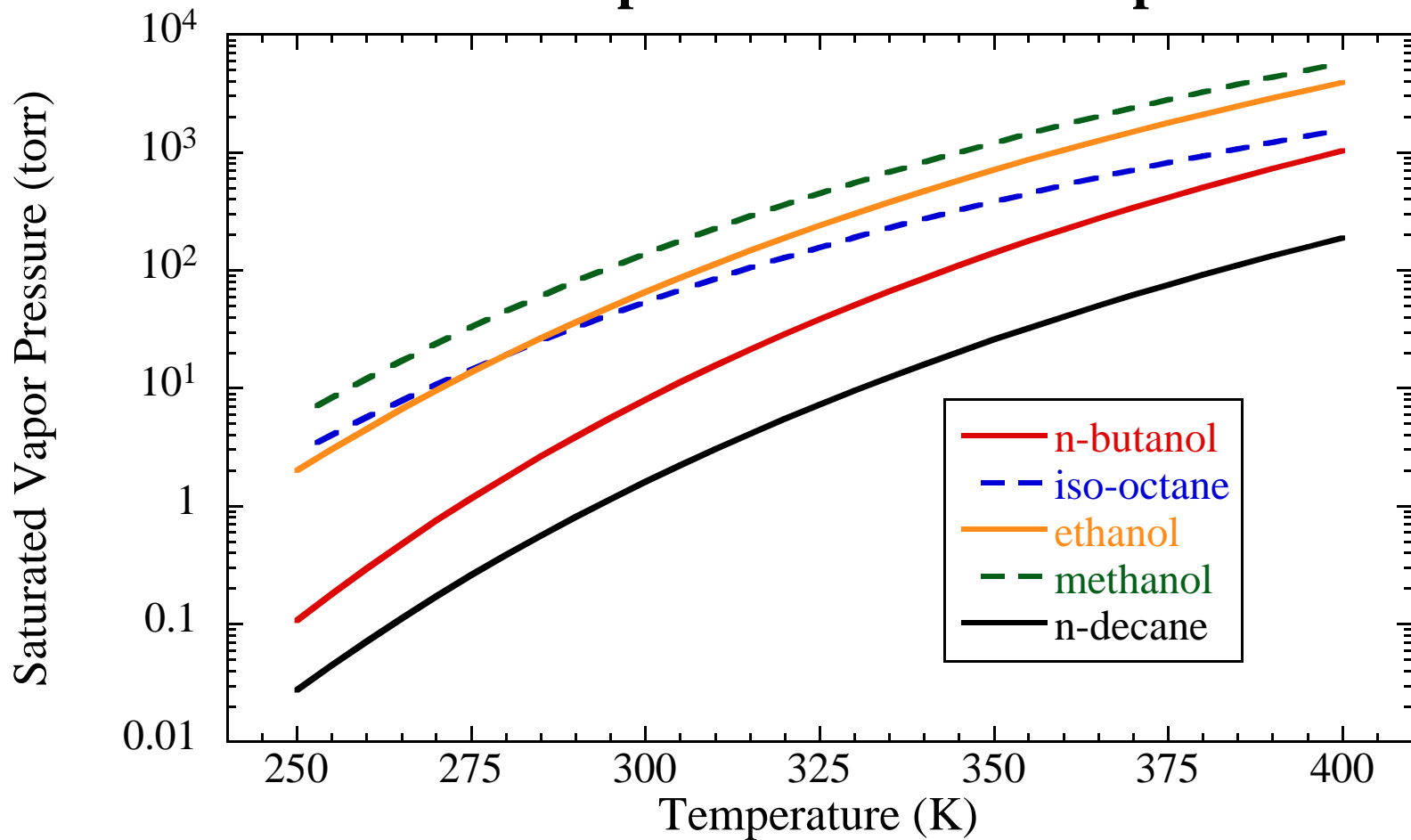 - Reducing evaporative emissions and risk of explosion

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Fuel	Lower Heating Value [MJ/kg]	Volumetric Energy Density [MJ/L]	Research Octane Number, RON	Motor Octane Number, MON
Gasoline	42.5	32	92-98	82-88
Methanol	19.9	16	136	104
Ethanol	28.9	20	129	102
1-Butanol	33.1	29	96	78

J.T. Moss, et. al, "An Experimental and Kinetic Modeling Study of the Oxidation of the Four Isomers of Butanol," *The Journal of Physical Chemistry A*, vol. 112, 2008, pp. 10843-10855.

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Saturated Vapor Pressure vs. Temperature

Legend:
- n-butanol (red solid)
- iso-octane (blue dashed)
- ethanol (orange solid)
- methanol (green dashed)
- n-decane (black solid)

Yaws, C.L. "Chemical Properties Handbook." McGraw-Hill, 1999

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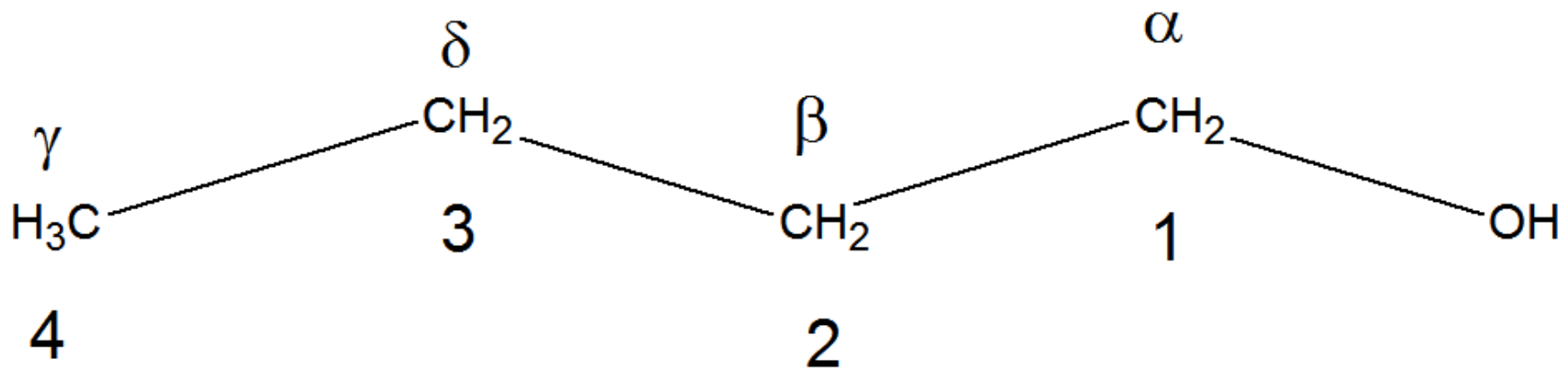
n-Butanol

- Carbons in the skeleton are numbered by their distance from the alcohol group

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- ~15 studies directly relevant to butanol kinetics.

- Dagaut *et al.*[1,2] have done JSR experiments at 1 and 10 atm, and laminar flame speed and opposed-flow diffusion flame experiments for n-butanol.

- Zhang *et al.*[3] performed a motored engine study with *n*-butanol and reported combustion intermediates in a temperature range similar to the one considered here

1. S.M. Sarathy, P. Dagaut, et. al., "An experimental and kinetic modeling study of n-Butanol combustion," *Combustion and Flame*, 2009.

2. P. Dagaut, et. al., "A chemical kinetic study of n-Butanol oxidation at elevated pressure in a jet stirred reactor," *Proceedings of the Combustion Institute*, vol. 32, 2009, pp. 229-237.

3. Y. Zhang, A.L. Boehman. "Oxidation of 1-butanol and a mixture of n-heptane/1-butanol in a motored engine." *Combustion and Flame*. In Press, 2010. doi:10.1016/j.combustflame.2010.04.017

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- Black *et al.*[4] (NUI) have done shock tube studies for *n*-butanol from 1100-1800 K and 1, 2.6 and 8 atm over ϕ=0.5, 1, 2 and fuel mole percents of 0.6%, 0.75% and 3.5%.

4. G. Black, et. al., "Bio-Butanol: Combustion properties and a detailed kinetic model," *Combustion and Flame,* vol. 157, 2010 pp. 363-373.

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- 243 species

- 1446 reactions

- Mechanism based on updated C_4 chemistry from the same group, with an added *n*-butanol sub-mechanism taken from EXGAS and modified as appropriate

- Validated against shock tube data

- Ignition delay validation range:
  - T = 1100 – 1800 K
  - P = 1 – 8 atm

- Black *et al.*[4] (NUI)

- Harper *et al.*[5] (MIT) have created a mechanism for *n*-butanol based on the previous experiments, a pyrolysis experiment and a butanol-doped methane flame experiment

4. G. Black, et. al., "Bio-Butanol: Combustion properties and a detailed kinetic model," *Combustion and Flame,* vol. 157, 2010 pp. 363-373.

5. M. Harper, W. Green, et. al., "Comprehensive Reaction Mechanism for n-Butanol Pyrolysis and Combustion", unpublished manuscript.

- 189 species

- 2022 reactions

- Created automatically from Reaction Mechanism Generator, open-source software from MIT

  – Initial "Seed" Mechanisms:

  – GRI-Mech (excluding Nitrogen chemistry)

  – Ethanol mechanism by Marinov (not discussed here)

- Validated against JSR, flame, shock tube and pyrolysis data

- Ignition delay validation range:

  – T = 1100-1800 K

  – P = 1 – 8 atm

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- Black *et al.*[4] (NUI)

- Harper *et al.*[5] (MIT)

- Grana *et al.*[6] (Milano) have performed counterflow diffusion flame experiments of *n*-butanol and *iso*-butanol and created a reaction mechanism

4. G. Black, et. al., "Bio-Butanol: Combustion properties and a detailed kinetic model," *Combustion and Flame,* vol. 157, 2010 pp. 363-373.

5. M. Harper, W. Green, et. al., "Comprehensive Reaction Mechanism for n-Butanol Pyrolysis and Combustion", unpublished manuscript.

6. R. Grana, *et al.* "An experimental and kinetic modeling study of combustion of isomers of butanol." *Combustion and Flame*. In Press, 2010. doi:10.1016/j.combustflame.2010.05.009.

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Milano Mechanism

- 354 species

- 10,127 reactions

- Includes all four isomers of butanol

- Based on C_0-C_{16} semi-detailed mechanism previously developed by the same group, which includes low temperature chemistry of most species but not the butanols

- Validated against JSR, flame, and shock tube data

- Ignition delay validation range:
  - T = 1100-1800 K
  - P = 1 – 8 atm

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- Black *et al.*[4] (NUI)

- Harper *et al.*[5] (MIT)

- Grana *et al.*[6] (Milano)

- Moss *et al.*[7] (RPI) have done shock tube studies for all four isomers of butanol at 1 and 4 bar and T=1200 to 1800 K over ϕ=0.5, 1, 2 and fuel mole percents of 0.25%, 0.5% and 1%.

4. G. Black, et. al., "Bio-Butanol: Combustion properties and a detailed kinetic model," *Combustion and Flame,* vol. 157, 2010 pp. 363-373.

5. M. Harper, W. Green, et. al., "Comprehensive Reaction Mechanism for n-Butanol Pyrolysis and Combustion", unpublished manuscript.

6. R. Grana, *et al.* "An experimental and kinetic modeling study of combustion of isomers of butanol." *Combustion and Flame*. In Press, 2010. doi:10.1016/j.combustflame.2010.05.009.

7. J.T. Moss, et. al, "An Experimental and Kinetic Modeling Study of the Oxidation of the Four Isomers of Butanol," *The Journal of Physical Chemistry A*, vol. 112, 2008, pp. 10843-10855.

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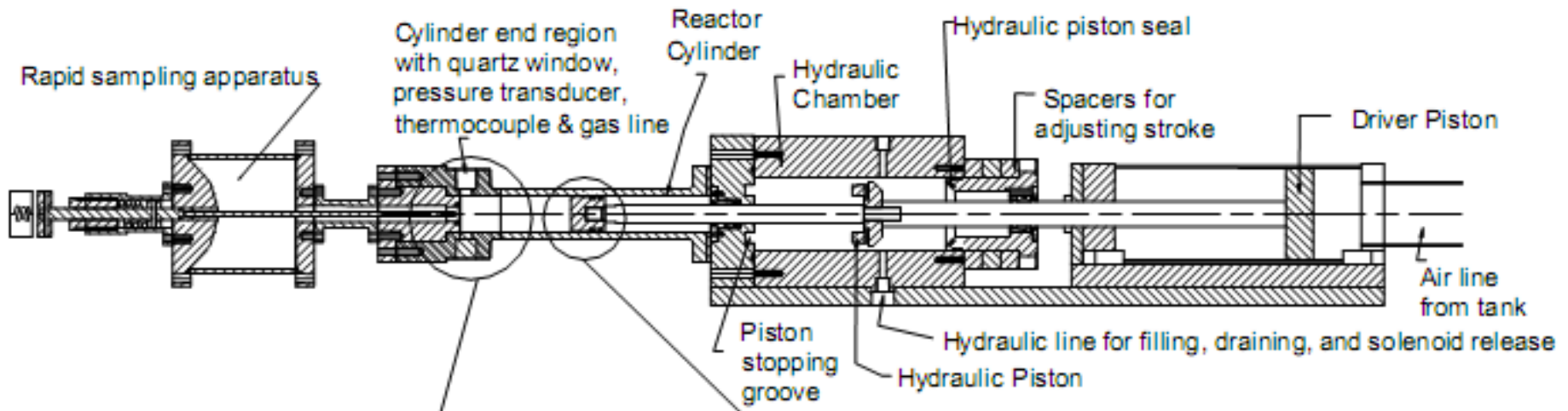
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- 161 species
- 1250 reactions
- Covers all four isomers of butanol
- Generated by EXGAS software which creates a 3 part mechanism
  - Primary mechanism: Initial organic compounds and oxygen
  - Lumped secondary mechanism: Reactions which consume the products of the primary mechanism, but not contained in the third mechanism
  - $C_0 - C_2$ complete reaction base coupled with a $C_3 - C_4$ unsaturated reaction base
- Validated against shock tube data
- Ignition delay validation range:
  - $T = 1200 - 1700$ K
  - $P = 1 - 4$ bar

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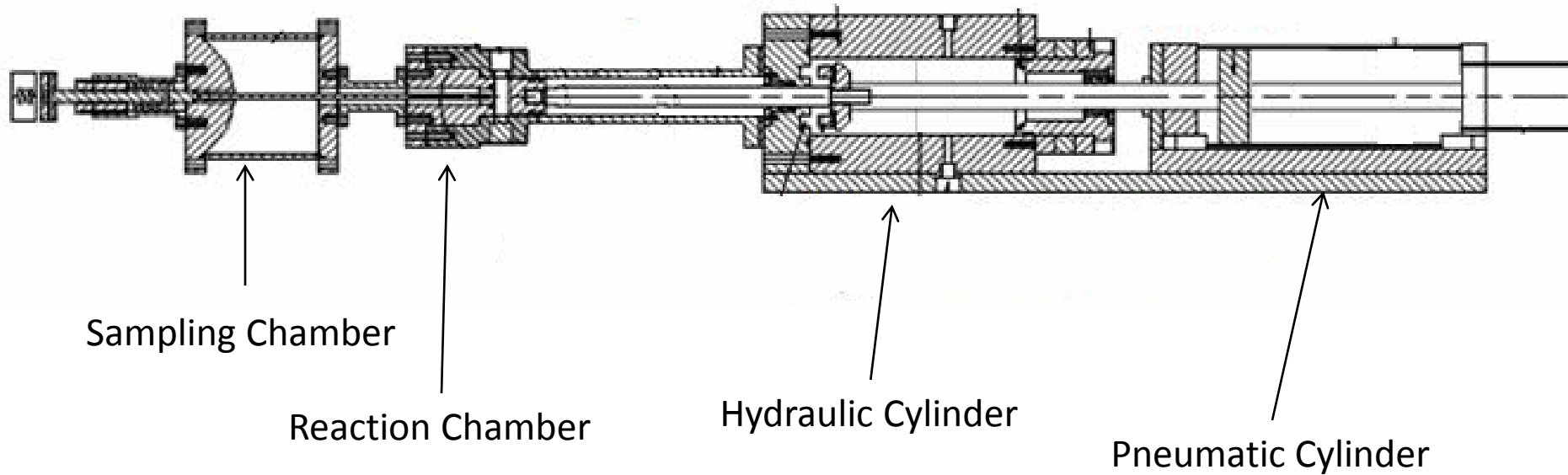
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- None of the mechanisms have been validated at lower temperature than 1100 K for ignition delay
- None of the mechanisms have been validated at pressures higher than 10 atm (for JSR) or 8 atm (for shock tube)
- High-pressure, low-temperature combustion conditions are relevant to several advanced low emissions engines
  - Homogeneous Charge Compression Ignition (HCCI)
  - Low Temperature Diesel engines
- Comprehensive reaction mechanisms require validation over a wide range of experimental conditions

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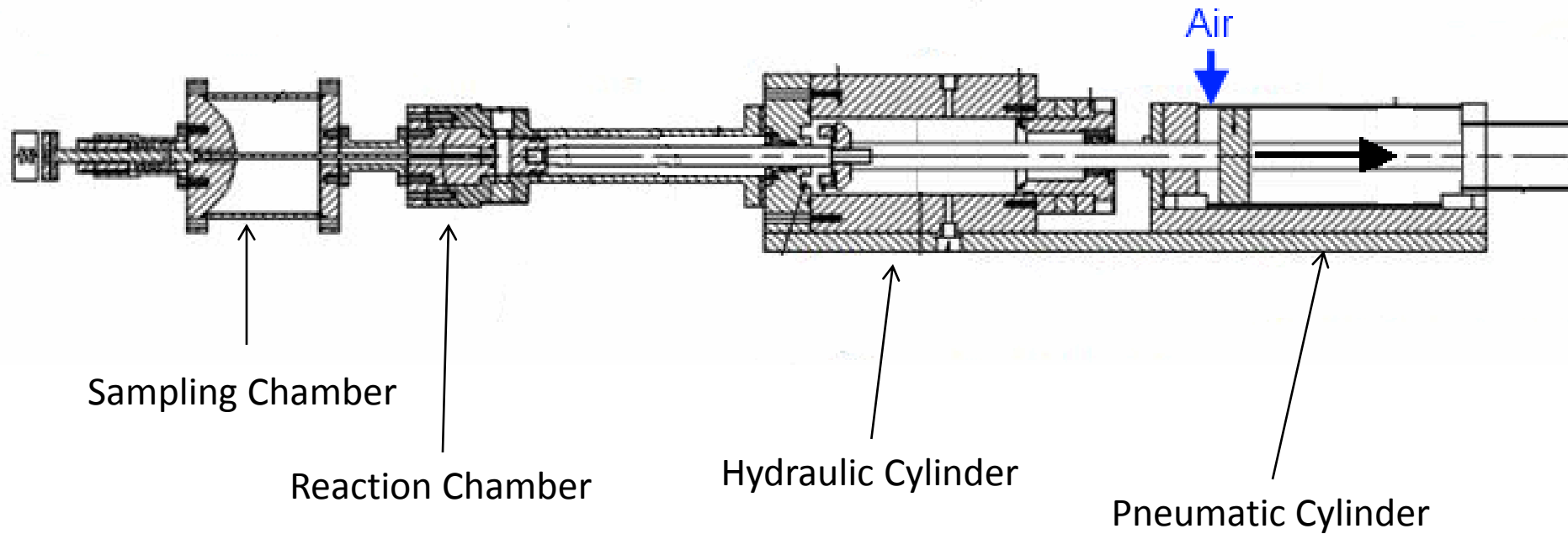
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- Obtain experimental data for autoignition delays at elevated pressures and low-to-intermediate temperatures, using a heated rapid compression machine

Cylinder end region with quartz window, pressure transducer, thermocouple & gas line

Reactor Cylinder

Hydraulic piston seal

Rapid sampling apparatus

Hydraulic Chamber

Spacers for adjusting stroke

Driver Piston

Piston stopping groove

Hydraulic Piston

Hydraulic line for filling, draining, and solenoid release

Air line from tank

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Operating Procedure of the Rapid Compression Machine (RCM)

Sampling Chamber

Reaction Chamber

Hydraulic Cylinder

Pneumatic Cylinder

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Operating Procedure of the Rapid Compression Machine (RCM)

Sampling Chamber

Reaction Chamber

Hydraulic Cylinder

Pneumatic Cylinder

Operating Procedure of the Rapid Compression Machine (RCM)

Sampling Chamber

Reaction Chamber

Hydraulic Cylinder

Pneumatic Cylinder

Operating Procedure of the Rapid Compression Machine (RCM)

Sampling Chamber

Reaction Chamber

Oil

Hydraulic Cylinder

Pneumatic Cylinder

Operating Procedure of the Rapid Compression Machine (RCM)

Sampling Chamber

Reaction Chamber

Hydraulic Cylinder

Pneumatic Cylinder

Operating Procedure of the Rapid Compression Machine (RCM)

Premixed Fuel and Air

Sampling Chamber

Reaction Chamber

Hydraulic Cylinder

Pneumatic Cylinder

Operating Procedure of the Rapid Compression Machine (RCM)

Sampling Chamber

Reaction Chamber

Hydraulic Cylinder

Pneumatic Cylinder

Operating Procedure of the Rapid Compression Machine (RCM)

Sampling Chamber

Reaction Chamber

Hydraulic Cylinder

Pneumatic Cylinder

Operating Procedure of the Rapid Compression Machine (RCM)

Sampling Chamber

Reaction Chamber

Hydraulic Cylinder

Pneumatic Cylinder

Operating Procedure of the Rapid Compression Machine (RCM)

Sampling Chamber

Reaction Chamber

Oil

Hydraulic Cylinder

Pneumatic Cylinder

Operating Procedure of the Rapid Compression Machine (RCM)

Sampling Chamber

Reaction Chamber

Hydraulic Cylinder

Pneumatic Cylinder

Operating Procedure of the Rapid Compression Machine (RCM)

Release the Puncture Mechanism

Sampling Chamber

Reaction Chamber

Hydraulic Cylinder

Pneumatic Cylinder

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Operating Procedure of the Rapid Compression Machine (RCM)

Sampling Chamber

Reaction Chamber

Hydraulic Cylinder

Pneumatic Cylinder

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- Compression Ratio: 8 to 12

- Initial Temperature: up to 140°C

- Compressed Pressure: 7 to 45 bar

- Compressed Temperature: 650-1100K

- Compression Time: ~30 ms

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- RCM Experimental Conditions for *n*-butanol
  - Compressed Pressure: P_C = 7, 15, 30 bar
  - Compressed Temperature: T_C = 650-900 K
  - Fuel/Air Equivalence Ratio: 0.5, 1.0, 2.0
  - Vary initial O_2 mole fraction at constant initial fuel mole fraction
  - Vary initial fuel mole fraction at constant initial O_2 mole fraction
  - Vary Inert Composition: Ar, N_2

- Shock Tube Experiments for *n*-butanol[4,7]
  - Fuel Mole Percent = 1-3.5%
  - Compressed Pressure: P_C = 1-8 bar
  - Compressed Temperature: T_C = 1100-1800 K

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Mole Percentage (%)				Equivalence Ratio	Pressure (bar)
n-Butanol	O_2	N_2	Ar	ϕ	P_C
2.96	20.39	76.65	0.00	0.87	30
2.96	20.39	0.00	76.65	0.87	7
3.38	20.30	76.32	0.00	1.0	15
3.38	20.30	76.32	0.00	1.0	30
1.72	20.65	77.63	0.00	0.5	15
6.54	19.63	73.83	0.00	2.0	15
3.38	40.60	56.02	0.00	0.5	15
3.38	10.15	86.47	0.00	2.0	15
1.69	20.30	78.01	0.00	0.5	15
6.76	20.30	72.94	0.00	2.0	15

Oxidizer = Air	Vary O_2 Mole Fraction	Vary Fuel Mole Fraction

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

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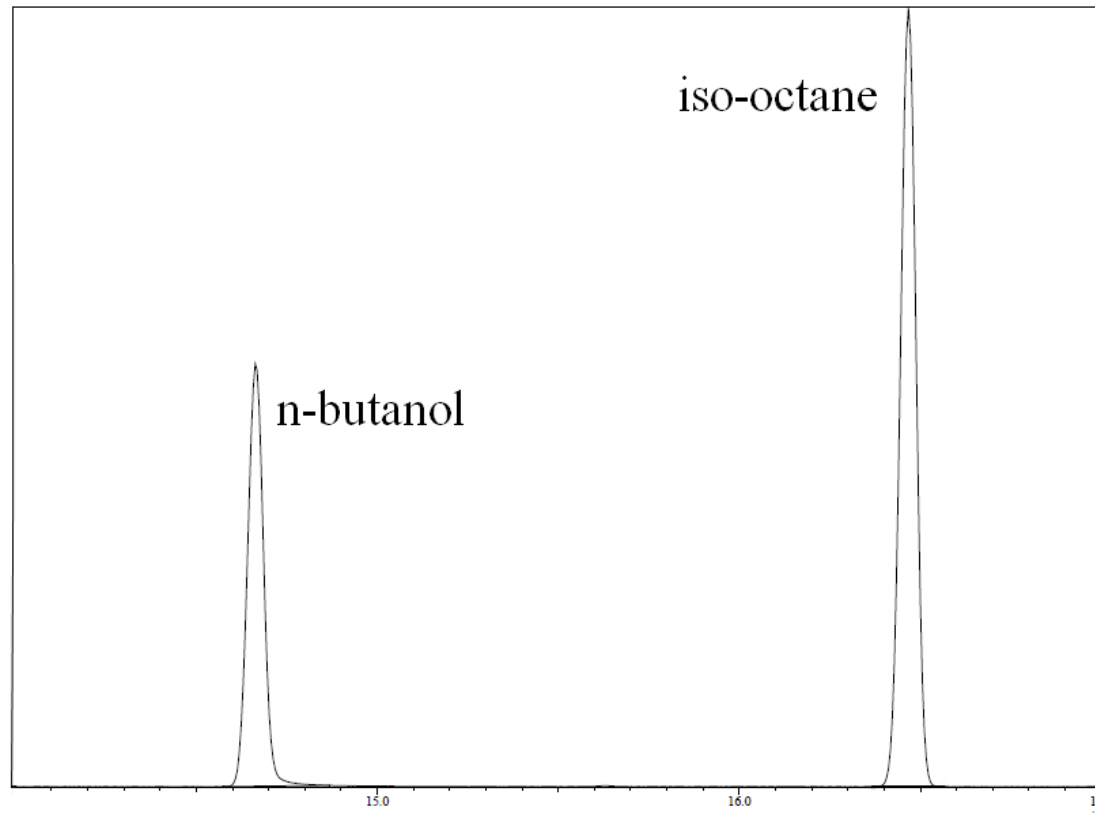
- RTX-1PONA column and temperature program used in this analysis provides good separation of *iso*-octane and *n*-butanol

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Liquid Calibration Sample

n- butanol

iso-octane

2,3-dimethyl-pentane

Ethyl Acetate

Sample from Mixing Tank

n-butanol

iso-octane

2,3-dimethyl-pentane

Ethyl Acetate
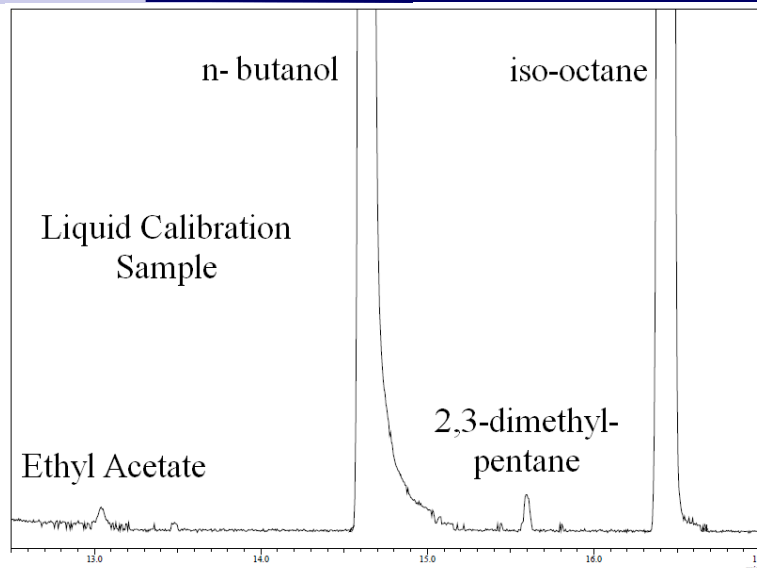
- Liquid standard is created with known concentrations of *n*-butanol and *iso*-octane
- Small peaks are impurities from *n*-butanol and *iso*-octane
- There are no extra peaks in the chromatogram of the sample withdrawn from the mixing tank
- No decomposition!
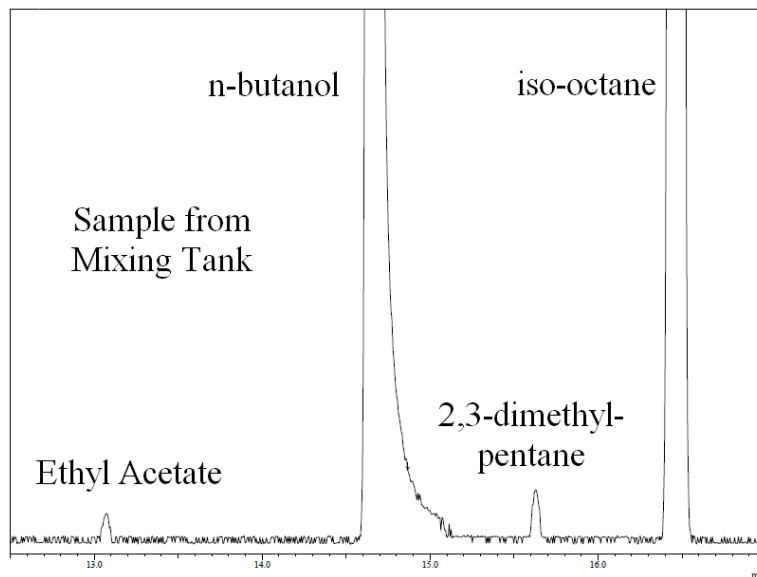
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- Response factor of *n*-butanol to *iso*-octane is calculated based on peak areas from the liquid sample

- Response factor and known concentration of *iso*-octane in the mixing tank are used to calculate the concentration of *n*-butanol in the mixing tank

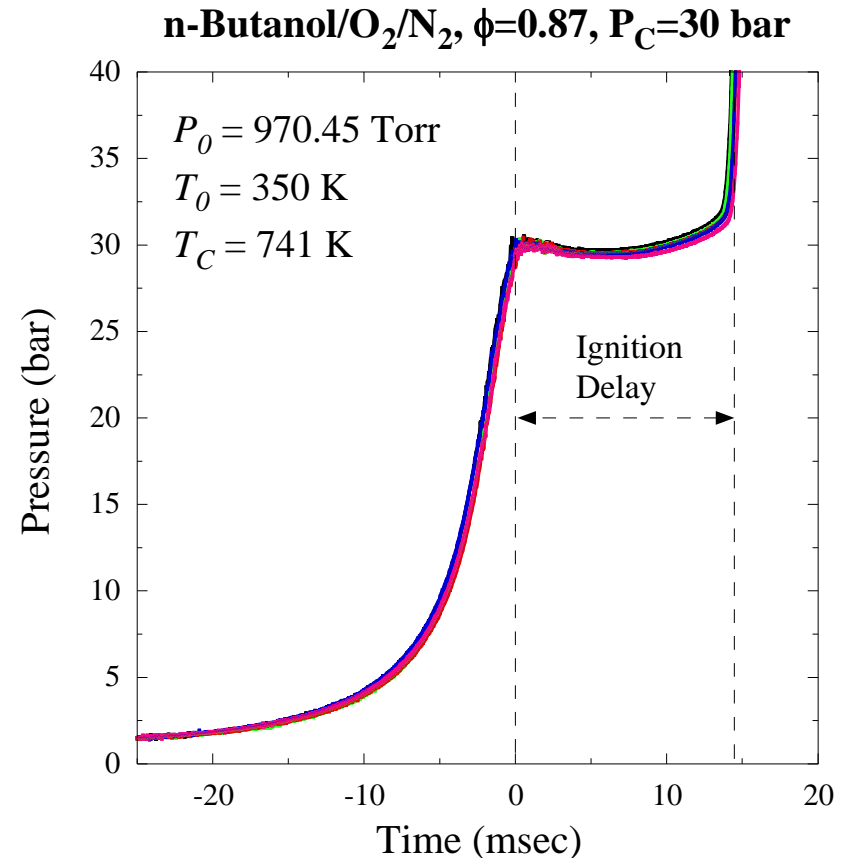- Concentration of *n*-butanol is within 4% of the expected value

Response Factor Determination		
1-butanol Peak Area	10788294	
iso-octane Peak Area	20061355	
Response Factor	**0.349076**	

Concentration of 1-Butanol		
Concentration of iso-octane in mixing tank		0.0111

Sample #	*1-butanol Peak Area*	*iso-octane Peak Area*	*Concentration of 1-butanol*
1	11165856	22824035	0.015653
2	8920318	19145108	0.014908
3	18182941	35118170	0.016566
4	15224721	27259402	0.01787
5	19145886	34907200	0.017549
		Average	**0.0165**
		Expected	**0.0172**
		Deviation (%)	**4.05**

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Experimental Reproducibility

- Representative trace from at least 6 concordant runs for determining ignition delay.

- Pressure is measured; P_C is the pressure at Top Dead Center (TDC)

- Temperature at TDC (T_C) is computed by matching the simulated and experimental pressure traces during compression stroke

n-Butanol/O_2/N_2, ϕ=0.87, P_C=30 bar

P_0 = 970.45 Torr
T_0 = 350 K
T_C = 741 K

Ignition Delay

Pressure (bar)

Time (msec)

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- End of Compression is determined to be at TDC

- The location of inflection point in the pressure trace (found by the maximum of the pressure derivative) identifies the point of ignition

- The ignition delay is the time difference between the end of compression and the point of ignition

n-Butanol/O_2/N_2, ϕ=1.0, P_C=15 bar

Pressure (bar) / Time Derivative of Pressure (bar/msec) vs. Time (msec)

— Pressure
— dP/dt (bar/msec)

P(t)
Maximum of dP/dt
End of Compression
τ
dP/dt

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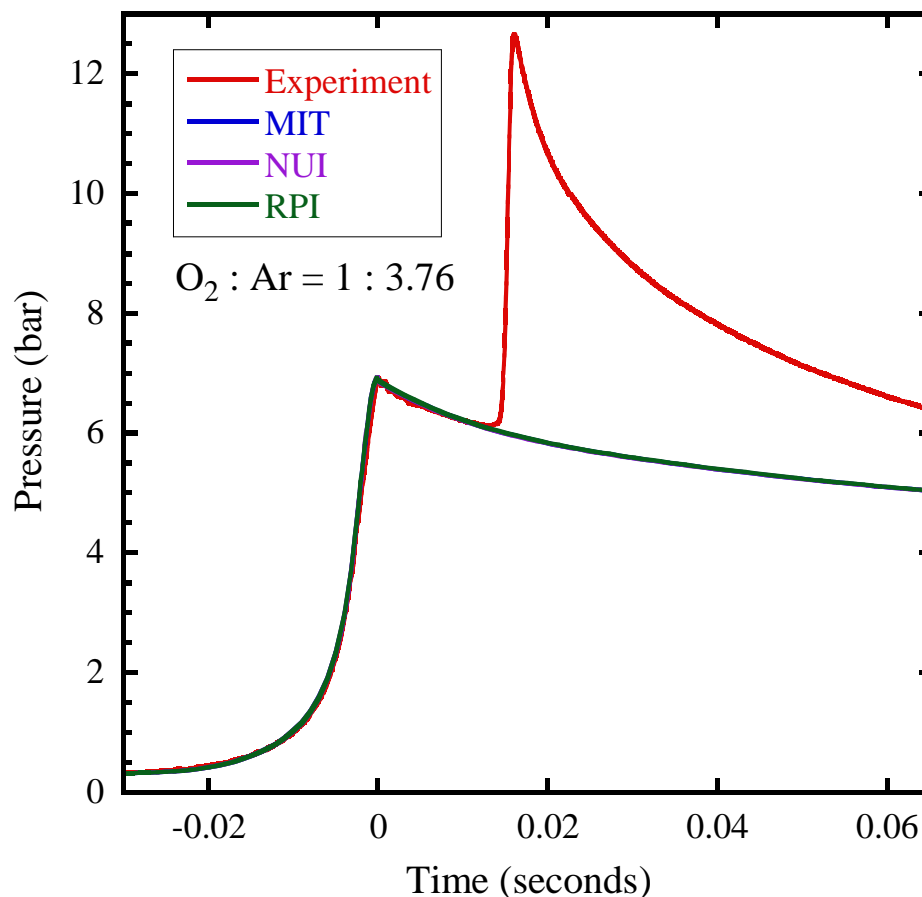University of
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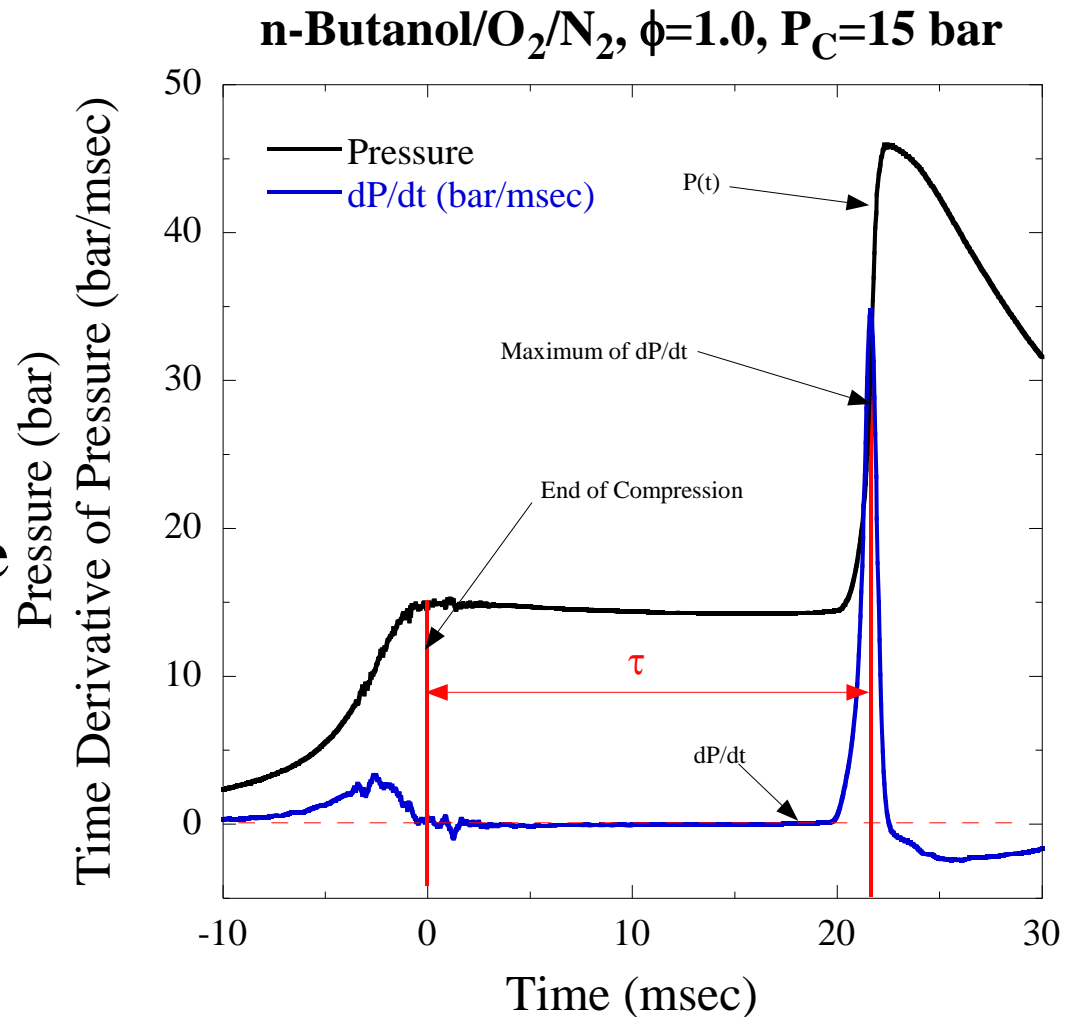
- SENKIN/CHEMKIN-III and CHEMKIN-PRO are used to model the ignition delay

- RCM Simulation

  – Reactor volume is a specified function of time

  – Includes compression stroke and post-compression events

- Shock Tube Simulation

  – Reactor is at constant volume and is adiabatic

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- During RCM simulations, none of the existing reaction mechanisms ignite within the limits of the experiment

n-Butanol/O$_2$/Ar, ϕ=0.87, P$_C$ =7 bar, T$_C$ =861K

O$_2$: Ar = 1 : 3.76

Legend: Experiment, MIT, NUI, RPI

Axes: Pressure (bar) vs Time (seconds)

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n-Butanol/O_2/N_2, ϕ=0.5, P_C =15 bar

Pressure (bar) vs Time (seconds)

906 K 898 K
924 K
879 K
866 K
853 K
834 K
T_C
824 K
813 K

$O_2 : N_2 = 1 : 3.76$

Time (seconds)
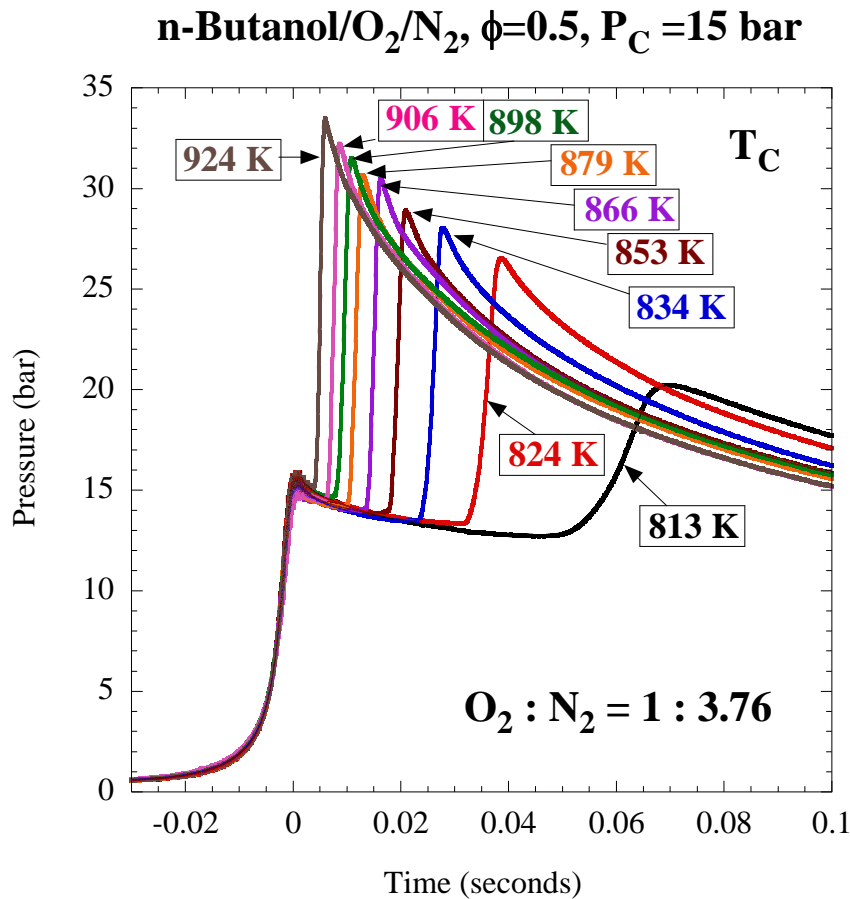
- Increasing compressed temperature reduces ignition delay monotonically

- No Negative Temperature Coefficient region found for *n*-butanol in these experiments
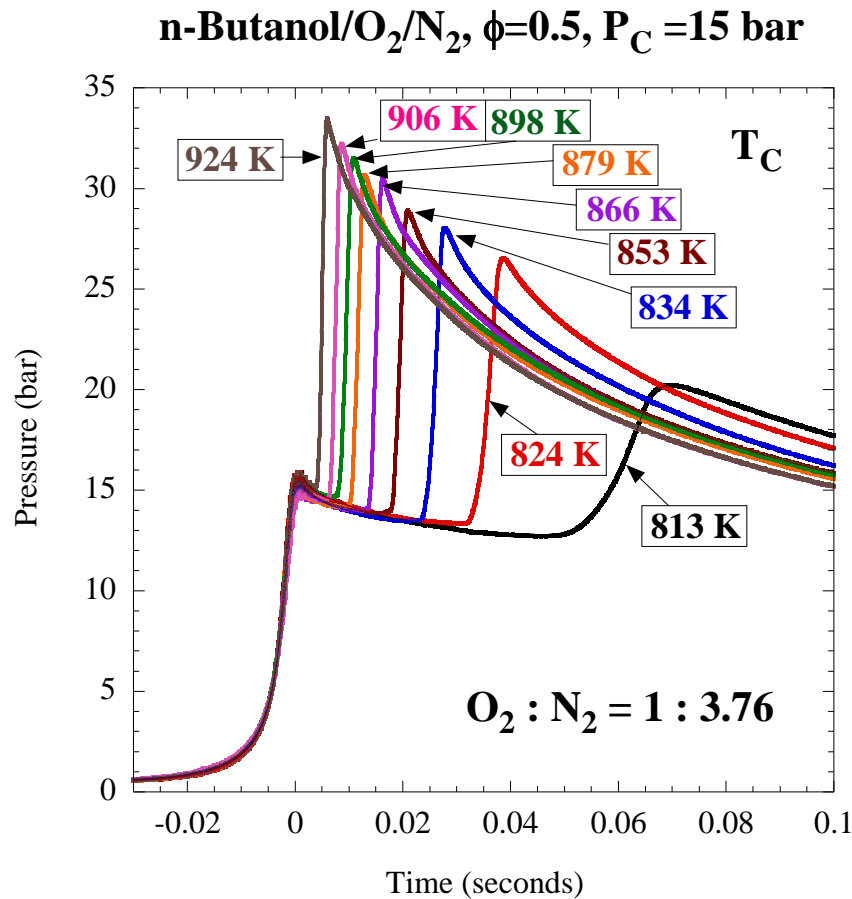
n-Butanol/O$_2$/N$_2$, ϕ=0.5, P$_C$ =15 bar

- No two stage ignition found for any condition in these experiments

This is a Typical 2-stage Ignition Delay
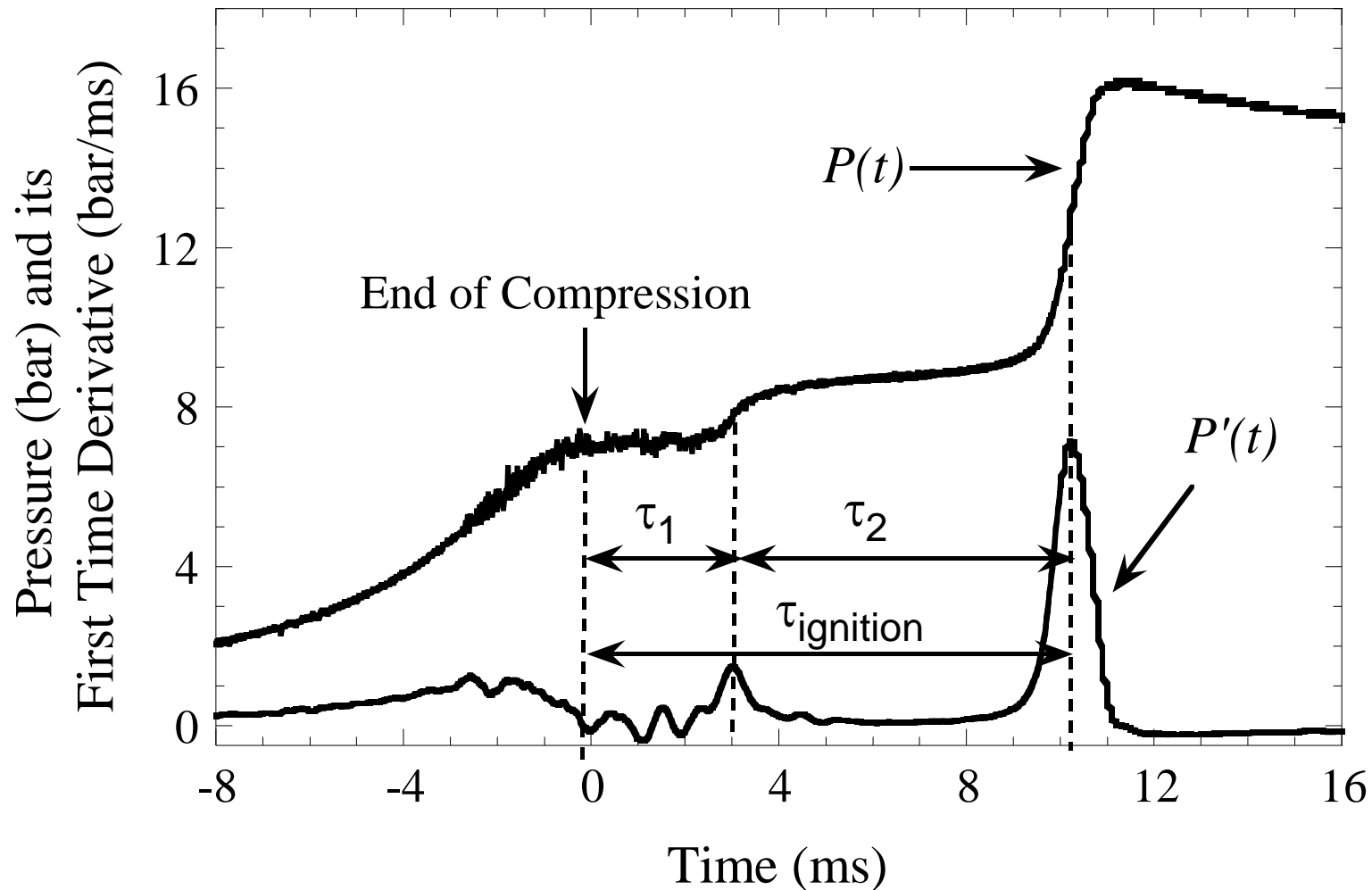
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n-Butanol/O$_2$/N$_2$, ϕ=0.5, P$_C$ =15 bar

Pressure (bar)

35

30

25

20

15

10

5

0

924 K
906 K 898 K
T$_C$
879 K
866 K
853 K
834 K
824 K
813 K

O$_2$: N$_2$ = 1 : 3.76

-0.02   0   0.02   0.04   0.06   0.08   0.1

Time (seconds)

- No two stage ignition found for any condition in these experiments

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n-Butanol/O$_2$/N$_2$, ϕ = 1.0, P$_C$ =15 bar

O$_2$: N$_2$ = 1 : 3.76

- - - - Current Data
—— MIT
—— NUI
—— RPI
—— Milano

Ignition Delay (seconds)

1000/T$_C$ (1/K)
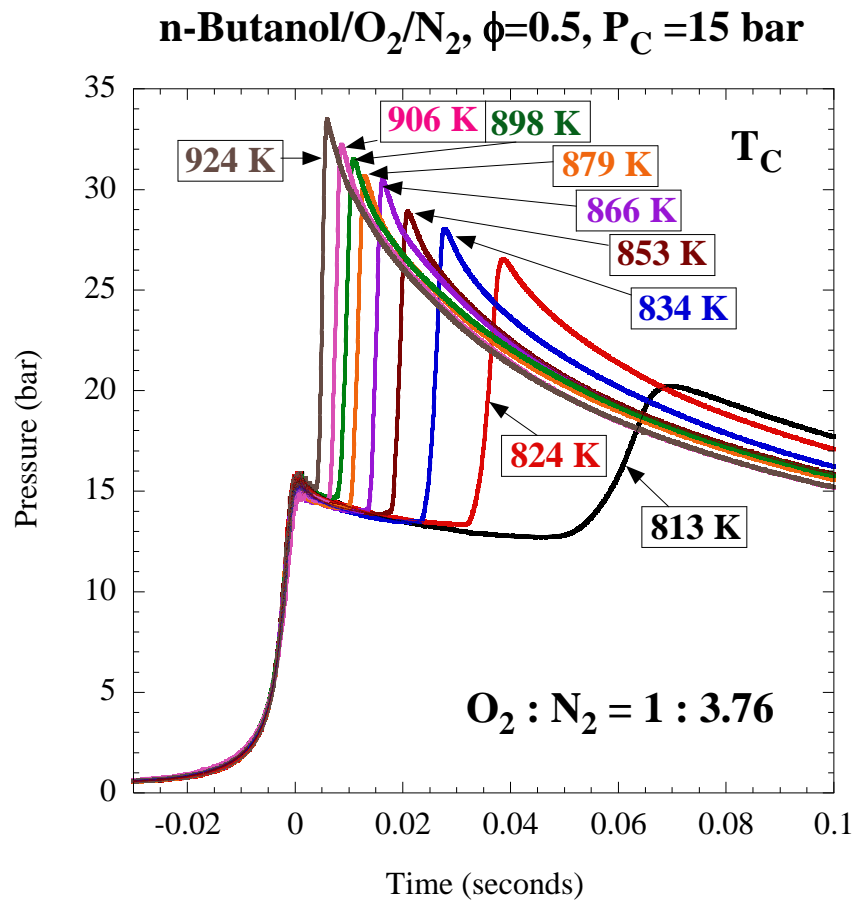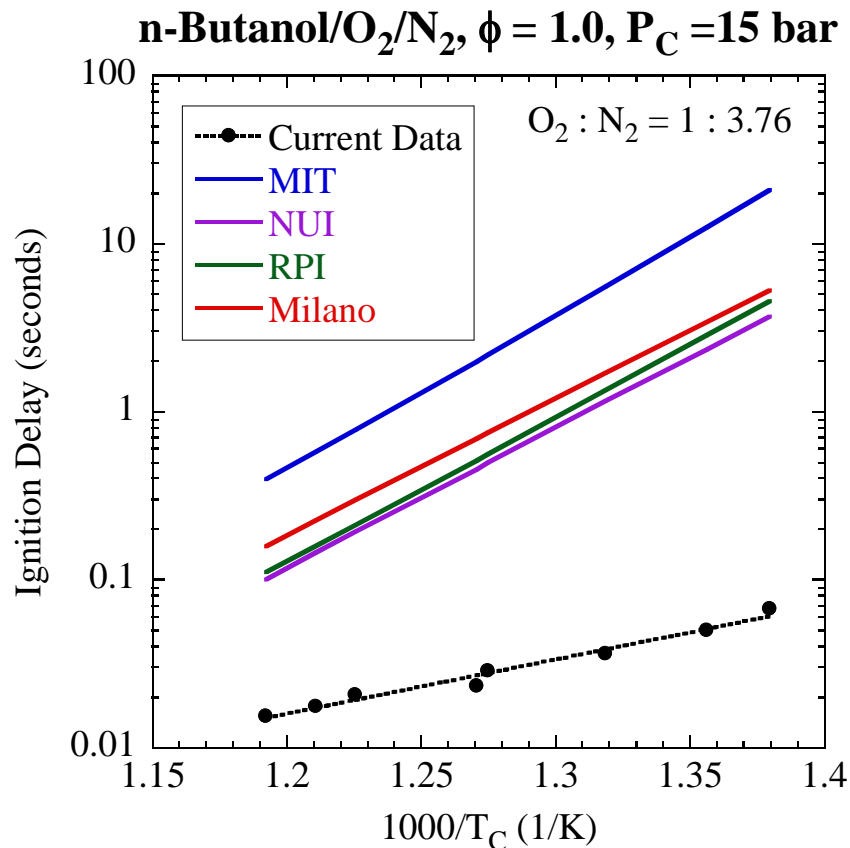
- Shock tube simulations are much longer than experiments

- MIT performs the worst; Harper *et al.* have a new mechanism to be published which corrects a serious error in their rate estimation database

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Autoignition of *n*-Butanol (4)

n-Butanol/O$_2$/N$_2$, P$_C$ =15 bar

- $\phi = 0.5$
- $\phi = 1.0$
- $\phi = 2.0$

Ignition Delay (seconds)

0.1

0.01

O$_2$: N$_2$ = 1 : 3.76

1   1.1   1.2   1.3   1.4   1.5

1000/T$_C$ (1/K)
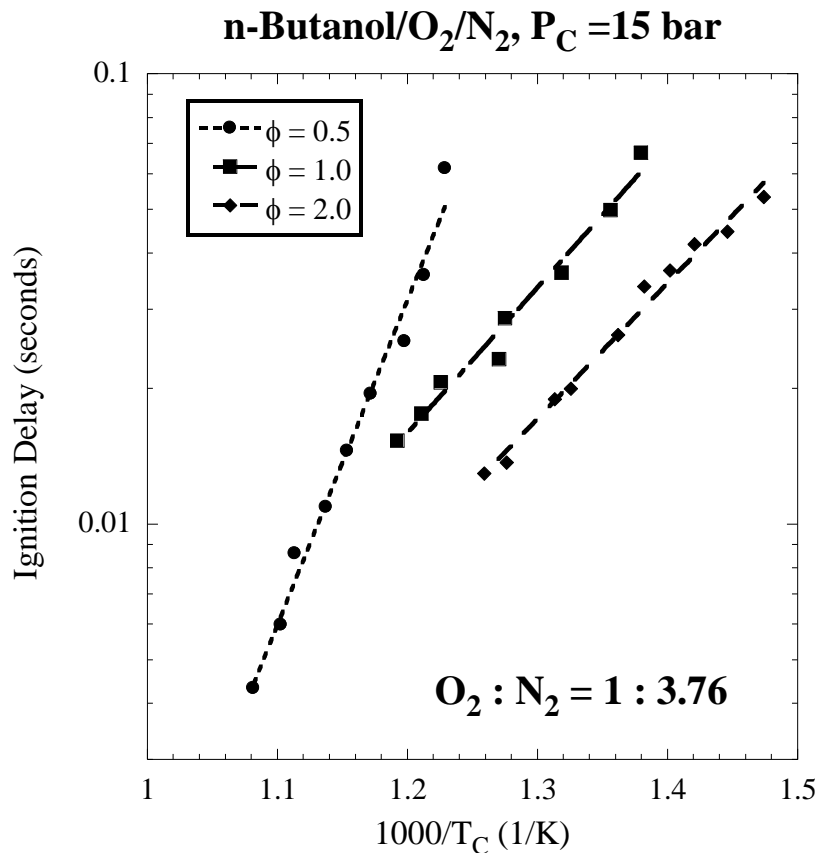
- Increasing equivalence ratio increases reactivity
- Shock tube results show the opposite trend[4]
- Reactivity dependence on equivalence ratio appears to be a function of temperature

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n-Butanol/O$_2$/N$_2$, P$_C$ = 15 bar

n-Butanol/O$_2$/N$_2$, P$_C$ = 15 bar

Left chart:
- Ignition Delay (seconds) vs 1000/T$_C$ (1/K)
- **Fuel Mole % = 3.38**
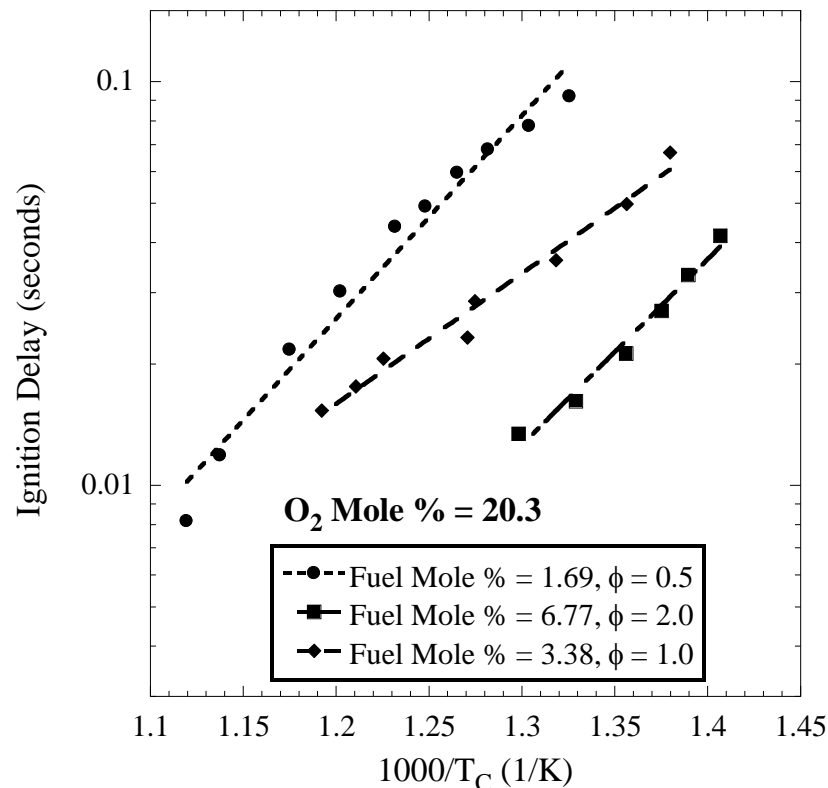 - O$_2$ Mole % = 40.6, ϕ = 0.5
  - O$_2$ Mole % = 10.2, ϕ = 2.0
  - O$_2$ Mole % = 20.3, ϕ = 1.0

Right chart:
- Ignition Delay (seconds) vs 1000/T$_C$ (1/K)
- **O$_2$ Mole % = 20.3**
  - Fuel Mole % = 1.69, ϕ = 0.5
  - Fuel Mole % = 6.77, ϕ = 2.0
  - Fuel Mole % = 3.38, ϕ = 1.0
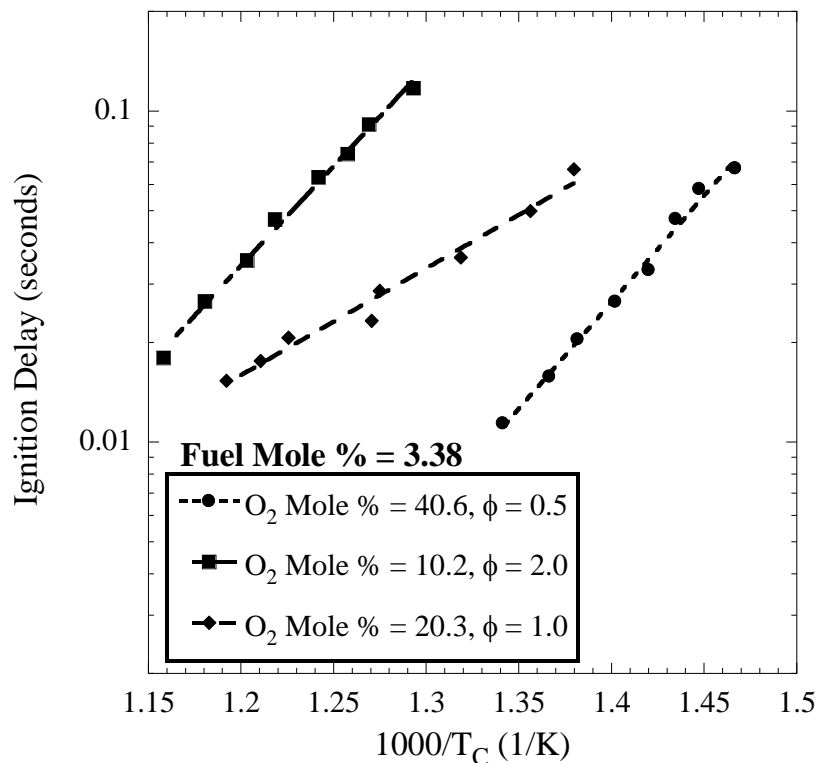
- Similar effect of varying initial oxygen mole fraction and initial fuel mole fraction

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n-Butanol/O$_2$/N$_2$, P$_C$ =15 bar

O$_2$: N$_2$ = 1 : 3.76

Ignition Delay (seconds)

1000/T$_C$ (1/K)

- ϕ = 2.0 Experiment
- ϕ = 2.0 Simulation
- ϕ = 1.0 Experiment
- ϕ = 1.0 Simulation
- ϕ = 0.5 Experiment
- ϕ = 0.5 Simulation
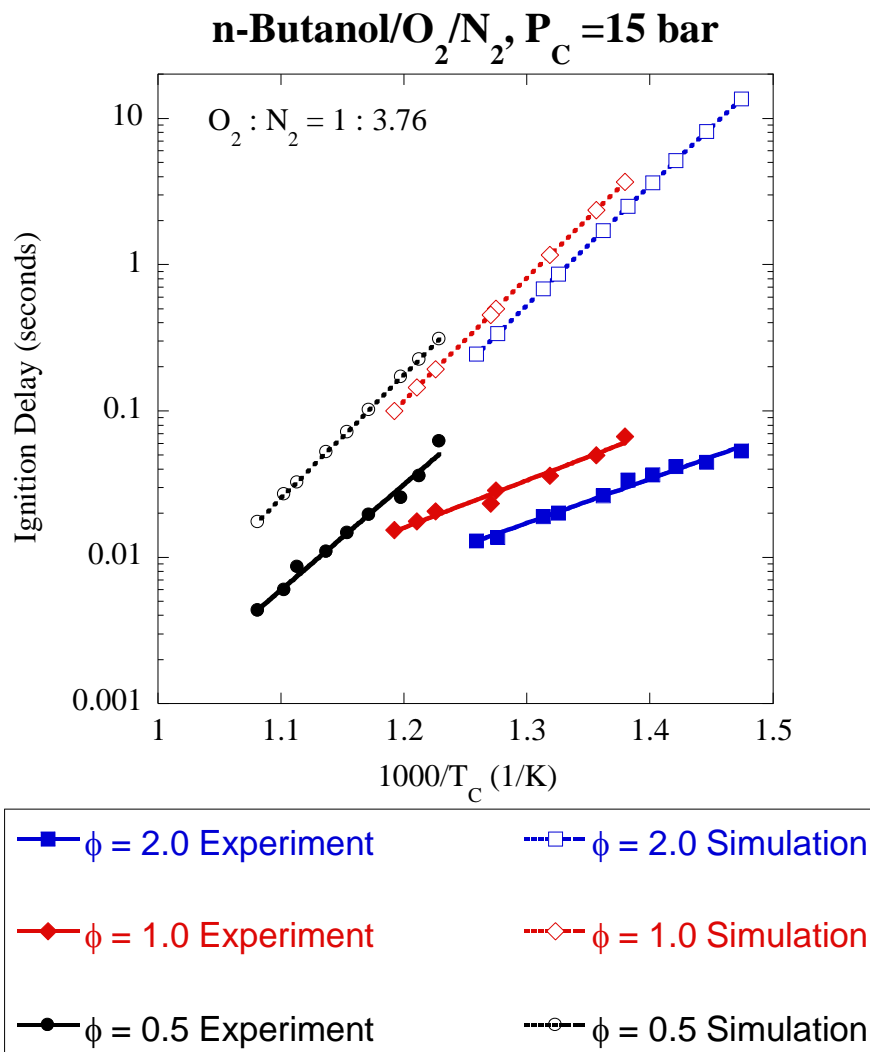
- Simulations capture the effect of equivalence ratio in that increasing equivalence ratio increases reactivity

- Simulations generally over-predict all results by at least one order of magnitude

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n-Butanol/O$_2$/N$_2$, ϕ = 1.0

Ignition Delay (seconds)

Current Data (30 bar)
NUI Sim (30 bar)
Current Data (15 bar)
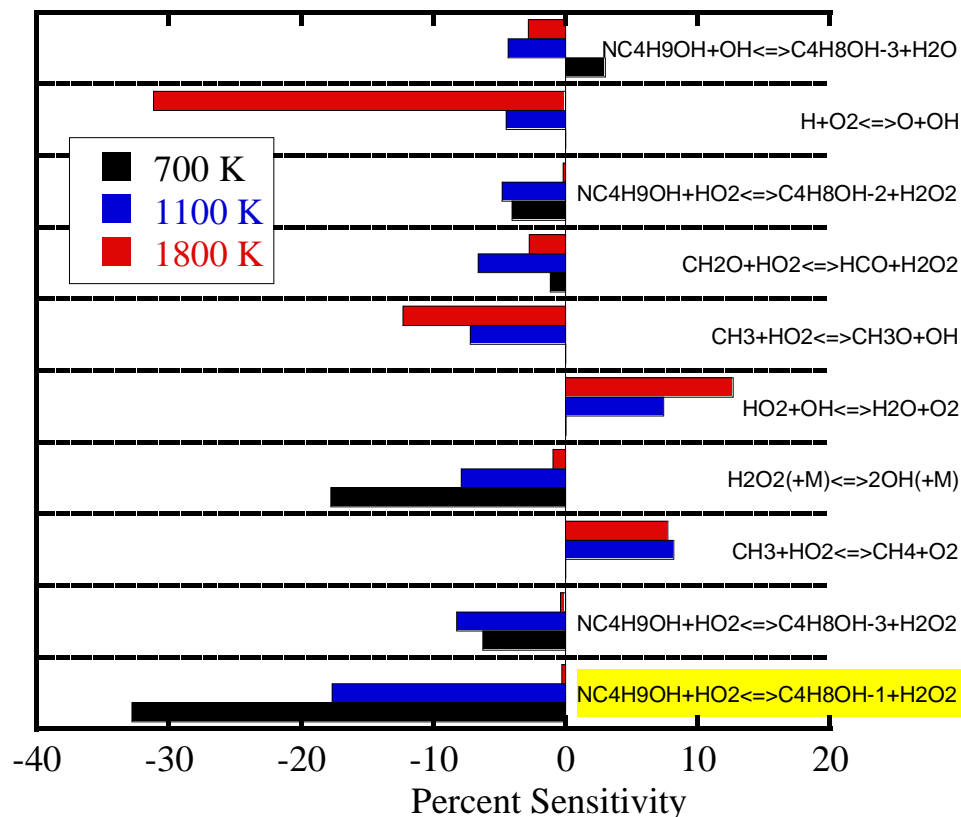NUI Sim (15 bar)

O$_2$: N$_2$ = 1 : 3.76

1000/T$_C$ (1/K)
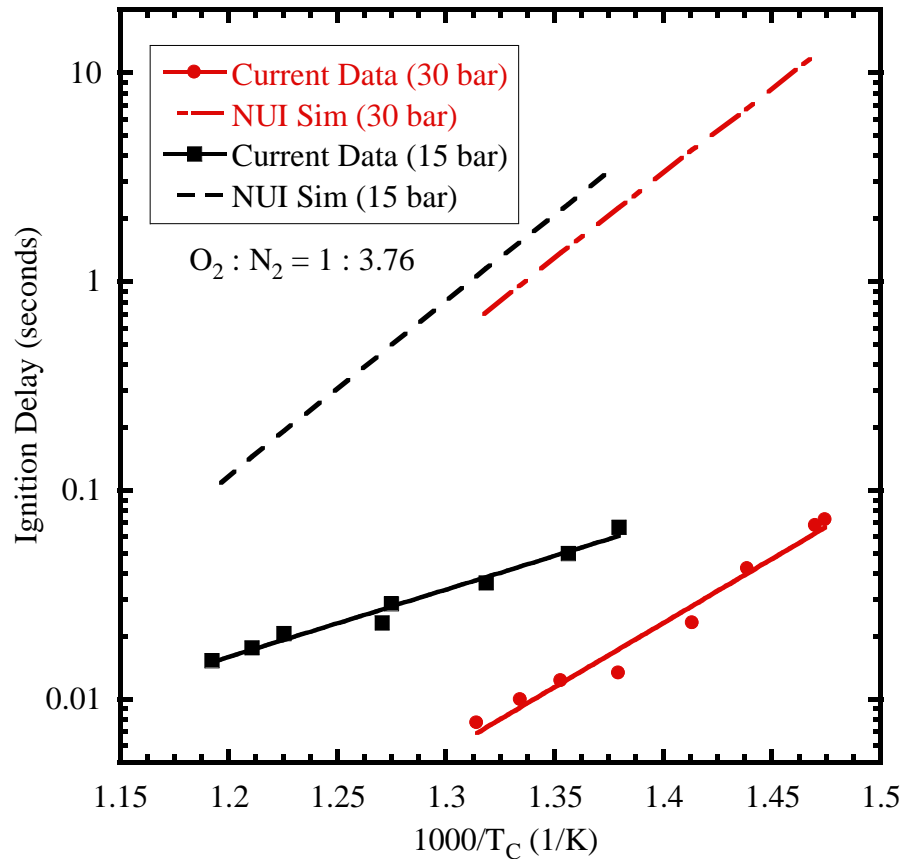
- Higher compressed pressure has higher reactivity

- Simulations unable to quantitatively capture the pressure dependence in this temperature range

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Brute Force Sensitivity

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

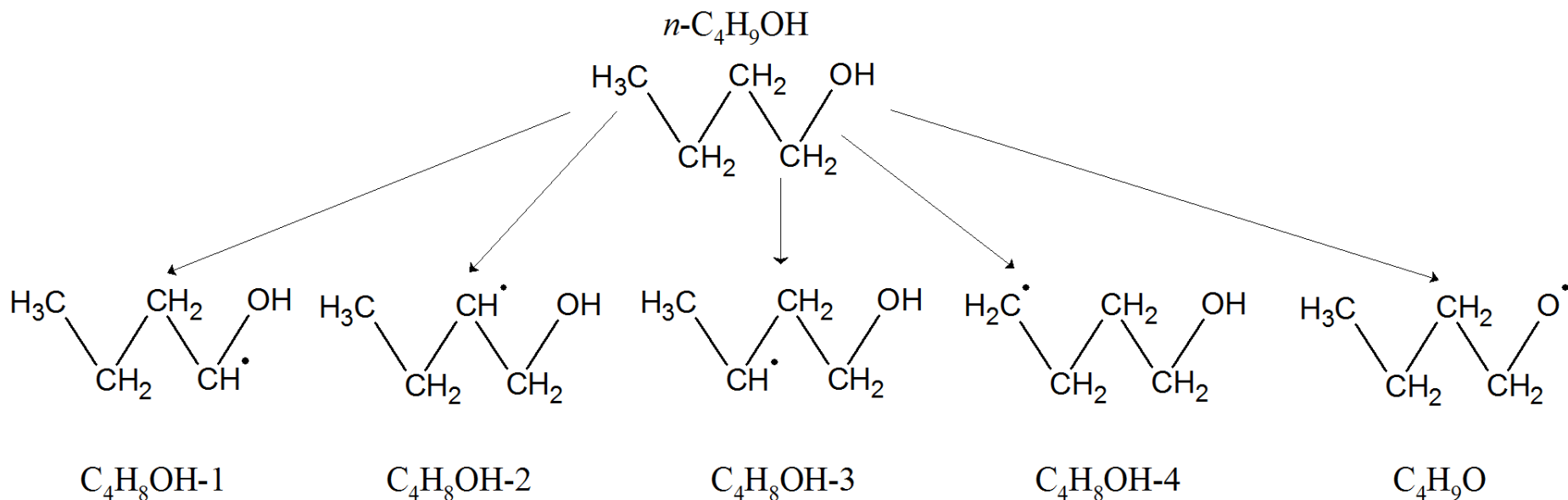**n-Butanol/O_2/N_2, ϕ=1.0, P_C =15 atm, O_2 : N_2 = 1 : 3.76**

- NUI mechanism is most sensitive to the reaction of fuel and HO_2 to form 1-hydroxybutyl

- The sensitivity is significantly reduced at higher temperatures

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- 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

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

n-C_4H_9OH

C_4H_8OH-1 C_4H_8OH-2 C_4H_8OH-3 C_4H_8OH-4 C_4H_9O

- These radicals are not equally produced

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800K, 15 atm, ϕ=1.0

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1600K, 15 atm, φ=1.0

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Modified Mechanism (1)

Reaction 1353: $NC4H9OH + HO2 \Leftrightarrow C4H8OH\text{-}1 + H2O2$
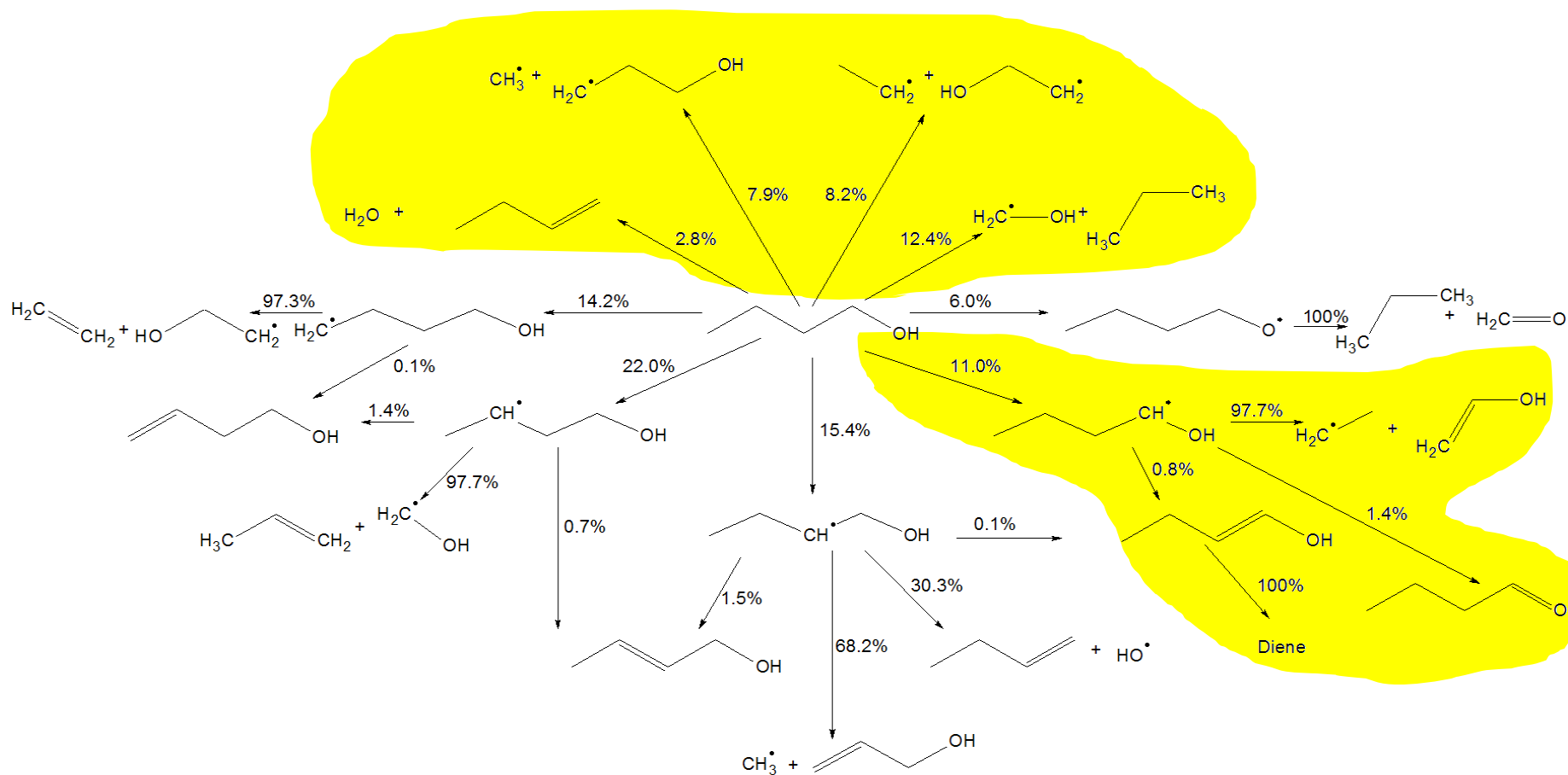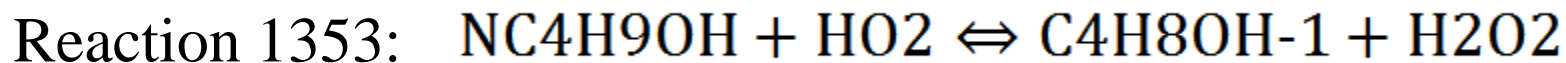
Ignition Delay vs. Multiplication Factor for Reaction 1353
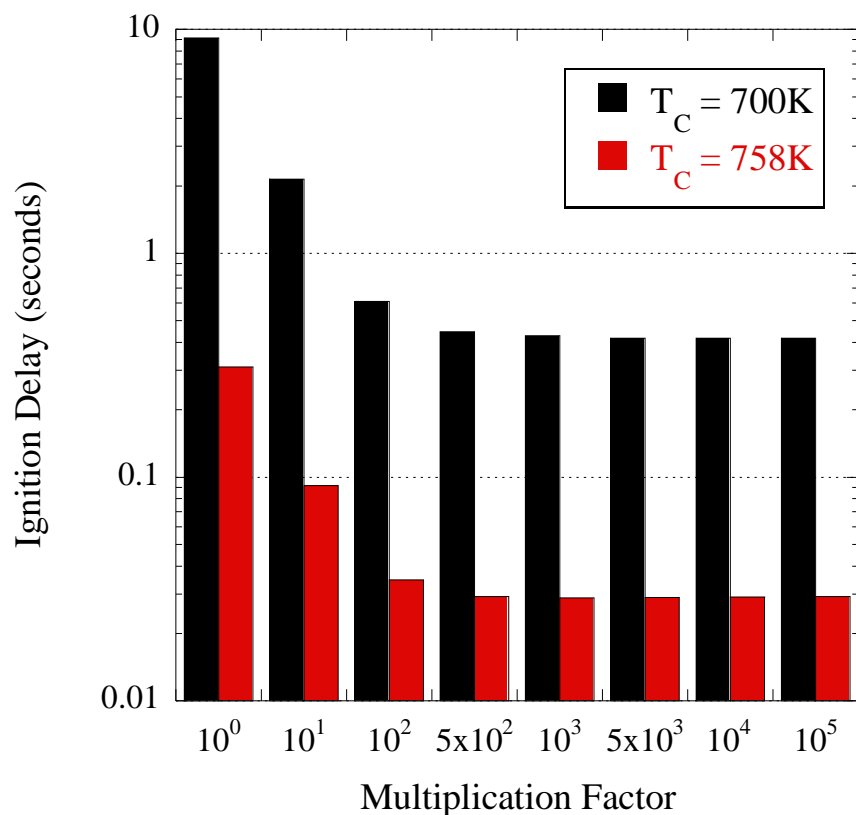
- Ignition delay becomes constant when the rate of 1-hydroxybutyl formation by R1353 is increased past a certain point

- This suggests a new rate limiting step has taken over

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Modified Mechanism (2)

Reaction 1353: $NC4H9OH + HO2 \Leftrightarrow C4H8OH\text{-}1 + H2O2$

n-Butanol/O_2/N_2, ϕ =1.0, P_C =15 bar
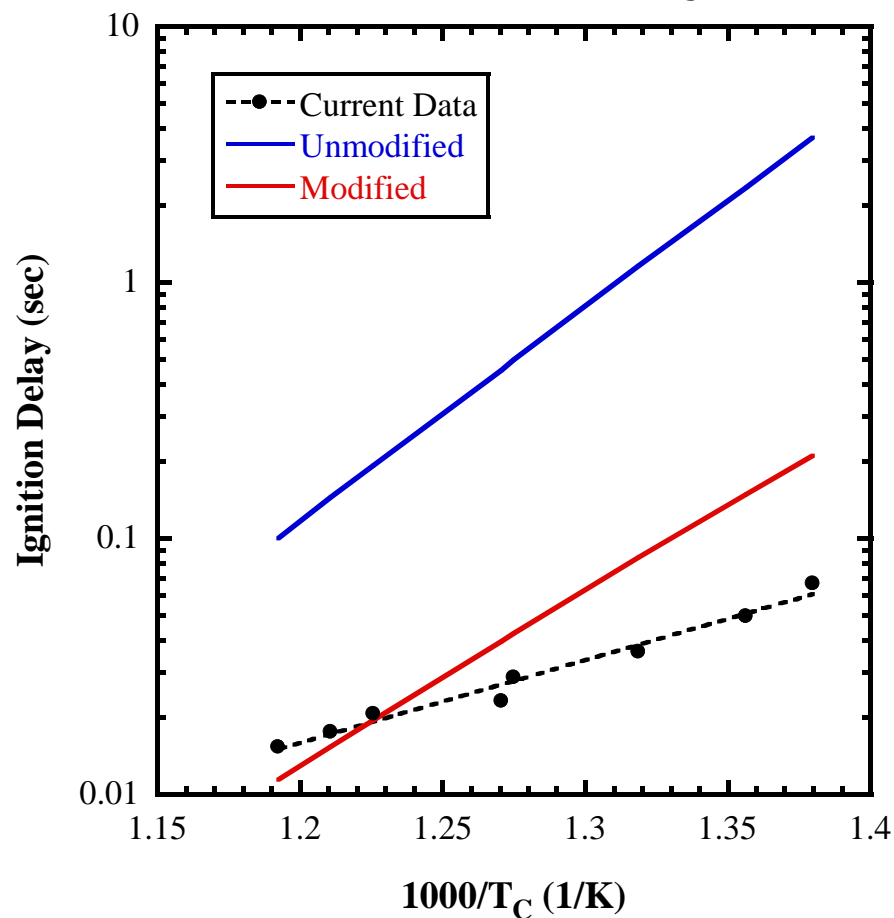
- The rate of R1353 is multiplied by 1000

- Ignition delays are recomputed

- Results are close, but the lowest temperature case is still over-predicted by 100 ms

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

Legend: ■ 700K ■ 758K (red)

Reactions (top to bottom):
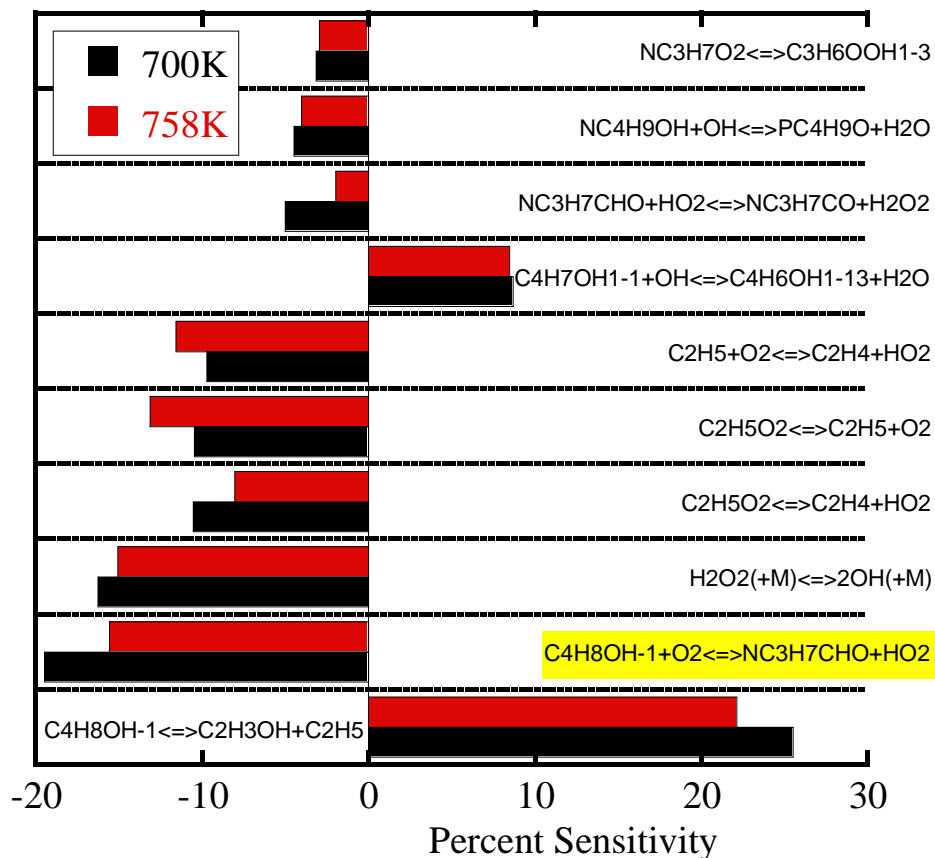- NC3H7O2<=>C3H6OOH1-3
- NC4H9OH+OH<=>PC4H9O+H2O
- NC3H7CHO+HO2<=>NC3H7CO+H2O2
- C4H7OH1-1+OH<=>C4H6OH1-13+H2O
- C2H5+O2<=>C2H4+HO2
- C2H5O2<=>C2H5+O2
- C2H5O2<=>C2H4+HO2
- H2O2(+M)<=>2OH(+M)
- C4H8OH-1+O2<=>NC3H7CHO+HO2
- C4H8OH-1<=>C2H3OH+C2H5

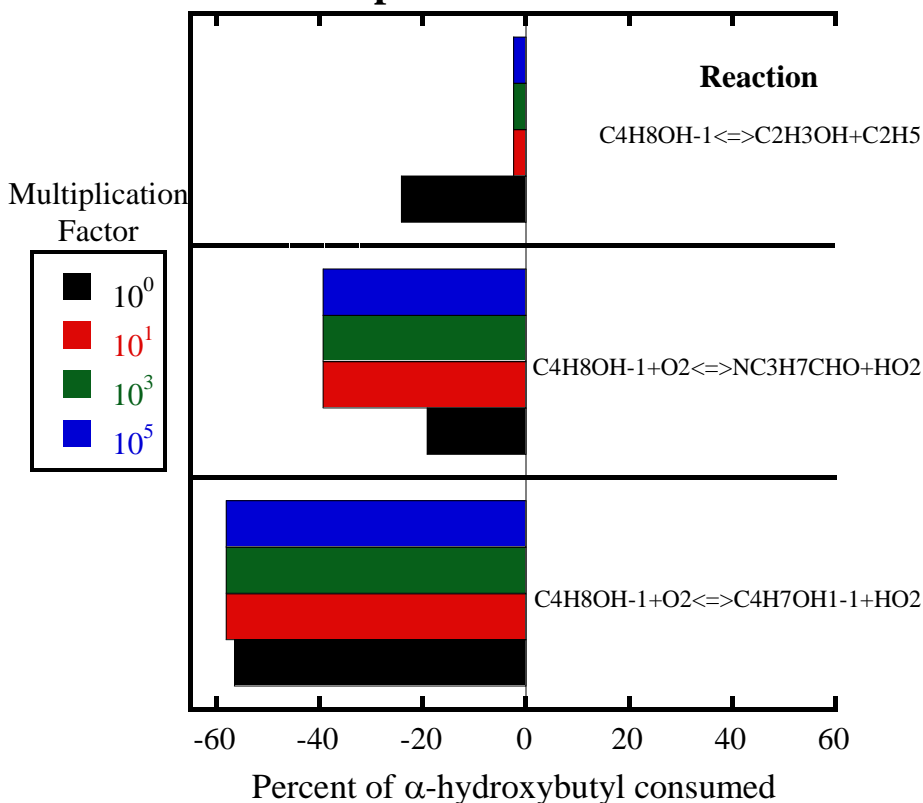X-axis: Percent Sensitivity (-20, -10, 0, 10, 20, 30)

- Brute force sensitivity is performed again on the modified mechanism

- System is sensitive to the formation of butanal (NC_3H_7CHO)

- Formation of 1-hydroxybutyl by R1353 has disappeared from the top ten reactions

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Reaction 1353: $NC4H9OH + HO2 \Leftrightarrow C4H8OH\text{-}1 + H2O2$

Percent of α-Hydroxybutyl Consumed vs. Multiplication Factor of R1353

Multiplication Factor

■	10^0
■	10^1
■	10^3
■	10^5

Reaction

C4H8OH-1<=>C2H3OH+C2H5

C4H8OH-1+O2<=>NC3H7CHO+HO2

C4H8OH-1+O2<=>C4H7OH1-1+HO2

Percent of α-hydroxybutyl consumed

- Upon first increasing the rate of R1353, production of butanal from 1-hydroxybutyl and fission of 1-hydroxybutyl change drastically

- Further increasing the rate does not change the percent directed into each pathway

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- This analysis suggests butanal formation is the next rate limiting step

- The entire pathway of 1-hydroxybutyl formation and destruction is clearly quite important

- Further speciation measurements are necessary to determine which pathways are most important

- Speciation data with Rapid Sampling Apparatus can confirm fuel decomposition pathways
- Expand experiments to other isomers of butanol

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- Autoignition delay data have been obtained for *n*-butanol at low to intermediate temperature and elevated pressure using a heated rapid compression machine

- Reactivity increased as equivalence ratio, initial oxygen mole fraction or initial fuel mole fraction increase in the temperature range studied

- Comparison of experimental results and reaction mechanisms available in the literature showed very poor agreement

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- Sensitivity analysis of one reaction mechanism revealed that the rates of certain fuel decomposition reactions strongly affect the ignition delay

- Further path analysis highlighted the importance of several fuel decomposition pathways

- Speciation data may be required to further improve reaction mechanisms by confirming fuel decomposition pathways

- Quantum calculations of the rates of important reactions is warranted based on this work, in particular the 1-hydroxybutyl system

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Colleagues: Kyle Brady, Apurba Das, Billal Hossain, Xin Hui

Additional Slides

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n-Butanol/O_2/N_2, ϕ=1.0, P_C =15 bar
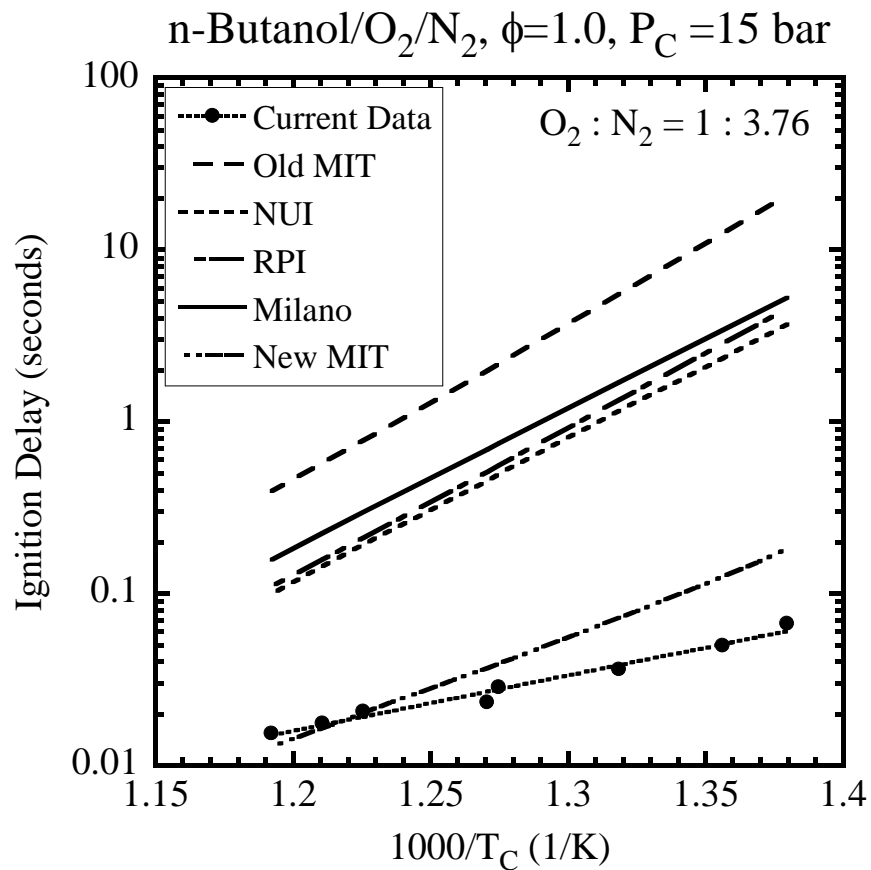
- New MIT mechanism corrects error in reaction rates of H-abstraction from the fuel by HO_2

- New MIT mechanism shows much improved results – comparable to the 1000*NUI results

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- Rapid Sampling Apparatus designed to sample the mixture from the reaction chamber at predetermined time

Holding/Release Mechanism

Sample Chamber

Diaphragm

Puncture Rod

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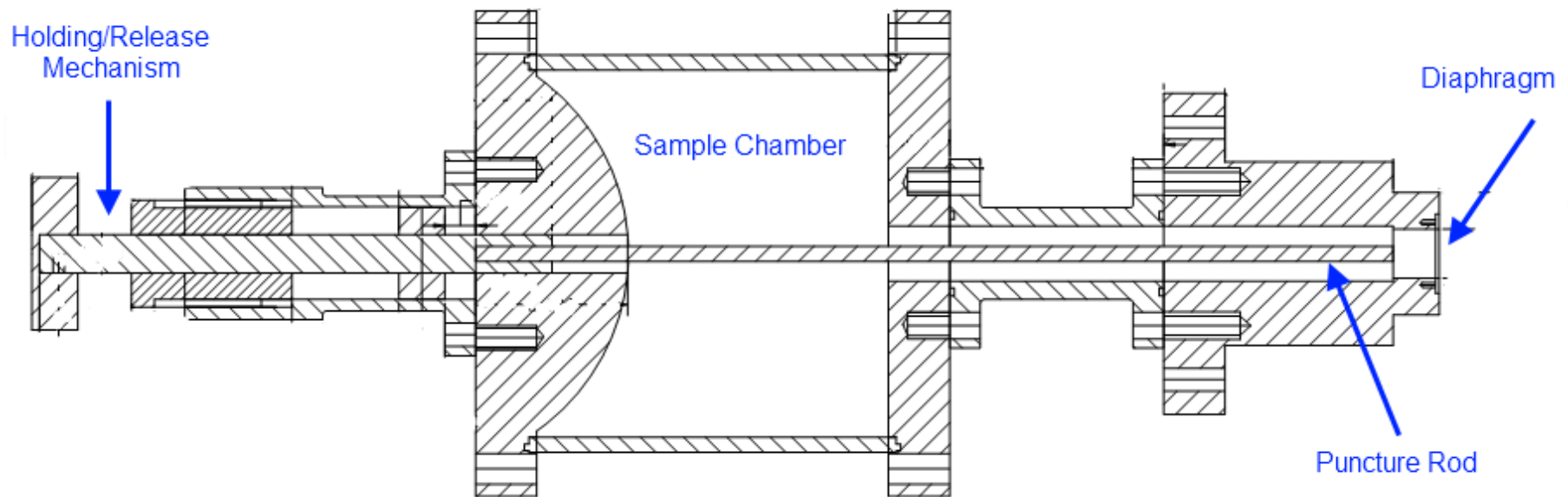
- Volume ratio between Sample Chamber and Reaction Chamber is about 50:1

- Expansion occurs within 2-3 milliseconds and quenches reactions

- Convex shape ensures shocks are diverged and weakened

- Samples are withdrawn and analyzed using GC-MS/FID/TCD

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- Previous design relied on opposed forces of a spring and electromagnet to hold the puncture rod above the diaphragm

- Several drawbacks:
  – Electromagnet was frequently deactivated accidentally
  – Rod could not be withdrawn from the diaphragm after puncture

- Requires disassembly to replace the diaphragm

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- New design aims to improve reliability of puncture control circuit

- Use "positive action" system to reduce risk of accidental puncture

- Combination of linear solenoid device with MOSFET transistor

- Advantages:
  - Reduced risk of premature puncture
  - Solenoid allows retracting of rod after puncturing

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Correlated Ignition Delay

$$\tau = 10^A [X_{O2}]^a [X_{n\text{-Butanol}}]^b P_C^{\ n} \exp(T_a / T_C)$$

$A = -(8.5 \pm 0.8)$
$a = -(1.7 \pm 0.2)$
$b = -(1.4 \pm 0.2)$
$n = -(1.5 \pm 0.3)$
$T_a = 9730.3 \pm 1035.5$

$0.0169 < X_{n\text{-Butanol}} < 0.0676$
$0.1015 < X_{O2} < 0.4060$
$15 < P_C < 30$ bar
$675 < T_C < 925$ K

Legend:
- $\circ$ $\phi=2.0$, Air — Correlation
- $\triangle$ $\phi=2.0$, Fuel — $\diamond$ $\phi=0.5$, Air
- $\boxplus$ $\phi=2.0$, Oxygen — $\triangleright$ $\phi=0.5$, Fuel
- $\square$ $\phi=1.0$, Air — $+$ $\phi=0.5$, Oxygen
- $\triangleleft$ $\phi=1.0$, $P_C=30$ bar

Y-axis: $\tau / (X_{O2}^{-1.7} X_{n\text{-Butanol}}^{-1.4} P_C^{-1.5})$

X-axis: $1000/T_C$ (1/K)
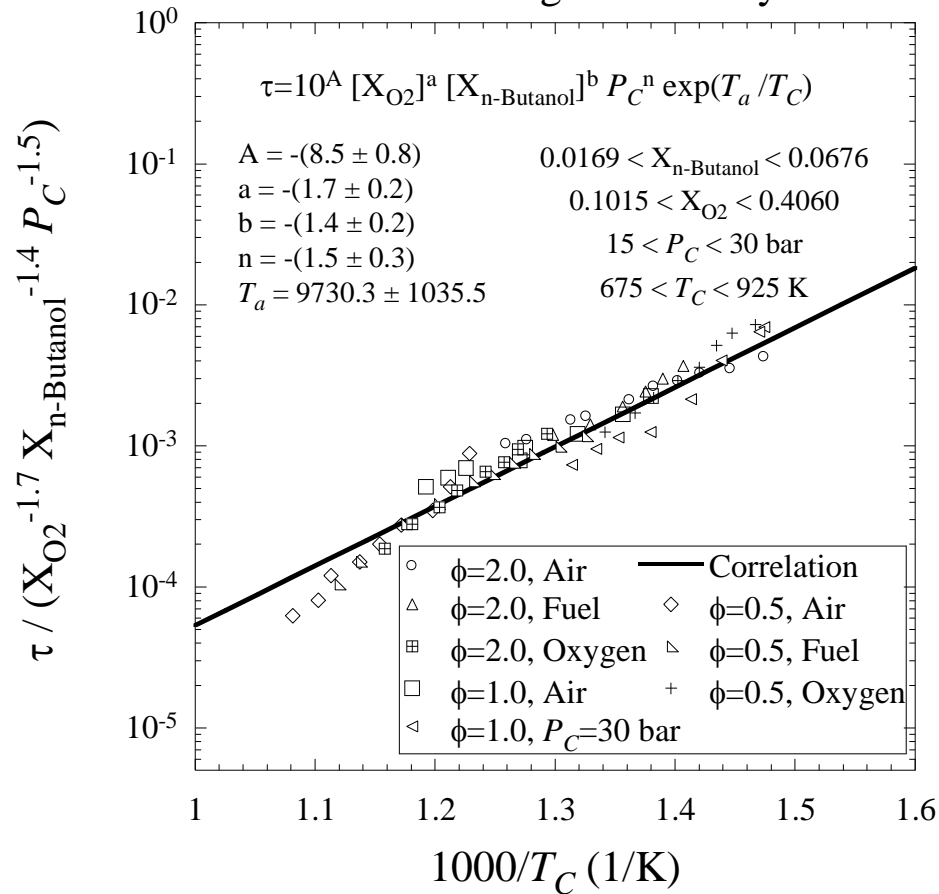
- Correlation shows slightly greater than first order dependence on initial fuel mole fraction and compressed pressure
- Nearly second order dependence on initial oxygen mole fraction

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