Autoignition of Methyl Valerate at Low to Intermediate Temperatures and Elevated Pressures in a Rapid Compression Machine

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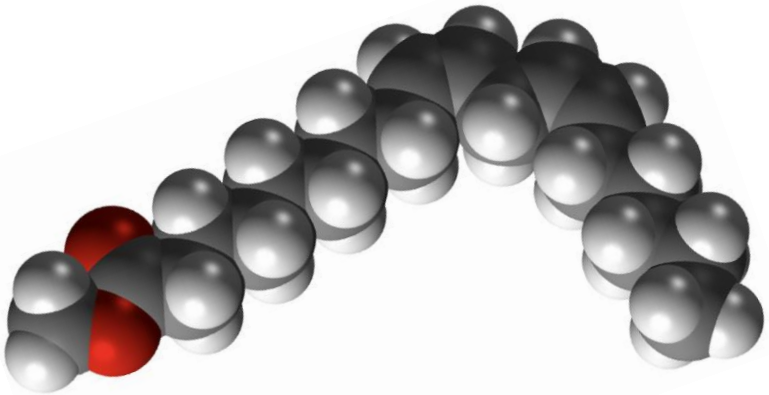
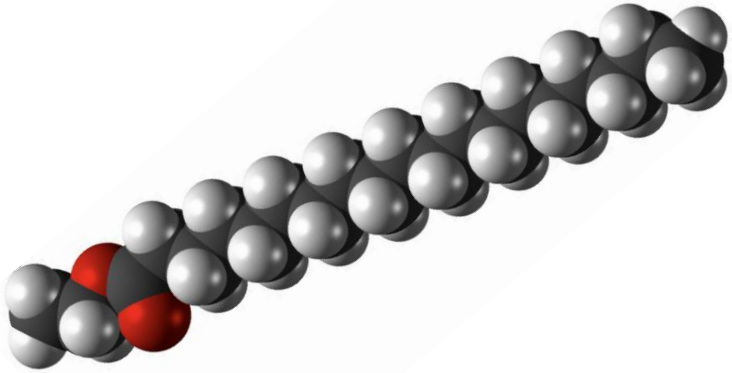
Methyl Esters are components of biodiesel

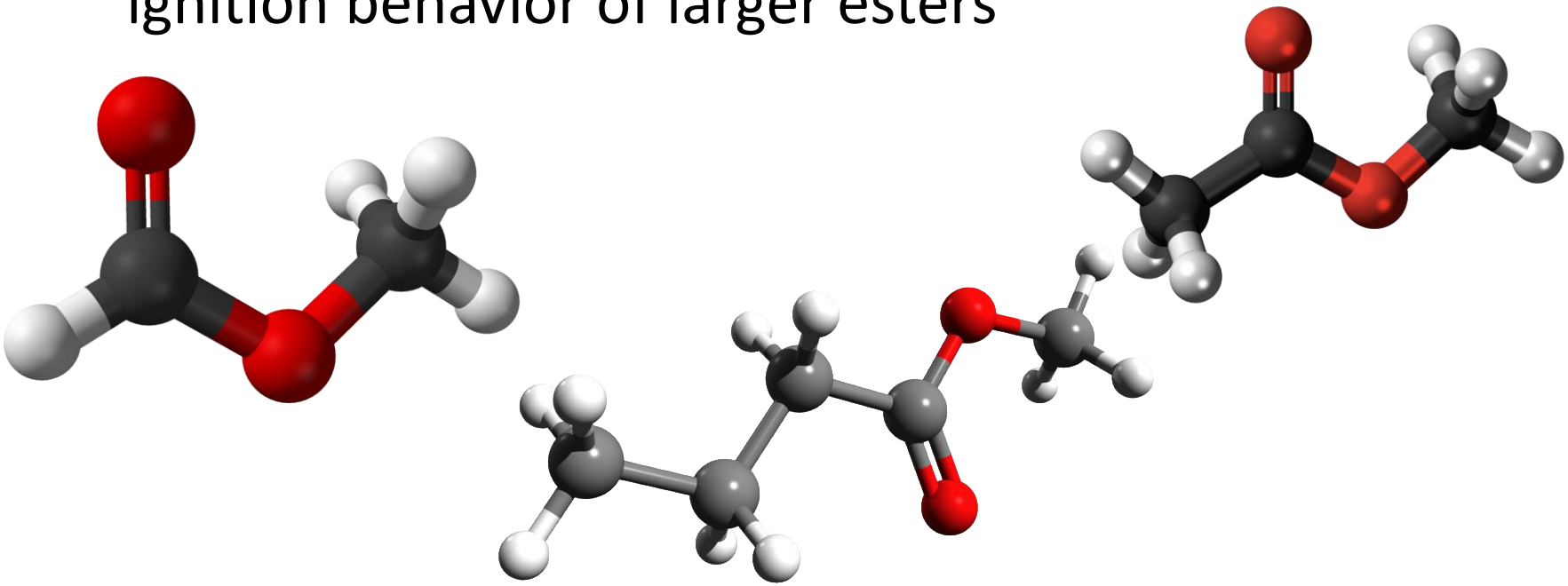




- But these long chain molecules are hard to study experimentally!

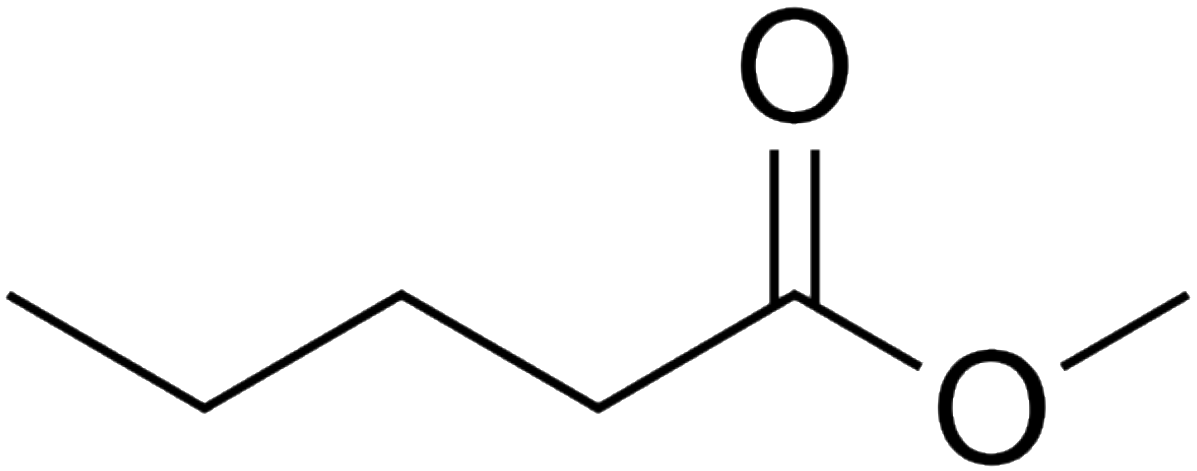
Use smaller methyl esters to understand the fundamentals

- Smaller methyl esters are easier to work with
- But they don't reproduce the low-temperature ignition behavior of larger esters



How many carbon atoms do we need to expect "good" behavior?

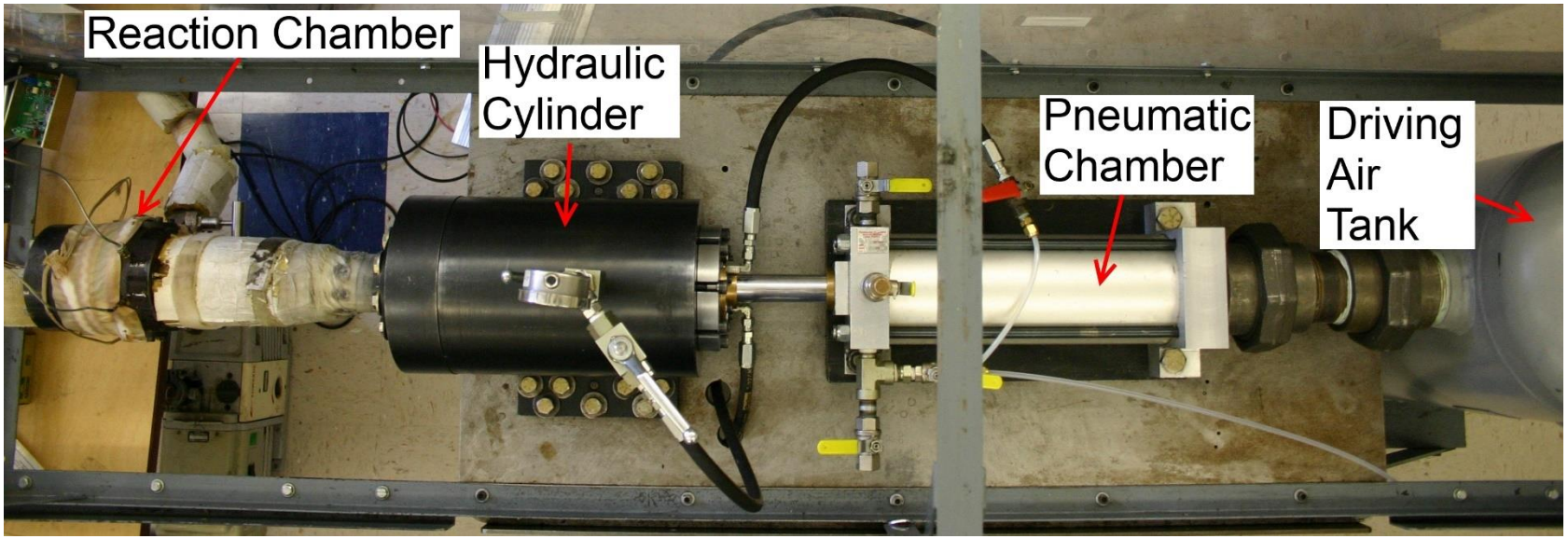
- Methyl valerate (MV, methyl pentanoate, $C_6H_{12}O_2$) seems promising
- Can still run experiments relatively easily



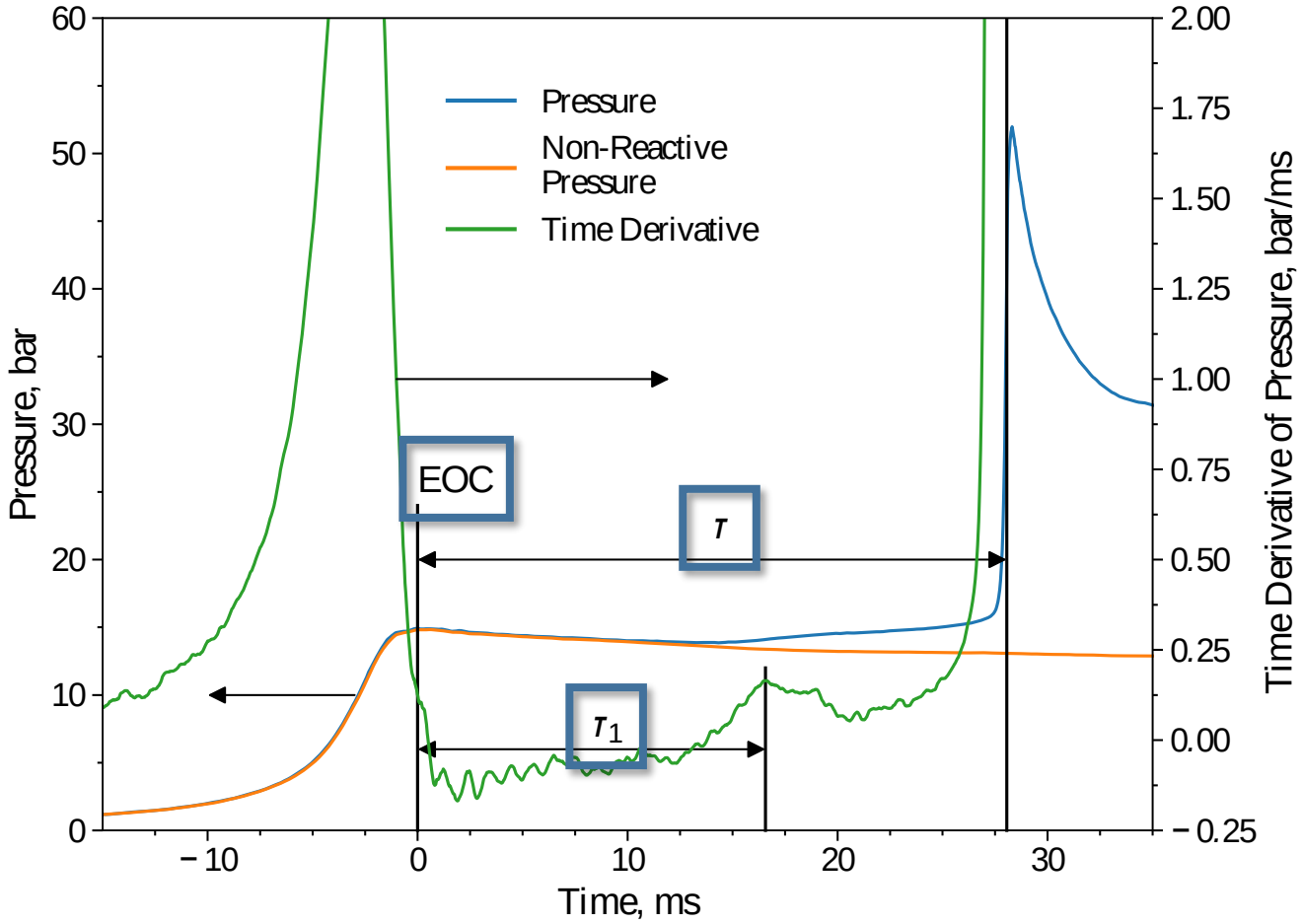
Hadj-Ali et al. (2009) DOI:10.1016/j.proci.2008.09.002.

Rapid Compression Machine

- Experiments are conducted in a heated Rapid Compression Machine (RCM)
- High pressure and low temperature conditions
- Minimize effects of fluid mechanics and inhomogeneity



Rapid Compression Machine

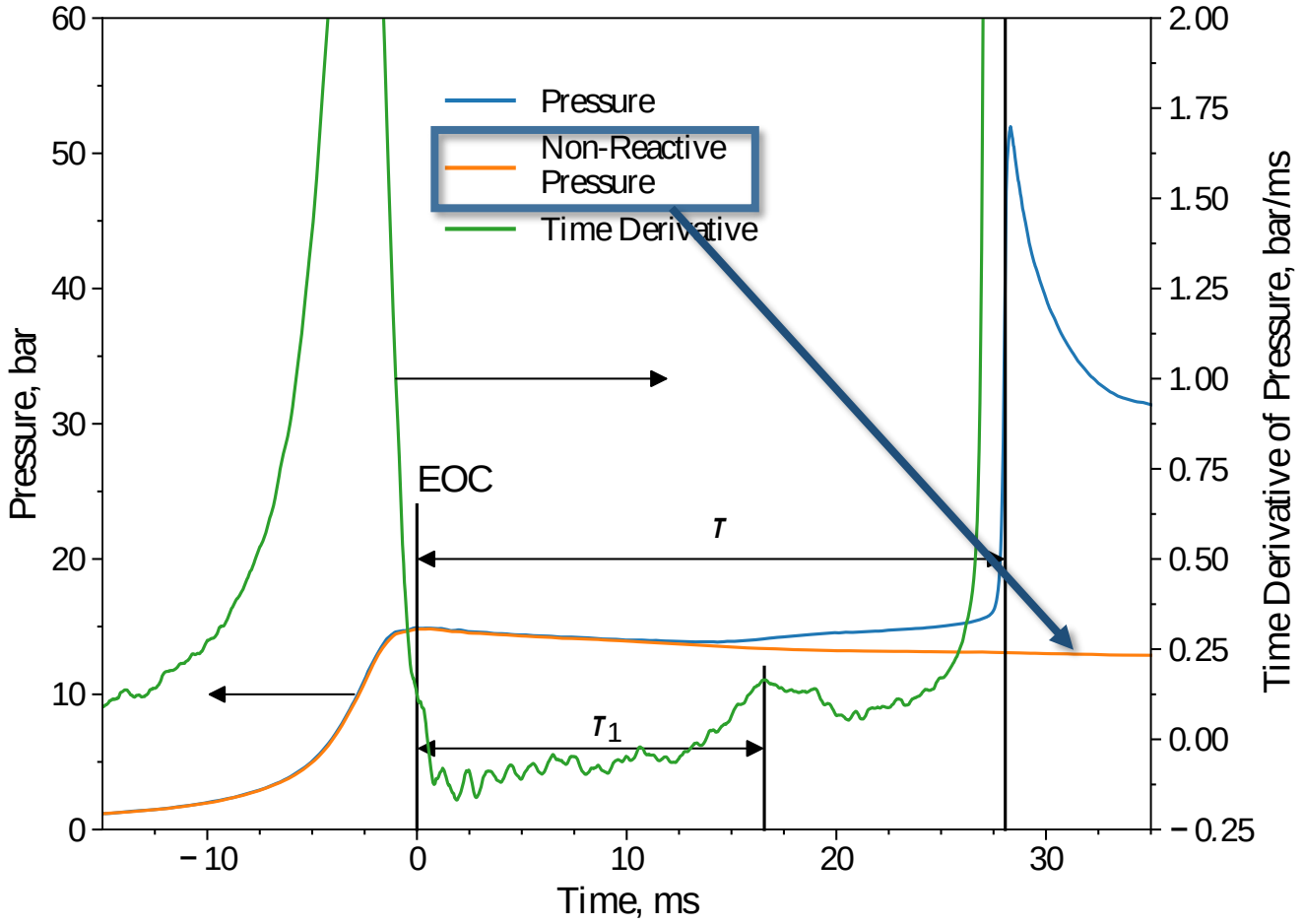


End of Compression (EOC) conditions are used to report experiments:

$$P_C, T_C$$

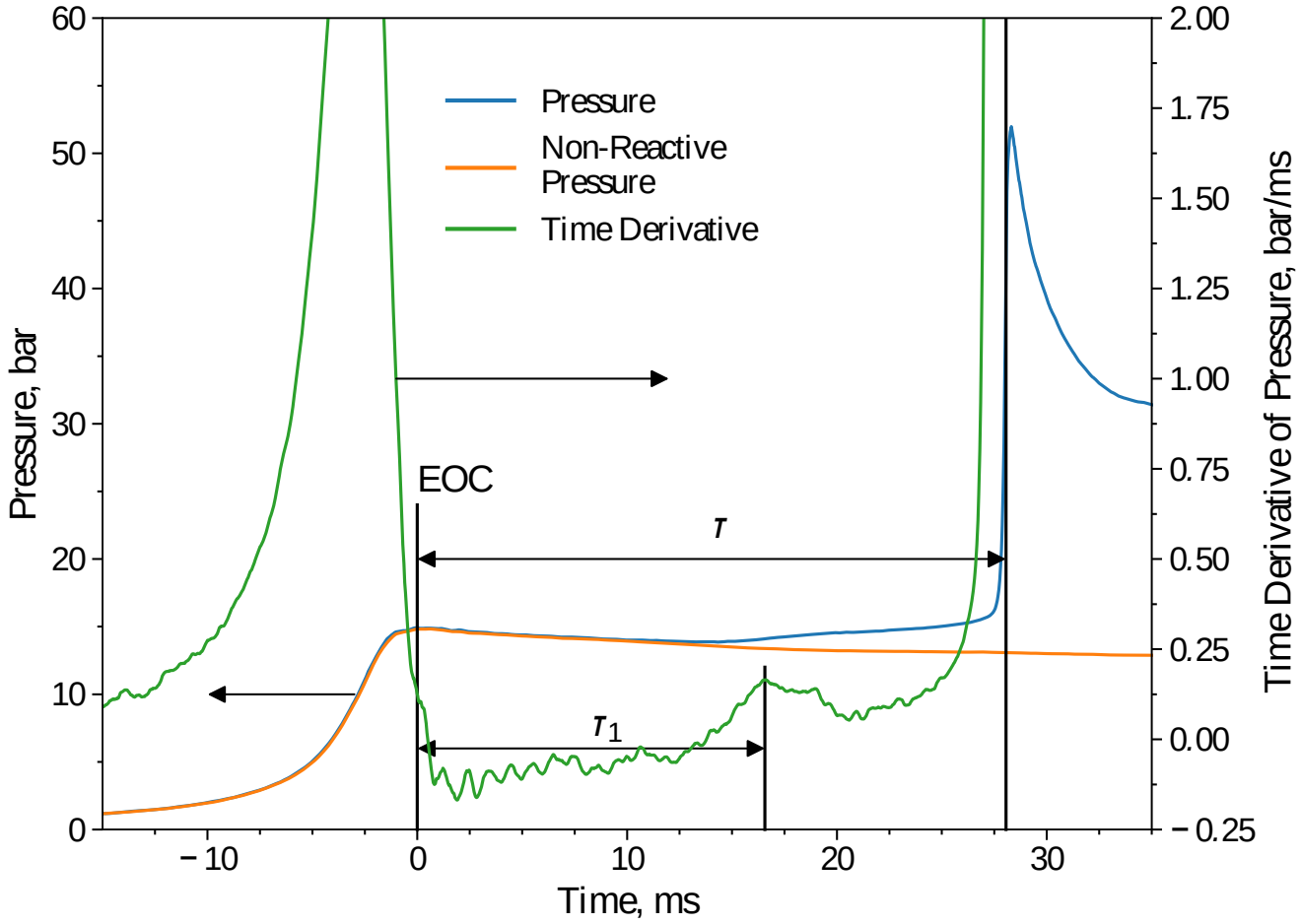
Ignition delays determined by peaks in dP/dt

Rapid Compression Machine



Non-Reactive experiments replace O_2 with N_2 to characterize machine-specific effects

Rapid Compression Machine



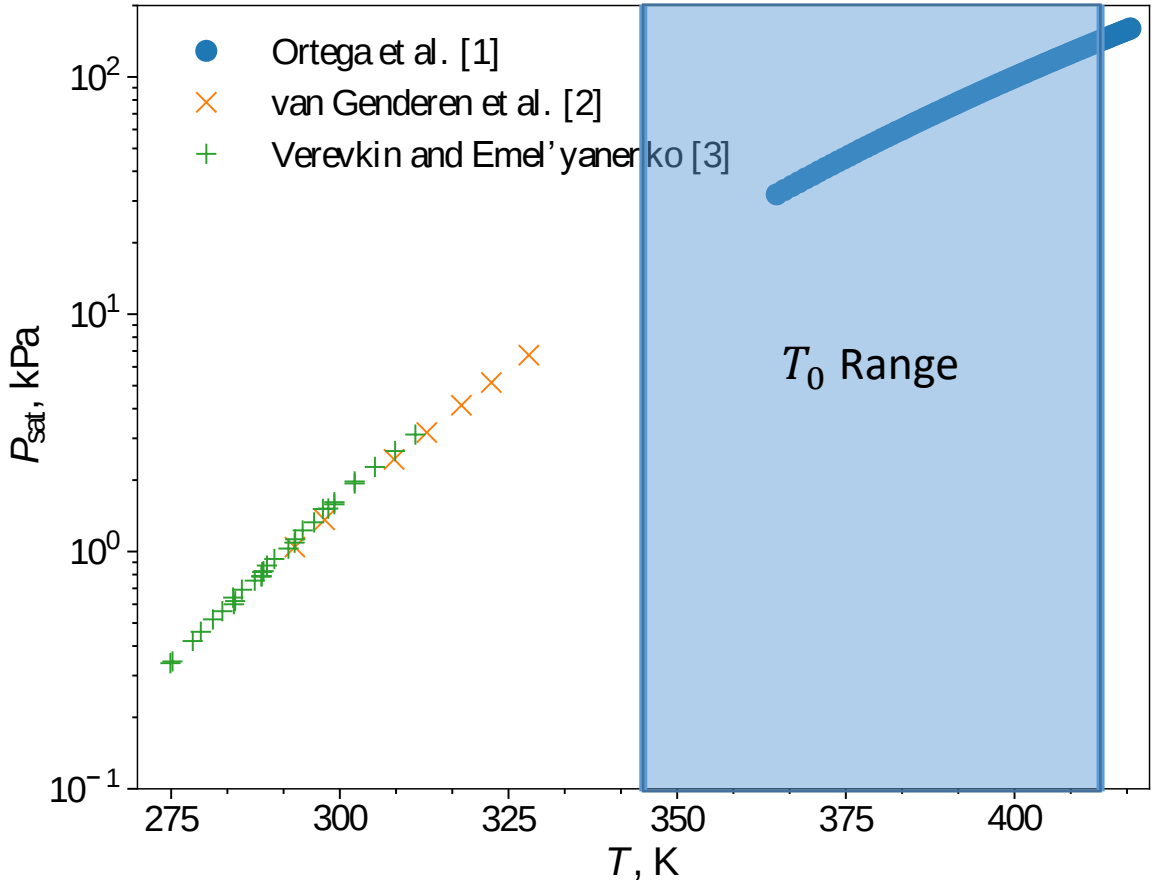
Data are processed by UConnRCMPy (2D19, today at 5:35 PM, Room 1102)

https://github.com/bryanwweber/UConnRCMPy

Experimental Conditions

- 17 L, stainless-steel mixing tanks to prepare homogeneous gas-phase fuel/air mixtures
- Equivalence Ratios: $\phi = 0.25 - 2.0$
- $P_C = 15 - 30$ bar
- $T_C = 680 - 1050$ K
- Initial temperature: $T_0 = 348 - 413$ K
  - Heated to prevent fuel condensation

Vapor pressure data is important to have homogeneous mixtures



1. Ortega et al. (2003) DOI: 10.1021/je030117d
2. van Genderen et al. (2002) DOI: 10.1016/S0378-3812(02)00097-3
3. Verevkin and Emel'yanerko (2008) DOI: 10.1016/j.fluid.2008.02.001

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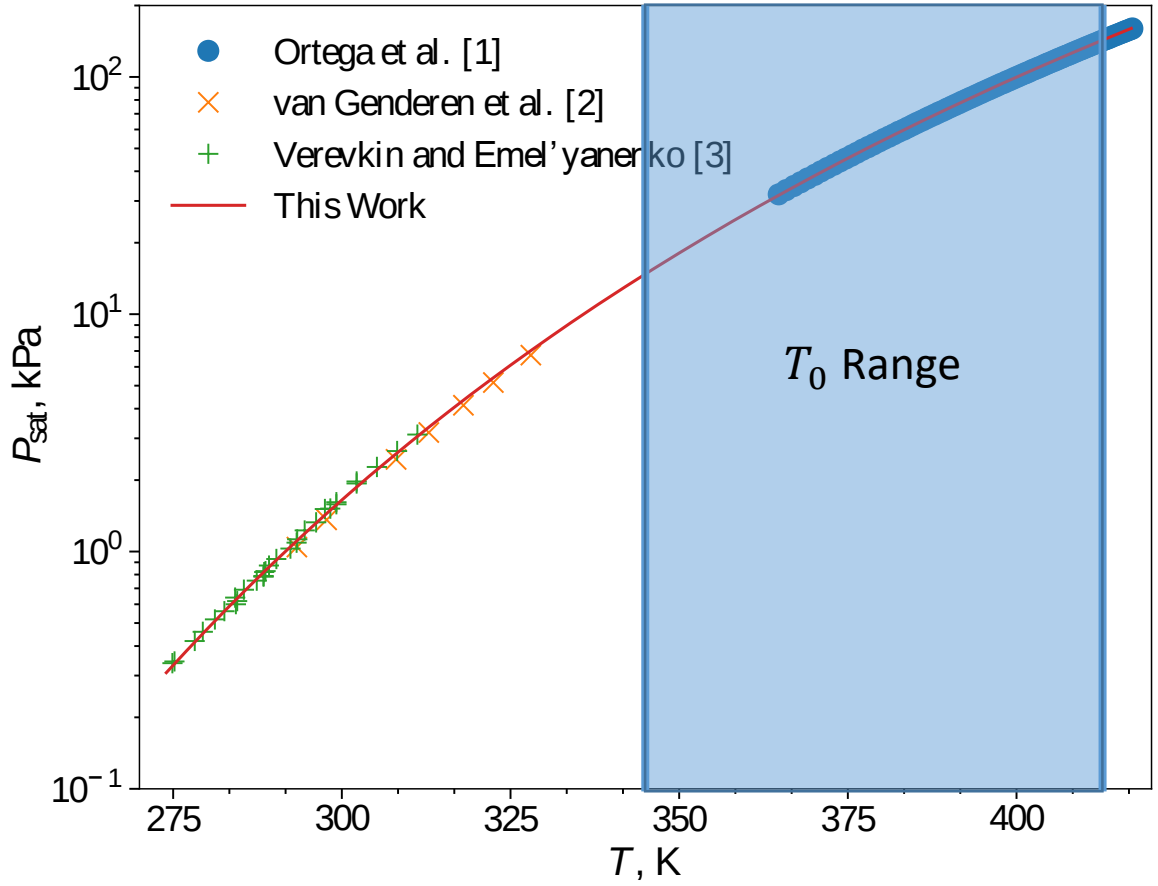

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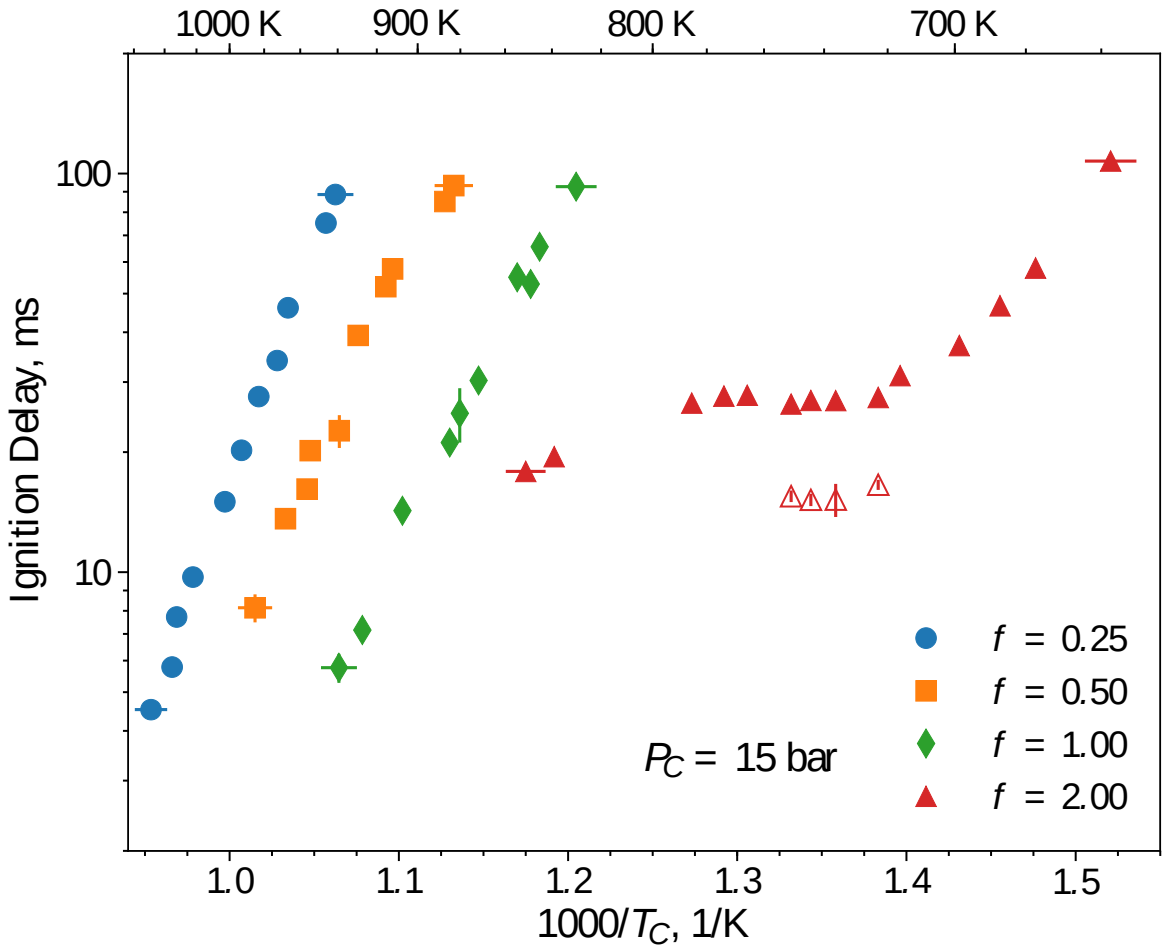
New fit with Antoine Equation fills in the missing range and agrees will with experimental data

Experimental Results



At $P_C = 15$ bar:

No Negative Temperature Coefficient (NTC) region of ignition delay for $\phi \leq 1.0$ in these experiments

$\phi = 2.0$ does have NTC from 720–775 K

First stage ignition measured from 720-750 K

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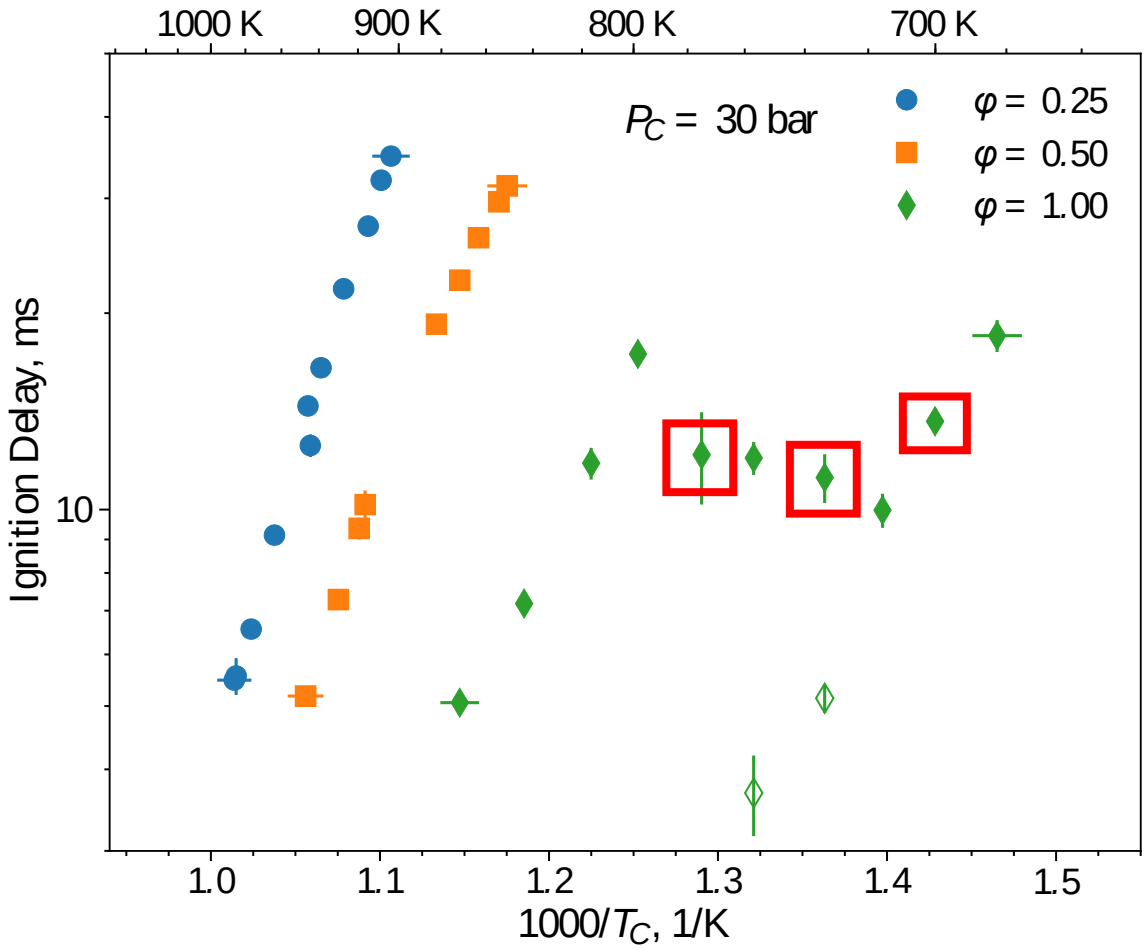
Experimental Results



At $P_C = 30$ bar:

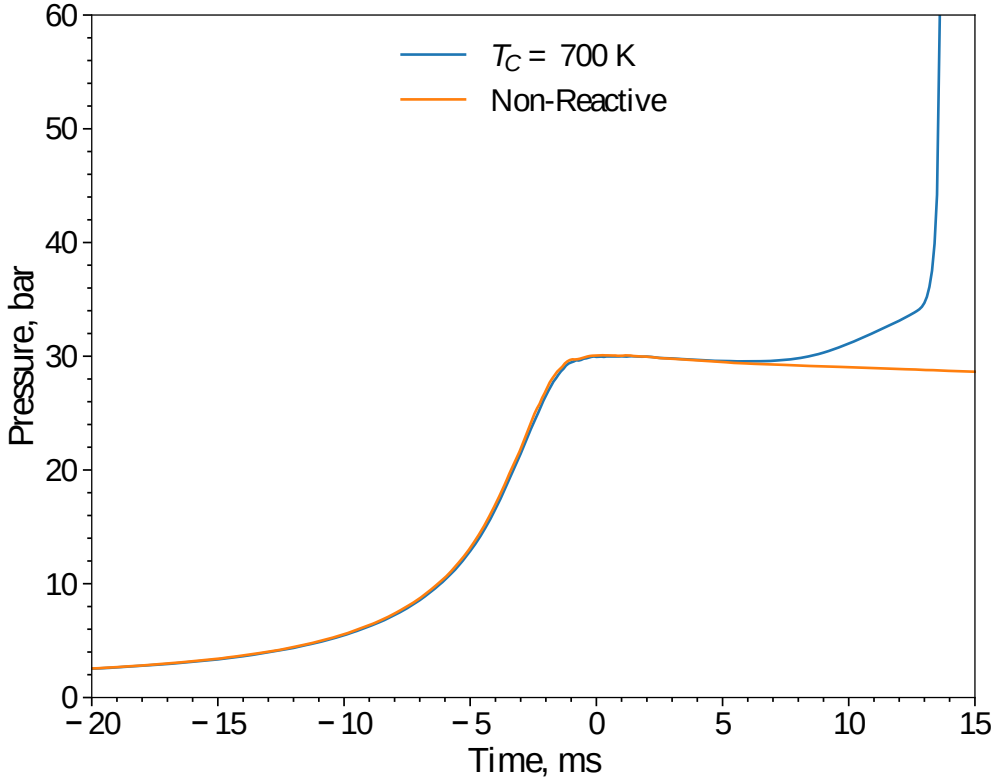
No NTC region of ignition delay for $\phi < 1.0$ in these experiments

$\phi = 1.0$ does have an NTC region from 720–800 K

First stage ignition measured from 734-757 K

Pressure traces show heat release for range of temperatures

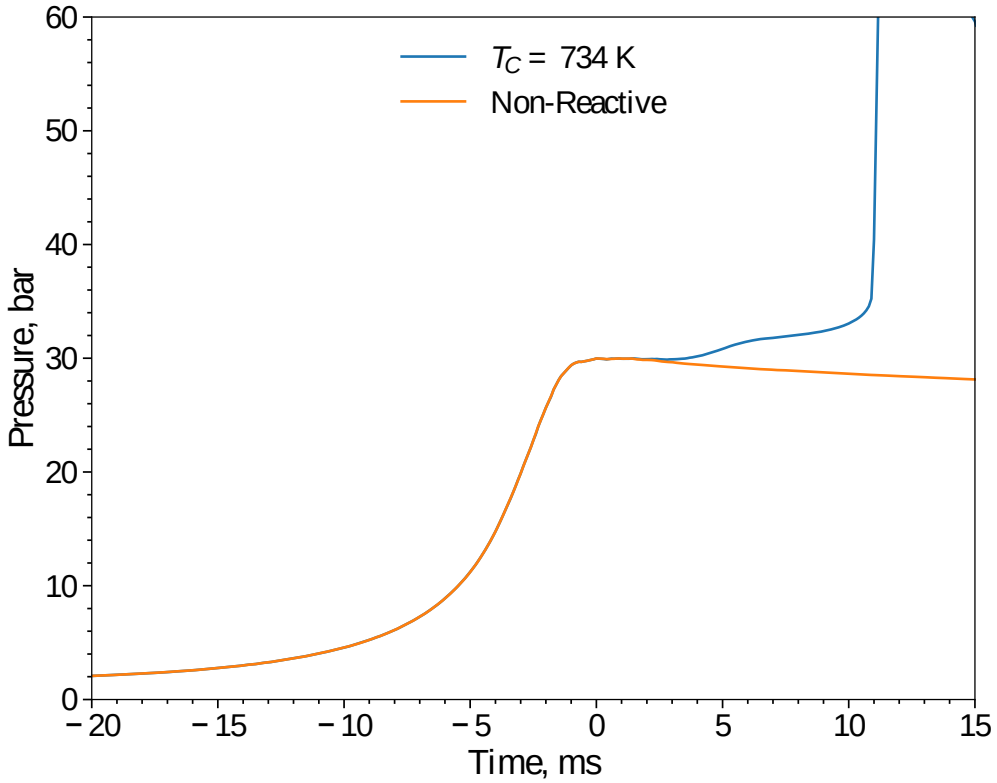
$\phi = 1.0, P_C = 30$ bar



- $T_C = 700$ K is on the low-temperature side of the NTC
- Heat release is present, as judged by the deviation of the reactive experiment from the non-reactive experiment
- Only one peak in the derivative is present → Single-stage ignition

Pressure traces show heat release for range of temperatures

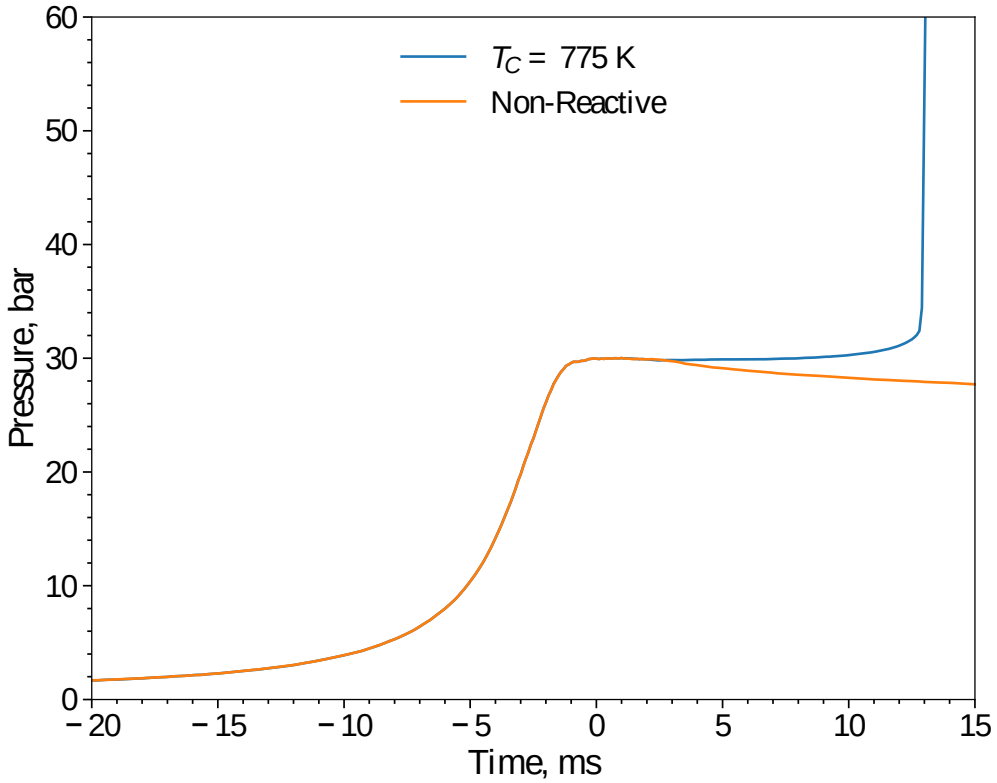
$\phi = 1.0, P_C = 30$ bar



- $T_C = 734$ K is a case with two-stages of ignition
- In this case, two peaks in the derivative are present → Two-stage ignition

Pressure traces show heat release for range of temperatures

$\phi = 1.0, P_C = 30$ bar



- $T_C = 775$ K is near the high-temperature limit of the NTC region
- The heat release is more gradual than the lower-temperature cases
- Only one stage of ignition

Models

- One model available in the literature includes low-temperature chemistry
  - Diévart et al. (2013) DOI: 10.1016/j.proci.2012.06.180
  - Validated by comparison to flame extinction limits
  - 1103 species, 7557 reactions
  - Includes reactions for many methyl esters

- New model with Reaction Mechanism Generator (RMG) 1.0.4 [5, 6], with version 1.10.0 of the RMG database
  - 483 species, 19990 reactions
  - MV-only reaction mechanism

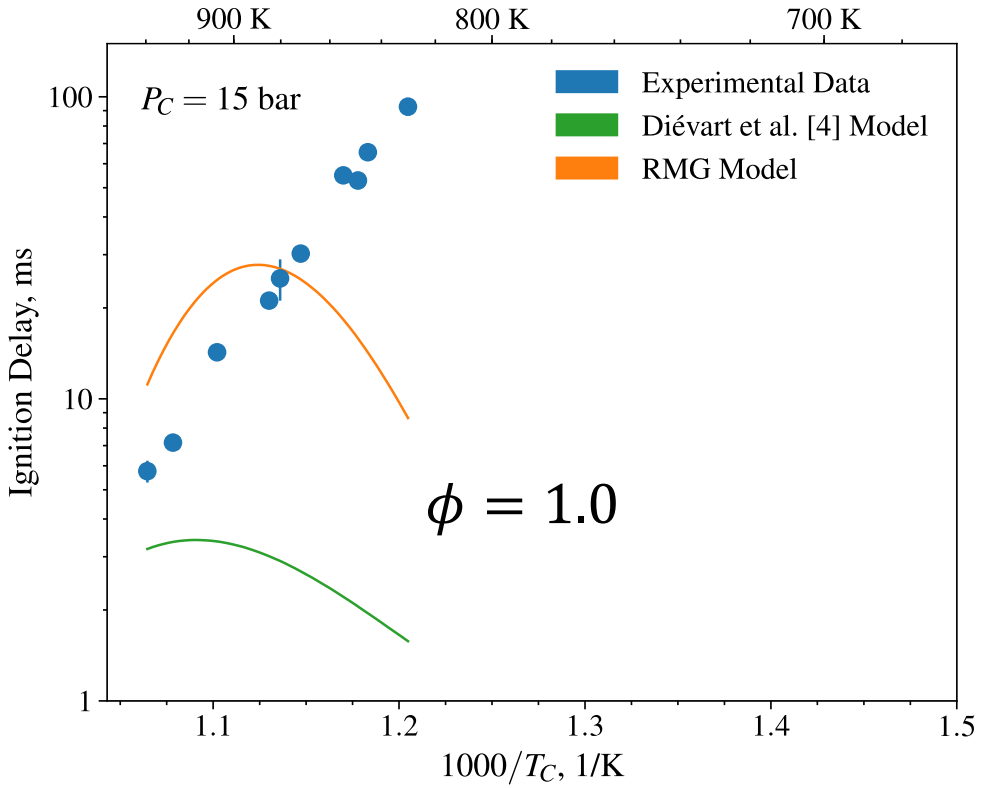
5. Gao et al. (2016) 10.1016/j.cpc.2016.02.013
6. Allen et al. (2012) 10.1039/c1cp22765c

Simulations

- Variable Volume
- Accounts for compression stroke and post-compression heat loss
- Used to compare ignition delays between experiments and simulations

- Constant Volume
- Adiabatic, fixed volume reactor
- No account for experimental effects
- Used to investigate chemistry without confounding experimental effects

Agreement of models with data

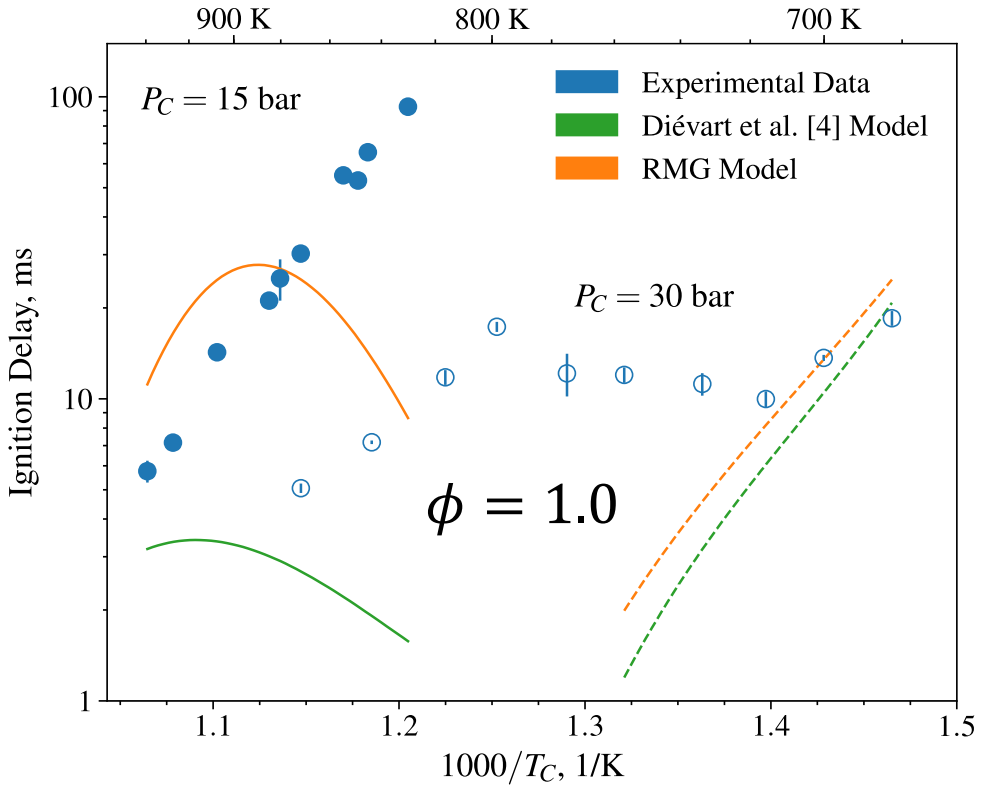


- Variable volume simulations
- Neither model is validated for these predictions

- Both models predict an NTC region where none is in the data at $P_C = 15$ bar

4. Diévart et al. (2013) DOI: 10.1016/j.proci.2012.06.180

Agreement of models with data



- Variable volume simulations
- Neither model is validated for these predictions

- Neither model predicts the experimental NTC at $P_C = 30$ bar
- Similar results for other equivalence ratios

4. Diévart et al. (2013) DOI: 10.1016/j.proci.2012.06.180

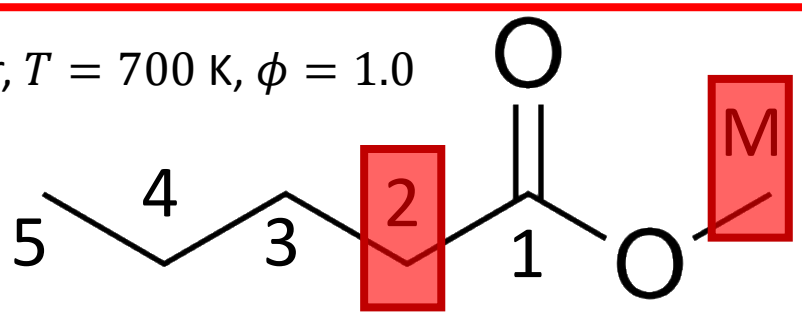
How can we improve the models?

- Include more reactions
  - RMG model has 19990 reactions
  - This may not be all the important one
- Estimate the reaction rates better
  - May affect construction of RMG model if rates are incorrectly estimated
- Estimate the thermodynamic properties better
  - How does the fuel react?

Path analysis shows differences between the models

Radical Site	Diévart et al. [4] (%)	RMG Model (%)
2	29.3	7.4
3	17.5	36.0
4	17.5	41.1
5	9.4	3.7
M	26.3	11.8

$P = 30$ bar, $T = 700$ K, $\phi = 1.0$



How much of the fuel is used to produce a fuel radical by H-abstraction?

Diévart et al. [4] model favors 2 and M radical sites

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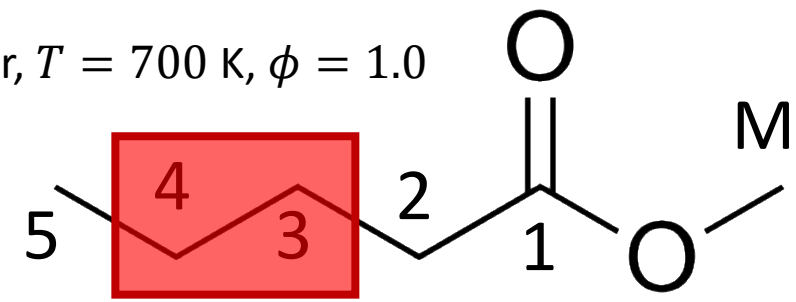

How much of the fuel is used to produce a fuel radical by H-abstraction?

RMG model favors the 3 and 4 radical sites

4. Diévart et al. (2013) DOI: 10.1016/j.proci.2012.06.180

Summary

- New experimental data for methyl valerate ignition at elevated pressure and low-to-intermediate temperature
- NTC region of ignition delay mapped for $\phi = 2.0$, $P_C = 15$ bar and $\phi = 1.0.$, $P_C = 30$ bar from 720 K to 800 K
- No existing models validated for low temperature ignition of methyl valerate
- Agreement for ignition delay between experiments and models isn't great

A series of interesting questions

- Why are the models so different from each other in terms of fuel radical production?
- Why do the models agree with the $P_C = 30$ bar, $\phi = 1.0$ data below 700 K but miss the NTC region?
- Why is there an NTC region predicted at $P_C = 15$ bar, $\phi = 1.0$ but no such experimental behavior?
- How is the chemistry of low temperature ester ignition different from alkane/alcohol ignition?

Thank you! Questions?

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