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$_6$H$_{12}$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 O₂ with N₂ 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’yanenko (2008)
   DOI: 10.1016/j.fluid.2008.02.001
Vapor pressure data is important to have homogeneous mixtures

![Graph showing vapor pressure data](image)

- Ortega et al. [1]
- van Genderen et al. [2]
- Verevkin and Emel’yanenko [3]

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

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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.
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

\[ \phi = 1.0, \ P_C = 30 \text{ bar} \]

- \( T_C = 700 \text{ K} \) 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

\[ \phi = 1.0, P_C = 30 \text{ bar} \]

- \( T_C = 734 \text{ K} \) is a case with two-stages of ignition
- In this case, two peaks in the derivative are present \( \rightarrow \) Two-stage ignition
Pressure traces show heat release for range of temperatures

\[ \phi = 1.0, P_C = 30 \text{ bar} \]

- \( T_C = 775 \text{ K} \) 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
  • Diévant 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

$P_C = 15$ bar

$\phi = 1.0$

$1000/T_C$, 1/K

Experimental Data
Diéwart et al. [4] Model
RMG Model

4. Diéwart 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. Diébart 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          |

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

\[ P = 30 \text{ bar}, \ T = 700 \text{ K}, \ \phi = 1.0 \]

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

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

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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