From Atom to Engine: Understanding Fundamental Effects of Structure on Combustion Using Tandem Experiment and Computation

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How do we identify a “good” fuel?

- Make and test it
- Predict its fuel properties
- Understand the fundamentals of its properties
Ignition needs vary with engine mode

Spark Ignition
Priority: **Spark**, not pressure, dictates ignition (knock resistance)

MultiMode Ignition
Priority: **Ease of mode-switching** between SI at high loads and CI at low loads

Compression Ignition
Priority: **Pressure** increase dictates ignition (minimize IDT)

Image sources: Co-Optima, Google Images
Fuel Combustion: Atomistic
Fuel Combustion: Atomistic

Fuel Molecule

- (H abstraction)
- (Oxidation)

alkyl radical
alkyl peroxy radical
internal H abstraction
hydroperoxyalkyl radical
second $O_2$ addition
internal H abstraction
ketohydroperoxide
chain branching

alkyl hydroperoxide
chain branching

$HO_2 + alkene$

$OH + O$-heterocycle

$ROOH + O_2$

$RO + OH$
Accurate understanding of the structure and chemistry = Accurate ignition models
Goal: Accurately describe fundamental chemistry that drives ignition and combustion

1. Identify products of unimolecular fuel pyrolysis

2. Produce PES’s of unimolecular breakdown and oxidation sites

3. Generate and compare ignition plots

Computed Potentials and Kinetics

Comparison to Experimental Ignition Data

Experimental Breakdown Pathway Identification


Approach

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<th>C2</th>
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**Ignition Promotion**
- OH production
- Chain propagating paths

**Ignition Suppression**
- HO₂ production
- Chain terminating paths
Computational kinetics of fuels provide a means of anticipating fuel properties related to combustion.

Ignition data estimations can be generated using rate constants typically produced using either:
- Reaction rate theory
- Computational chemistry

Zhang 2012 (model), Sarathy 2014 (model), Stranic 2012 (measured)
The computational piece of work presents a hybrid approach

1. First $O_2$ addition; assuming lowest E for subsequent QOOH pathways
2. Correct subsequent $O_2$ additions
3. Identify global trends
4. Connect fundamental reasoning to the global trends

\[
\text{n-butanol} \quad \rightarrow \quad \text{isopropanol} \quad + \quad O_2 \quad \rightarrow
\]

\[
\begin{align*}
\text{n-butanol ROO1} \\
\text{isopropanol ROO1}
\end{align*}
\]
N-butanol PES: ROO1

Lockwood & Stutzman et al. 2020 (in preparation)
<table>
<thead>
<tr>
<th>Isopropanol PES: ROO1</th>
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<tbody>
<tr>
<td>12.86</td>
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<tr>
<td>11.41</td>
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<td>36.15</td>
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<td>38.38</td>
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Huo et al. 2020 (in preparation)
N-butanol vs. isopropanol

First pass model expected to over-estimate IDTs

Assumed mostly HO2 downstream

Lockwood & Stutzman et al. 2020 (in preparation), Stranic 2012 (measured), Man 2014 (measured)
N-butanol

P = 19 atm

\[ \text{P = 1.5 atm} \quad (\varphi = 0.5) \]

\[ \text{P = 19 atm} \quad (\varphi = 0.5) \]

- Experimental
- Sarathy
- New

Lockwood & Stutzman et al. 2020 (in preparation); Sarathy 2014 (model), Stranic 2012 (measured)
N-propanol

$P = 16$ atm

\[ \text{OH} \]

$\phi = 0.5$

$\phi = 1.0$

New

Experimental

Sarathy

Huq et al. 2020 (in preparation), Sarathy 2014 (model), Noorani 2010 (measured), Man 2014 (measured)
Changes in chain length

Huq et al. 2020 (in preparation), Sarathy 2014 (model), Man 2014 (measured)
Ongoing and Upcoming Work

- Completing downstream QOOH calculations to improve rate accuracy
- Evaluating full subset of small alcohols of varied structure
- Identify ignition trends and identify structural/radical origins
- Compare our computations to experimental AFIDA data
- Validate trends against measured properties of biobased fuel candidate molecules
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NREL/PR-5100-77595
References

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• Sarathy butanol model- S.M. Sarathy et al., A comprehensive chemical kinetic combustion model for the four butanol isomers, Combustion and Flame 159 (2012) 2028-2055
• C.K. Law model propanol model- X. Man et al., An experimental and kinetic modeling study of n-propanol and i-propanol ignition at high temperatures, Combustion and Flame 161 (2014) 644-656

• Expt. Data of slide 1: X. Man et al., An experimental and kinetic modeling study of n-propanol and i-propanol ignition at high temperatures, Combustion and Flame 161 (2014) 644-656
• Expt. Data of slide 3: X. Man et al., An experimental and kinetic modeling study of n-propanol and i-propanol ignition at high temperatures, Combustion and Flame 161 (2014) 644-656
• Expt Data of slide 4: I Stranic et al., Shock tube measurements of ignition delay times for the butanol isomers, Combustion and Flame 159 (2012) 516-527