Fuel Chemistry and Combustion Kinetics

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Requirements for experiments to used in kinetic model validation

- Observed phenomenon is governed primarily by chemical kinetics
- Transport processes are sufficiently decoupled from chemical kinetics
- Physical boundary conditions are well known
- Uncertainties are documented

Need Fundamental Experiments to Validate Models

- Validate models against a wide range of data from idealized systems

Fundamental Experimental Tools for Kinetic Model Validation (0-D and 1-D)

- Ignition delay measurements
  - Shock tubes and rapid compression machines
  - Speciation measurements
- Premixed well stirred reactors
  - Speciation measurements
- Premixed flames
  - Low pressure flame speciation
  - Laminar flame propagation rates
- Counter-flow diffusion flames
  - Flame ignition and extinction
  - Speciation measurements
Shock Tube Reactors

Shock Tubes are ideal for measuring homogeneous gas phase reaction kinetics

Ideally a zero-dimensional system after reflected shock departs from the end wall

ST Ignition Delay Results

Simulation of shock tube reactor

- Simulate as a 0-D batch reactor
- Ideally as a constant volume reactor, but may be constant pressure
Reactive Gasdynamics Modeling: A Problem

- Most current reflected shock modeling assumes Constant-Volume or Constant-Pressure

But:
- **Exothermic** energy release during oxidation or **endothermic** cooling during pyrolysis changes T & P behind reflected shocks
  - not a Constant-V or Constant-P process!
- **Example:** Heptane Ignition

3 Proposed Solutions to Enable Modeling through Entire Combustion Event

1. Minimize fuel loading to reduce exothermically- or endothermically-driven T and P changes
   - enabled by high-sensitivity laser diagnostics
2. Modified gasdynamics modeling to account for P and T change during combustion
   - work in progress (but computationally intensive: 1-D, 3-D)
3. Use new constrained reaction volume concept to minimize pressure perturbations
   - enables constant P (or specified P) modeling

Examples:
- 1) Use of dilute reactive mixtures
- 2) Use of constrained reaction volume

Example 1: Benefit of Dilute Mixtures 3-Pentanone Oxidation

- Low Fuel Loading Experiment
- **OH Mole Fraction**

  - Pressure nearly constant throughout experiment
  - Good agreement between Constant H,P model and expt.
  - Model successfully includes temperature change
Example 2: Constrained Reaction Volume Approach
Hydrogen Ignition at 950 K

Conventional Shock Tube
- Pre-Shock
- Test Mixture
- Reflected Shock Wave
- Large Region of Energy Release

Constrained Reaction Volume
- Pre-Shock
- Helium
- Non-Reactive Mix
- TM
- Small Region of Energy Release

- Large reaction volume gives large energy release $\to \Delta P$ & $\Delta T$
- CRV gives reduced energy release $\to$ near-constant $P$

- Conventional ST exhibits large pressure change!
- CRV pressure nearly constant throughout experiment!
- Allows kinetics modeling through ignition and combustion!

Simulated ignition under conditions in a rapid compression machine

Rapid Compression Machine

Vanhoue, Minetti, Ribaucour, and coworkers, Lille, France
Diesel relevant n-heptane fuel exhibits low temperature ignition

![Graph showing n-heptane ignition delay](image)

Ignition delay test times

![Graph showing ignition delay test times](image)

Pressure Traces

![Pressure traces for ST and RCM](image)

Data processing for RCM simulation

**Step 1: Non-reactive experiment**

Experiment where O₂ is replaced by N₂ to characterize the compression and heat loss for a specific mixture
**Data processing for RCM simulation**

**Step 2: Volume profile**

- A volume profile is deduced from the pressure profile assuming isentropic behaviour (isentropic exponent not constant but temperature dependent).
- Heat loss effects are modelled as change in volume (Assumption of adiabatic core in RCM chamber).

**Step 4: Simulating reactive experiment**

Input for simulation (CHEMKIN PRO): Volume profile, gas mixture, initial temperature and pressure.

Perturbation of the constant volume reactor by the given volume profile

Non-constant volume simulation

Example: n-pentanol, φ = 1.0

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**Premixed Well Stirred Reactor (JSR)**

CNRS Orleans, P. Dagaut

- The zero dimensional perfectly stirred system is ideal for modeling.
- The products species profiles are dependent on chemical kinetics due to the perfectly mixed homogeneous environment.

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**JSR Boundary Conditions**

- The residence time of the gas in the reactor is actually a mean residence time (or space time) which is defined as the ratio of the volume of the reactor, V, and of the volume flow rate of the gas flowing through the reactor, Q, which is also the volume flow rate at the outlet of the reactor, Q⁺.
- To verify that the reactor can be considered as a continuous stirred-tank reactor, one can measure the residence time distribution (RTD) by doing a short injection of a very small amount of tracer at the inlet and by recording the evolution of the concentration of the tracer at the outlet. The reactor is an ideal continuous stirred-tank reactor if the residence time distribution E(t) can be represented by the expression given by the ideal equation.

\[ \tau = \frac{V}{Q} \]

\[ E(t) = \frac{1}{\tau} \exp \left( -\frac{t}{\tau} \right) \]
RTD measurement in jSR

\[ \tau = \frac{V}{Q} \]

\[ E(t) = \frac{1}{\tau} \exp\left(-\frac{t}{\tau}\right) \]

Fig. 2 - E(t) plots of the different JIRs against normalized time. The upper and lower dashed lines - or error bars - represent the region containing all the experimental data. The error bars of the experimental E(t) are generated from the error propagation in measuring the residence time in triplicate. The error bars of the ideal E(t) are sourced from the uncertainty in the volumetric flow rate (i.e., ±1% of the mass flow controller's full scale).


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JSR Results
CNRS Orleans, P. Dagaut

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JSR Results
CNRS Orleans, P. Dagaut
Premixed low pressure flames

Low pressure (10-100 Torr) premixed burner stabilized flames are ideal for measuring combustions intermediates and stable products.

Premixed low pressure flames results

➢ **T profile** for optical or MBMS sampling must be considered in comparison with models – no shifts!
➢ **Example:** butanol flames.

![Image of butanol flames](image)

Premixed Laminar Flame Speed

Univ Southern California, F. Egolfopoulos

![Graph showing laminar flame speed vs. equivalence ratio](image)

Laminar Flame Speed, Suo (cm/s)

- n-octane
- 2-methylheptane

Equivalence Ratio

0.6 0.8 1.0 1.2 1.4 1.6

n-octane/2-methylheptane in air, 353 K, 1atm
Premixed Laminar Flame Speed for n-octane

![Graph showing laminar flame speed for n-octane with equivalence ratio on the x-axis and laminar flame speed on the y-axis. The graph includes data points for 1 atm and 2 atm, with labels for Princeton and USC.]

Strained extinction and ignition

- Stable lower and upper branches are common in diffusive-convective reacting flows
- NTC-affected ignition phenomenon has also been observed

![Graph showing temperature vs. maximum temperature for different pressures (7 atm, 10 atm, 8 atm, 7 atm).]


Counterflow Extinction/Ignition Results for branched alkanes

![Diagram showing extinction and ignition of 2-methylheptane and 2,5-dimethylhexane.]

Opposed-flow Diffusion Flame (OPPDIF)

- The one-dimensional flame structure is ideal for modeling.
- The emissions and temperature profiles are dependent on chemical kinetics due to the non-turbulent flame.

![Diagram of opposed-flow diffusion flame with oxidizer and fuel mixture. Port diameter = 25.4 mm, Port Gap = 20 mm.]

Santhy et al. Combust Flame (2011)
OPPDIF Experimental Setup

OPPDIF Plots

OPPDIF Results

OPPDIF Minor Species Results
Fuel Chemistry and Combustion Kinetics

S. Mani Sarathy, Clean Combustion Research Center, KAUST

Reaction classes for oxidation chemistry

**High temperature mechanism**
1: Unimolecular fuel decomposition
2: H atom abstractions from fuel
3: Alkyl radical decomposition
4: Alkyl radical isomerization
5: H atom abstraction from alkenes
6: Addition of radical species to alkenes
7: Alkenyl radical decomposition
8: Alkene decomposition
9: Retroene decomposition reactions

**Low and High Temperature Reactions**

At high temperatures, the alkyl radical R decomposes, producing olefin and smaller alkyl radicals.

\[ \text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH} \]

is the dominant chain branching reaction.

At lower temperatures, alkyl radicals add to O2 forming PEROXY RADICALS:

\[ \text{R} + \text{O}_2 \rightarrow \text{RO}_2 \]

The equilibrium constant is strongly temperature dependent and is in favor of RO2 at low T, shifting toward R + O2 as T increases.

The Ceiling Temperature is the temperature above which this equilibrium favors the dissociation path.

RO2 radicals isomerize to produce a QOOH radical species:

\[ \text{RO}_2 \rightarrow \text{QOOH} \]

Isomerization depends sensitively on the size and structure of the original fuel molecule and the site where the O2 group is located.

Successive reactions of peroxy radicals form the very reactive 'ketohydroperoxide' species

Keto-/Carbonyl-hydroperoxides fastly decompose to form two radicals:
Explosion Diagrams: C₃H₈/O₂ mixture

The Ceiling Temperature
R + O₂ ↔ RO₂
rules the transition between
Low and High T Mechanisms

High Temperature Mechanism
Alkyl radicals

Low Temperature Mechanism
Peroxy radicals

TEST molecule

Bond dissociation energies
Primary: ~103 kcal/mol
Secondary: ~98 kcal/mol
Tertiary: ~94 kcal/mol

Comprehensive Combustion Chemistry

Fast High Temperature Combustion

Long Chain Alkanes

Low T Chemistry

NTC

HI T Chemistry

Degenerate Branching Path
Detailed chemical kinetic models for the combustion of hydrocarbon fuels

John M. Simmie

Lumping procedures in detailed kinetic modeling of gasification, pyrolysis, partial oxidation and combustion of hydrocarbon mixtures

E. Ranzi, M. Dente, A. Goldaniga, G. Bozzano, T. Faravelli

Low temperature combustion chemistry

Low temperature combustion chemistry

What is the reason for NTC reactivity?

Detailed chemical kinetic models for the low-temperature combustion of hydrocarbons with application to gasoline and diesel fuel surrogates

F. Reitz-Loeber
Reaction classes for oxidation chemistry

Low temperature mechanism
10: Alkyl radical addition to O₂ (R + O₂ = ROO)
12, 13, and 14: R + RO = RO + RO
15: Alkylperoxo radical isomerization (ROO=QOOH)
16: Concerted eliminations (RO₂ = alkene + HO₂)
17: RO₂ + HO₂ = ROOH + O₂
18: RO₂ + H₂O₂ = ROOH + HO₂
19: RO₂ + CH₃O₂ = RO + CH₂O + O₂
20: RO₂ + RO = RO + RO + O₂
21: ROOH = RO + OH
22: RO decomposition
23: QOOH = cyclic ether + OH (cyclic ether formation)
24: QOOH = alkene + RO₂ (radical beta to OOH)
25: QOOH = alkene + carbonyl + OH (radical gamma to OOH)
26: Addition of QOOH to molecular oxygen O₂ (QOOH+O₂=QOOH)
27: Q₂QOOH isomerization to carbonylhydroperoxide + OH
28: Carbonylhydroperoxide decomposition
29: Reactions of cyclic ethers with OH and HO₂

10: Alkyl radical addition to O₂ (R+O₂=ROO)

- The addition of molecular oxygen to alkyl radicals is the first step in the low temperature chain branching process.
- Each unique fuel radical leads to an alkylperoxy (ROO) radical.
- The chemistry of alkylperoxy radicals governs tropospheric oxidation of organic species. In combustion chemistry however, the R+O₂ reaction displays much more complex behavior.

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Table 1. Detailed Mechanism of α-Alkene Oxidation: Number of Primary Propagation Reactions

<table>
<thead>
<tr>
<th>Reaction Class</th>
<th>α-CH₃</th>
<th>α-CH₂-CH₃</th>
<th>α-CH₂-CH₂-CH₃</th>
<th>α-CH₃-CH₂-CH₂-CH₃</th>
<th>α-CH₃-CH₂-CH₂-CH₂-CH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>10</td>
<td>18</td>
<td>24</td>
<td>30</td>
<td>36</td>
</tr>
<tr>
<td>B2</td>
<td>6</td>
<td>9</td>
<td>11</td>
<td>13</td>
<td>15</td>
</tr>
<tr>
<td>B3</td>
<td>10</td>
<td>13</td>
<td>16</td>
<td>18</td>
<td>20</td>
</tr>
<tr>
<td>B4</td>
<td>10</td>
<td>13</td>
<td>16</td>
<td>18</td>
<td>20</td>
</tr>
<tr>
<td>B5</td>
<td>10</td>
<td>13</td>
<td>16</td>
<td>18</td>
<td>20</td>
</tr>
<tr>
<td>B6</td>
<td>10</td>
<td>13</td>
<td>16</td>
<td>18</td>
<td>20</td>
</tr>
<tr>
<td>B7</td>
<td>10</td>
<td>13</td>
<td>16</td>
<td>18</td>
<td>20</td>
</tr>
<tr>
<td>B8</td>
<td>10</td>
<td>13</td>
<td>16</td>
<td>18</td>
<td>20</td>
</tr>
<tr>
<td>B9</td>
<td>10</td>
<td>13</td>
<td>16</td>
<td>18</td>
<td>20</td>
</tr>
<tr>
<td>total</td>
<td>10</td>
<td>13</td>
<td>16</td>
<td>18</td>
<td>20</td>
</tr>
</tbody>
</table>

Table 2. Detailed Mechanism of α-Alkene Oxidation

<table>
<thead>
<tr>
<th>Primary Propagating Radicals</th>
<th>α-CH₃</th>
<th>α-CH₂-CH₃</th>
<th>α-CH₂-CH₂-CH₃</th>
<th>α-CH₃-CH₂-CH₂-CH₃</th>
<th>α-CH₃-CH₂-CH₂-CH₂-CH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-CH₃</td>
<td>15</td>
<td>21</td>
<td>27</td>
<td>33</td>
<td>39</td>
</tr>
<tr>
<td>α-CH₂-CH₃</td>
<td>6</td>
<td>9</td>
<td>11</td>
<td>13</td>
<td>15</td>
</tr>
<tr>
<td>α-CH₂-CH₂-CH₃</td>
<td>6</td>
<td>9</td>
<td>11</td>
<td>13</td>
<td>15</td>
</tr>
<tr>
<td>α-CH₃-CH₂-CH₂-CH₃</td>
<td>6</td>
<td>9</td>
<td>11</td>
<td>13</td>
<td>15</td>
</tr>
<tr>
<td>α-CH₃-CH₂-CH₂-CH₂-CH₃</td>
<td>6</td>
<td>9</td>
<td>11</td>
<td>13</td>
<td>15</td>
</tr>
</tbody>
</table>


10: Alkyl radical addition to O₂ (R+O₂=ROO)

- Recent rate calculations from Miyoshi et al. suggest that these rates are temperature dependent.
10: Alkyl radical addition to O₂ (R+O₂=ROO)

- Why do we have NTC?
- RO₂ dissociation becomes competitive with RO₂ isomerization as temperature increases.
- This competition leads to a decrease in OH production and thus reduction in overall reactivity.

BDEs of RO₂ radicals
- P = ~35 kcal/mol
- S = ~37 kcal/mol
- T = ~39 kcal/mol

15: Alkylperoxy radical isomerization (RO₂=QOOH)

- The intramolecular H-abstraction of an alkyl peroxy radical (i.e., ROO) to form a hydroperoxyalkyl radical (i.e., QOOH) is the second step in the low temperature chain branching process.
- Include isomerization reactions involving 5-member, 6-member, and 7-member, and 8-member transition state rings.
- Exclude radical isomerizations involving fewer than five and greater than eight members because they are much slower.

Rate Rules from Bugler et al JPCA 2015

<table>
<thead>
<tr>
<th>Addition Site</th>
<th>A (cm³ mol⁻¹ s⁻¹)</th>
<th>n</th>
<th>E (cal mol⁻¹)</th>
<th>Uncertainty (Upper, Lower)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary</td>
<td>1.301 x 10¹¹</td>
<td>0.230</td>
<td>-1580</td>
<td>1.7, 2.2</td>
</tr>
<tr>
<td>Secondary</td>
<td>1.507 x 10¹³</td>
<td>-0.920</td>
<td>-130</td>
<td>2.1, 1.7</td>
</tr>
<tr>
<td>Tertiary</td>
<td>2.464 x 10¹¹</td>
<td>0.400</td>
<td>-880</td>
<td>1.4, 1.7</td>
</tr>
</tbody>
</table>

15: Alkylperoxy radical isomerization (RO₂=QOOH)

- The rate constant depends on the nature of the broken C-H bond (i.e., primary, secondary, or tertiary) and on the ring strain energy barrier.
Alkylperoxy isomerization (RO₂=QOOH)

How would these new rate rules affect low T ignition delay predictions?


RO₂=QOOH isomerization rate effect on shock tube ignition delay time

Modifying the rate rules the rate rules does appear to decrease ignition delay times.

Rate Rules from Bugler et al JPCA 2015

<table>
<thead>
<tr>
<th>reaction</th>
<th>A₀ (s⁻¹)</th>
<th>α</th>
<th>E (cal mol⁻¹)</th>
<th>uncertainty (upper, lower)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,4p</td>
<td>2.563 x 10¹⁴</td>
<td>-0.130</td>
<td>34360</td>
<td>2.4, 3.3</td>
</tr>
<tr>
<td>1,4s</td>
<td>2.332 x 10⁷</td>
<td>1.000</td>
<td>78860</td>
<td>4.2, 5.1</td>
</tr>
<tr>
<td>1,4t</td>
<td>5.639 x 10⁷</td>
<td>0.530</td>
<td>36700</td>
<td>1.9, 3.0</td>
</tr>
<tr>
<td>1,5p</td>
<td>7.849 x 10⁷</td>
<td>0.780</td>
<td>21850</td>
<td>2.5, 3.7</td>
</tr>
<tr>
<td>1,s</td>
<td>8.204 x 10⁷</td>
<td>0.130</td>
<td>19470</td>
<td>2.2, 3.3</td>
</tr>
<tr>
<td>1,5t</td>
<td>1.819 x 10⁷</td>
<td>1.190</td>
<td>15000</td>
<td>2.1, 3.0</td>
</tr>
<tr>
<td>1,6p</td>
<td>3.065 x 10⁷</td>
<td>1.000</td>
<td>21070</td>
<td>1.8, 1.7</td>
</tr>
<tr>
<td>1,6s</td>
<td>7.154 x 10⁸</td>
<td>0.510</td>
<td>17690</td>
<td>1.6, 2.3</td>
</tr>
<tr>
<td>1,6t</td>
<td>1.847 x 10⁷</td>
<td>0.960</td>
<td>14290</td>
<td>1.5, 1.6</td>
</tr>
<tr>
<td>1,7p</td>
<td>3.968 x 10⁷</td>
<td>0.800</td>
<td>21400</td>
<td>1.2, 1.2</td>
</tr>
<tr>
<td>1,7s</td>
<td>1.143 x 10⁷</td>
<td>0.040</td>
<td>19780</td>
<td>1.8, 3.6</td>
</tr>
<tr>
<td>1,7t</td>
<td>2.956 x 10⁹</td>
<td>0.040</td>
<td>16330</td>
<td>1.2, 1.3</td>
</tr>
</tbody>
</table>

16: Concerted eliminations (RO₂ = alkene + HO₂)

- This concerted (direct) elimination of HO₂ from the alkyl peroxy radical (i.e., ROO) occurs via a 5-membered transition state.
- The O-O moiety leaves the ROO molecule, and takes an H atom from the adjacent C atom with it.
- Competes directly with the alkyl peroxy radical isomerization pathway, so it reduces overall low temperature reactivity. It is also responsible for the majority of HO₂ and high molecular weight alkenes formed in the low and intermediate temperature regimes.
16: Concerted eliminations (RO₂ = alkene + HO₂)

- This reaction class was a hot topic of debate for many years.
- It was finally put to rest in 2003 with an elegant combination of experiments and theory.

De Sain et al., J Phys Chem A 2003

16: Concerted eliminations (RO₂ = alkene + HO₂)

- The rate constant depends on the nature of the C-H bond broken (i.e., primary, secondary, or tertiary) during the direct elimination reaction.
- How many possible concerted eliminations are there?

Quirk et al., J. Am. Chem. Soc.

16: Concerted eliminations (RO₂ = alkene + HO₂)

- The rate constant depends on the nature of the C-H bond broken (i.e., primary, secondary, or tertiary) during the direct elimination reaction.
- Existing rules are are quite good agreement with theory for primary and secondary sites. No theoretical calculations for tertiary C-H.

Rate Rules from Bugler et al JPCA 2015

<table>
<thead>
<tr>
<th>RO₂ =&gt; Olefin + HO₂</th>
<th>Aₚ (s⁻¹)</th>
<th>n</th>
<th>E (cal mol⁻¹)</th>
<th>uncertainty (upper, lower)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.685 x 10⁻⁹</td>
<td>0.930</td>
<td>29000</td>
<td>2.8, 2.2</td>
<td></td>
</tr>
</tbody>
</table>
23: QOOH = cyclic ether + OH (cyclic ether formation)

- The cyclization of a hydroperoxyalkyl radical (i.e., QOOH) to form a cyclic ether plus an OH radical is an important pathway that competes with the critical chain branching channel.
- A first approximation assumes that the rate constant only depends on the ring size of the cyclic ether formed.
- 3-member (oxirane), 4-member (oxetane), and 5-member (oxolanes) are important ethers that can be formed.
- How many possible cyclic ether species are there?

\[
\begin{align*}
\text{QOOH} & \rightarrow \text{Cyclic Ether} + \text{OH} \\
\text{QOOH} & \rightarrow \text{Cyclic Ether} + \text{OH}
\end{align*}
\]

23: QOOH = cyclic ether + OH (cyclic ether formation)

- The A factor for oxirane (3m) formation is a factor of \( \sim 8-9 \) higher than that for oxetane (4m), which in turn is a factor of \( \sim 8-9 \) higher than for oxolanes (5m) due to the loss in entropy as one extra rotor is getting frozen with progressive increase of ring size.
- The activation energy decreases with increasing ring size.

<table>
<thead>
<tr>
<th>Cyclic Ether</th>
<th>A</th>
<th>( n )</th>
<th>( E_a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3m</td>
<td>1.0E+01</td>
<td>0.0</td>
<td>22.000</td>
</tr>
<tr>
<td>4m</td>
<td>7.500E+00</td>
<td>0.0</td>
<td>15.250</td>
</tr>
<tr>
<td>5m</td>
<td>9.183E+00</td>
<td>0.0</td>
<td>7.000</td>
</tr>
<tr>
<td>6m</td>
<td>1.173E+09</td>
<td>0.0</td>
<td>1.800</td>
</tr>
</tbody>
</table>

Cyclic ether formation rate: Effect on jet stirred reactor species profiles

- More refined treatments consider the nature of the radical center.
- Activation energy is smaller for tertiary carbon radical, followed by the secondary and then by the primary ones.
- Substitution of alkyl groups adjacent to the OOH group or the radical-bearing carbon decreases the activation energy because of release of alkyl strain in the cyclic TS.

What effect will substitution have on low temperature reactivity?

[Diagrams showing the effect of substitution on cyclic ether formation rate at different temperatures.]
26: Addition of QOOH to molecular oxygen $O_2$  
(QOOH+$O_2$=O$_2$ QOOH)  
- The addition of molecular oxygen to hydroperoxy alkyl radicals (i.e., QOOH) is the third step in the low temperature chain branching process.  
- The rate of $O_2$ addition to a QOOH radical depends on whether the radical carbon is a primary, secondary, or tertiary site. The prescribed rate constants are the same as the $R + O_2 = RO_2$ reactions (i.e., class 11).

27: O$_2$QOOH isomerization to carbonylhydroperoxide + OH  
- In this reaction class an O$_2$QOOH radical isomerizes, releases an OH, and then forms a carbonylhydroperoxide (i.e., keto hydroperoxide).  
- This is the fourth step in the low temperature chain branching process.

27: O$_2$QOOH isomerization to carbonylhydroperoxide + OH  
- A basic assumption is that atom being abstracted is bound to the carbon atom bonded to the hydroperoxy (OOH) group, which has a lower C-H bond strength than a normal C-H bond and makes it easier to abstract.  
- The reaction rate constant is the same as the RO$_2$=QOOH isomerizations, except the activation energies have been reduced by 3 kcal/mol to account for the weakened C-H bond.  
- Alternate isomerization may also be possible, and should be included for for branched molecules.
27: $O_2QOQOH$ isomerization to carbonylhydroperoxide + OH

- The reaction rate constant is the same as the $RO_2\to QOQOH$ isomerizations, except the activation energies have been reduced by 3 kcal/mol to account for the weakened C-H bond.
- Some theoretical calculations provide actual rates for these site-specific isomerizations, but their accuracy and testing are yet to be researched.

28: Carbonylhydroperoxide decomposition

- The decomposition of a carbonylhydroperoxide forms an OH radical, a carbonyl radical, and a stable carbonyl (i.e., aldehyde or ketone).
- This reaction pathway is the final step in the low temperature chain branching process because it forms two radical species from one stable reactant.

Prescribe an estimated rate constants of $1.0\times10^{16}$ exp (-39,000/RT) s$^{-1}$

Low temperature combustion chemistry

Pressure dependence of low T pathways

- Pressure dependence of all low temperature channels may affect reactivity.
- Solid lines are high pressure rate constants while dashed lines are 10 bar rate constants.
- Simulation results suggest that important species profiles are not significantly different when using P-dependent rate constants.

**Generic Fuel Reaction Scheme**

- Fuel
- H
- olefin + R
- high T
- β-scission
- R
- O₂
- RO₂
- cyclic ether + OH
- olefin + HO₂
- β-scission products
- O₂
- O₂ OOH
- carboxyhydroperoxide + OH
- carbonylalkoxy + OH radical

**The Effect of Substitution on Ignition**

<table>
<thead>
<tr>
<th>Research Octane Number</th>
<th>Derived Cetane Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-octane</td>
<td>0</td>
</tr>
<tr>
<td>2-methylheptane</td>
<td>42.4</td>
</tr>
<tr>
<td>3-methylhexane</td>
<td>52.0</td>
</tr>
<tr>
<td>2,4-dimethylpentane</td>
<td>83.1</td>
</tr>
<tr>
<td>n-octane</td>
<td>-19.0</td>
</tr>
<tr>
<td>2-methylheptane</td>
<td>21.7</td>
</tr>
<tr>
<td>3-methylhexane</td>
<td>36.8</td>
</tr>
<tr>
<td>2,5-dimethylhexane</td>
<td>55.5</td>
</tr>
</tbody>
</table>

**The Effect of Substitution on Ignition**
Using shock tubes experiments and kinetic modeling

- n-octane: -19.0
- 2-methylheptane: 21.7
- 3-methylhexane: 36.8
- 2,5-dimethylhexane: 55.5
- iso-octane: 100

**Correlating RON with ignition delay time**

- n-octane: -19.0
- 2-methylheptane: 21.7
- 3-methylhexane: 36.8
- 2,5-dimethylhexane: 55.5

The existence of a correlation between RON and ignition delay time exists using the present model.
Low Temperature (700 K) Chain Branching Reaction Pathways

~22 kcal barrier

6-member ring aromatization

~19 kcal

6-member ring aromatization

Effects of Substitution on JSR Reactivity

2-methylheptane is generally more reactive than 3-methylheptane

3-methylheptane

2-methylheptane

Volumetric heat of production rate (mg/cm³/s°C)

100 150 200 250 300 350 400

1.00-10 1.50-10 2.00-10 2.50-10 3.00-10

5.00E-08 6.00E-08 7.00E-08 8.00E-08 9.00E-08

2-methylheptane

3-methylheptane

45

27% beta scission

16%

12% O, O₂

79% (CH₃)₂CHCH₂CH₂CH₂CH₂OH

17% OOH

17% (CH₃)₂CHCH₂CH₂CH₂CH₂OH

17% OOH

40% alkenes

66% O₂

24%

76% (CH₃)₂CHCH₂CH₂CH₂CH₂OH

-temp scission

35% (CH₃)₂CHCH₂CH₂CH₂CH₂OH

32%

57% O₂

12% O, O₂

60% (CH₃)₂CHCH₂CH₂CH₂CH₂OH

100%

2.5-dimethyl-2-ethyl-THF

LCB

100%

Low Temperature Branching

100%

Low Temperature Branching

Low Temperature Branching

47
Real fuels are extremely complex

Low carbon number
Less complex

High carbon number
More complex

Kinetic Models

Conventional transportation fuels are complex mixtures

Gasoline
C5-C9

Jet Fuel
C9-C14

Diesel
C12-C20
Current combustion modeling requires surrogate fuels chemical kinetics

- Palette represents the carbon number range, carbon types, PIONA, and kinetic features
- A chemical kinetic model for mixtures of these fuels has been developed.
- We can use the model to determine surrogate mixture combustion properties.

We have automated tools for surrogate formulation


**Chemical Kinetic Models**


In 2017, we started wondering if there was a more simple and elegant approach to modeling real fuel combustion chemistry.

Dooley S. et al., Combust. Flame. 2012

Can a fuel's functional group information be used to predict its combustion characteristics?

Real fuels can have hundreds of components, but only a limited number of functional groups

Some of the molecules present in gasoline fuels

Functional groups present in gasoline fuels
Simple surrogates when formulated with knowledge of a fuel's functional groups can emulate fuel characteristics.

The MFG approach \[1\]

1. Formulate surrogates by matching the functional groups in the fuel

2. Use minimum number of species (1-2) to simplify the surrogate palette and also to test the approach unambiguously

The following key functional groups were chosen as a criteria for matching,

1. Paraffinic \( \text{CH}_2 \) groups
2. Paraffinic \( \text{CH}_3 \) groups
3. Paraffinic \( \text{CH} \) groups
4. Naphthenic \( \text{CH}_2\text{CH}_3 \) groups
5. Aromatic \( \text{C-CH} \) groups


We can identify and quantify functional groups using \(^1\text{H} \)NMR spectroscopy

\(^1\text{H} \)NMR spectra are accurate, predictable and can be acquired in a few minutes.

NMR spectra are represented in terms of chemical shifts, the number and position of the shifts is diagnostic of the molecular structure.

The various functional groups appear as peaks in their characteristic regions.

Functional groups that closely resemble also give distinct signals.

The functional groups can be quantified by integrating the peaks.

\(^1\text{H} \)NMR spectra of FACE gasolines

MFG surrogates have only 1 or 2 species

The gasoline surrogates reported in the literature tend to add more species thereby increasing the complexity.

Mehl et al. \[7\] have used 4 species (TPRF, 2-panterne) for RD-387 gasoline

Naik et al. \[8\] have used 5 species (TPRF, 1-panterne and methyl cyclohexane)

Ahmed et al. \[9\] have used 6 species (TPRF, n-butane, 2-methylbutane and 2-methylxylene) to represent FACE A and C

Elwardany et al. \[4\] have used 7 species to represent FACE A gasoline.

In the present minimalist approach we have used minimum number of species to match the functional groups, thereby simplifying the surrogates.

\[7\] Mehl, M. E.; Dumesic, J. A. Science 2013, 341, 322-324


MFG surrogates match the functional groups of real fuels

[Graphs showing comparison of surrogates with real fuels for FACE A, FACE B, and others]
MFG surrogates can match the combustion characteristics of real fuel

Fuel properties can be predicted using machine learning

Ignition quality can be predicted using NMR spectra as input

DCN of 71 pure compounds and 54 blends was collected/measured using IQT.

Dataset was used to study the relationship between CN/DCN and 8 structural parameters:

1) Paraffinic CH\(_2\) groups
2) Paraffinic CH\(_3\) groups
3) Paraffinic CH groups
4) Olefinic CH-CH\(_2\) groups
5) Naphthenic CH-CH\(_3\) groups
6) Aromatic C-CH groups
7) Molecular weight
8) A new parameter called as Branching Index (BI)

Slide credit: Abdul Jameel (Energy Fuels 2016)
Prediction of fuel combustion is good when using molecular features as inputs to ANNs

ANN models were developed to predict fuels research octane number (RON), motor octane number (MON) and cetane number (CN) using the fuel functional groups (7 types), molecular weight and branching index as input features to the model.

A dataset of 281 fuels for RON and MON, and 500 fuels for CN was used to in order to learn the complex relationship between the 9 inputs and the output.

Nuclear magnetic resonance (NMR) spectroscopy was used to identify and quantify the functional groups in the fuel.

The average absolute error of prediction was around one which is close to the range of experimental uncertainty.

A fully predictive lumped kinetic model for real fuels was developed

- **Lumped mechanism for fuel (oxidative) pyrolysis in HyChem model**

\[
\begin{align*}
C_{12}H_8 &= r_{C}(C_{12}H_{16} + 2C_6H_{12} + C_8H_8) \\
+ r_{C}(C_{12}H_{16} + 2C_6H_{12} + C_8H_8) + xH_2O + (2 - x)CH_3O & \text{(R2-R7)}
\end{align*}
\]

where

\[
\begin{align*}
\Sigma_p &= \gamma C_{12}H_8 + r_{C}(C_{12}H_{16} + 2C_6H_{12} + C_8H_8) \\
&+ xH_2O + (2 - x)CH_3O + (1 - z)CH_3
\end{align*}
\]

- **Experiments**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r )</td>
<td>number of H atoms produced in the “C-C fission reaction” (R1) per ( C_{12}H_8 )</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>number of H atoms produced in the H-abstraction reactions (R2-R7) per ( C_{12}H_8 )</td>
</tr>
<tr>
<td>( x )</td>
<td>CH_yield per ( C_{12}H_8 ) in addition to H abstraction by CH_3</td>
</tr>
<tr>
<td>( z )</td>
<td>( [C_6H_6]/[C_{12}H_8] )</td>
</tr>
<tr>
<td>( \lambda )</td>
<td>( [C_6H_6]/[C_{12}H_8] )</td>
</tr>
<tr>
<td>( \rho )</td>
<td>( [C_6H_6]/[C_{12}H_8] )</td>
</tr>
</tbody>
</table>

**Alternative approach**

- Fully predictive w/o need for exp. data

A real, Multi-component fuel + \( O_2 \)

Schematic of HyChem approach

- Surrogate fuel strategy: limited components to represent real fuels
- HyChem approach: lumped steps for fuel pyrolysis + detailed mech. for oxidation

FGM Mech philosophy

**Using functional groups for mechanism (FGMech) development**

- **Thermodynamic data:**

\[
\Delta_f H(298) = \sum_{X_i} GAV_{Th}(X_i)
\]

\[
S(298) = \sum_{X_i} GAV_{Th}(X_i) - R \ln(\eta/\eta_{app})
\]

\[
C_{pr}(T) = \sum_{X_i} GAV_{Th}(X_i)
\]

- **Kinetic data:**

\[
k(T) = \sum_{X_i} k_{1T}(X_i)
\]

Fuel characterization

Stoichiometric parameters

Thermodynamic data

Kinetic rate constants

Transport data

MLR Correlation

Benson GA

Rate rules

Jacobian method
Model construction: stoichiometric parameters

- **C$_2$H$_4$, C$_3$H$_6$, C$_4$H$_8$ isomers, H and CH$_3$ from a lumped mechanism**
  - H-atom abstraction, isomerization and decomposition are lumped
  - 50 fuels include $n$-$C_6$-alkanes, cycloalkanes and aromatics

\[ \text{C}_{6} \text{H}_{14}+H \rightarrow \text{C}_{6} \text{H}_{13} \text{H}+\text{H}_2 \]

- **CH$_4$, C$_2$H$_6$ and C$_3$H$_8$ from pyrolysis experiments**
  - Mainly secondary products from fuel decomposition
  - The yield of CH$_4$ in experiments is close to $\gamma$
  - The ratio of [C$_2$H$_6$]/([C$_3$H$_8$]+[C$_2$H$_4$]) in exp. is close to $\chi$

<table>
<thead>
<tr>
<th>Chemical class</th>
<th>Carbon number</th>
<th>P (atm)</th>
<th>T (K)</th>
<th>Time (ms)</th>
<th>Number of datasets</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$-alkane</td>
<td>C$_2$-C$_6$</td>
<td>1-50</td>
<td>1000-1600</td>
<td>1-300</td>
<td>33</td>
</tr>
<tr>
<td>iso-alkane</td>
<td>C$_3$-C$_8$</td>
<td>1-50</td>
<td>1023-1500</td>
<td>1-300</td>
<td>23</td>
</tr>
<tr>
<td>cycloalkane</td>
<td>C$_5$-C$_10$</td>
<td>1-200</td>
<td>1073-1587</td>
<td>2-300</td>
<td>38</td>
</tr>
<tr>
<td>aromatics</td>
<td>C$_5$-C$_10$</td>
<td>0.04-50</td>
<td>1083-1700</td>
<td>1-300</td>
<td>29</td>
</tr>
</tbody>
</table>

**Distribution of 123 datasets from pyrolysis speciation data**


Model validation: Model performance

- **Validation against real fuels: FACE gasoline fuels**
  - FGMech-Aramco (solid lines) better predicts the ignition delay at lower temperatures
  - FGMech-USC (dotted lines) better predicts the ignition delay at higher temperatures
Model validation: Model performance

- Validation against real fuels: Jet and rocket fuels

- Generally, the predicted results by the present model are in reasonable agreement with the experimental data

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Introduction to heavy residue gasification

Residues with heavy avg MW
Eg.: C46H66, C80H90, etc.

\[ + \text{O}_2 \text{ (sub-stoichiometric, } \lambda=0.4) + \text{H}_2\text{O} \]

Main products:
- CO, H\textsubscript{2}, CO\textsubscript{2}, H\textsubscript{2}O, CH\textsubscript{4}

Down-draft gasifier

\[ T \sim 1000 \text{ }-\text{ } 2000 \text{ }^\circ\text{C}, \text{ } P \sim 15\text{-}80 \text{ }\text{bara}, \tau \sim 10\text{-}30\text{ }\text{s} \]

---

Example pilot plant (Orimulsion, Japan*)

Feed \sim C\textsubscript{46}H\textsubscript{66} (avg molecular formula)

\[ \text{O}_2 \text{ } = \text{ sub-stoichiometric (}\lambda\sim 0.38\text{ of stoichiometry)} \]

Water content = 30% of liquid feed

Gasifier length = 3 m

Gasifier diameter = 1 feet

Gasifier residence time \sim 12 s

Gasifier pressure = 19 bara

Gasifier temperature profiles given

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Vacuum residue gasifier modeling using FGMech

FGMech strategy to model vacuum residue gasifier

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* Ashizawa, et al., Gasification characteristics of extra-heavy oil in a research-scale gasifier, Energy 30 (2005) 2194–2205
Formulation of the FGMech for Heavy Residual Oils

C_{m-n}H_n + R → e_o[C_2H_4] + λ_aC_2H_6 + λ_aC_4H_8 + θC_4H_8 + b_o[C_6H_6] + (1 - λ_a)C_5H_8 + (1 - θ)C_7H_8 + αA_2 + (1 - α)A_3CH_3 + alH_2 + (2 - α)CH_4

Gas-phase $C_{m-n}H_n$

Surface-phase $\gamma C$ (CHAR)

- Gas-phase kinetics: FGMech+base reduced model
- Char kinetics: Global or detailed chemistry

Derived from the MLR

$e_o, b_o, e_w, b_w$

Derived from the exp.

$\xi = [C_2H_4]/[C_2H_2]$  
$\lambda_a = [C_2H_2]/[C_2H_4]$  
$\lambda_a = [C_2H_2]/[C_2H_6]$  
$\theta = [C_4H_8]/[C_4H_6]$  
$\chi = [C_4H_6]/([C_2H_2]+[C_2H_4])$  
$\omega = [A_3]/([A_2]+[A_3])$

Key products and their stoichiometric parameters

**Gas-phase products from VRO pyrolysis experiment**

- Primary products:
  - Ethylene (C_2H_4)
  - Propylene (C_3H_6)
  - Ethane (C_2H_6)

- Secondary products:
  - Methane (CH_4)
  - Propane (C_3H_8)

- Not included in the lumped reactions:
  - They can be predicted by the base model

**Liquid-phase products from VRO pyrolysis experiment**

- Bicyclic aromatic HC
  - Naphthalene (A_2)
  - Methyl napthalene (A_2CH_3)

- Bicyclic aromatic HCs are considered as the secondary products and can be predicted by the base PAH mechanism

**Solid-phase products from VRO pyrolysis experiment**

- The products in solid phase are all considered as char, i.e. C

- $\gamma = 7.25$
For various VROs: Determine $\alpha$, $\beta$, $\lambda$, $\theta$, $\chi$, $\omega$

- The intermediate pools change little for the same fuel class

Use constant $\alpha$, $\beta$, $\lambda$, $\theta$, $\chi$, $\omega$ for all the VROs

Validation using Orimulsion gasifier data

Conclusions

- A functional-group-based approach is proposed to model real-fuel combustion
- Stoichiometric parameters based on MLR model
- Thermodynamic data based on Benson group additivity method
- Kinetic rate parameters based on rate rules developed for pure fuels
- 14 surrogate and 12 real fuel models were constructed based on FGMech;
  Reasonable model performances show that the present model approach can be applicable to model real-fuel combustion

Perspectives

- Improve the model performance:
- Improve correlation results to obtain more accurate stoichiometric parameters
- More accurate thermodynamic data obtained using machine learning
- Extend the FGMech to modeling low-temperature combustion
- Quantifying model uncertainties
- Provide smaller reduced/skeletal models for high-fidelity CFD simulations

XY. Zhang et al., Combust. Flame. https://doi.org/10.1016/j.combustflame.2020.10.038