Detailed Studies on the Oxidation of Surrogate Fuel Components, Surrogate Mixtures and Real Fuels

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Generation of Comprehensive Surrogate Kinetic Models and Validation Databases for Simulating Large Molecular Weight Hydrocarbon Fuels

MULTI AGENCY COORDINATION COMMITTEE FOR COMBUSTION RESEARCH (MACCCR)
FUELS RESEARCH REVIEW
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Motivation

- Develop an experimental and kinetic modeling validation database at high pressures and high temperatures for
  - Individual surrogate fuel components
    - n-alkanes, iso-alkanes and aromatics
  - Surrogate fuel component mixtures
  - Jet A POSF 4658
Experimental Approach

- Provide high pressure experimental data and speciation data for
  - Oxidation and pyrolysis of individual surrogate fuel components
    - Iso-octane
    - n-decane
    - n-dodecane
    - n-propylbenzene
    - 1,3,5-trimethylbenzene
  - Oxidation of 1st generation surrogate mixture
    - iso-octane/decane/toluene
  - Oxidation of 2nd generation surrogate mixture
    - iso-octane/n-dodecane/n-propylbenzene/1,3,5-trimethylbenzene
  - Oxidation of Jet A POSF 4658
- Comparison of speciation data between Jet A POSF 4658 and 1st and 2nd generation surrogates
- Measurement of polycyclic aromatic hydrocarbons (PAHs), precursors to soot
Modeling Approach

• Testing published models against high pressure experimental results of
  – Iso-octane, decane, dodecane, and 1st generation surrogate
• Advanced detailed modeling of iso-octane, decane and dodecane based on speciation data
• Develop models for oxidation and pyrolysis of alkylaromatics
  – n-Propylbenzene and 1,3,5-trimethylbenzene
• Testing published soot models against the experimentally measured PAHs
• Advanced detailed modeling of PAHs leading to soot formation
High Pressure Single Pulse Shock Tube (HPST)

- HPST Operating Conditions
  - Temperatures: 800 - 2500 K
  - Pressures: 15 – 1000 bar
  - Reaction times: 1.0 – 4.0 ms
- Single Pulse Shock Tube heated to 100°C

- Analytical Setup
  - Stable species analyzed using the GCs
    - TCD and FID x2 (used for quantification)
    - MS (used only for identification)
  - GC transfer lines heated to 150°C
**Carbon Totals and Measured Species**

- **Common species found in the oxidation and pyrolysis experiments of all the three fuels**
  - Major intermediates:
    - C1: CO, CO$_2$, Methane (CH$_4$),
    - C2: Ethene (C$_2$H$_4$), Ethane (C$_2$H$_6$), Acetylene (C$_2$H$_2$),
    - C4: Vinylacetylene (C$_4$H$_4$), Diacetylene (C$_4$H$_2$),
    - C6: Triacetylene (C$_6$H$_2$), Benzene (C$_6$H$_6$),
    - C7: Toluene (C$_6$H$_5$CH$_3$), Benzaldehyde (C$_6$H$_5$CHO),
    - C8: Styrene (C$_6$H$_5$C$_2$H$_3$)
  - Minor intermediates:
    - C3: Allene (C$_3$H$_4$), Propyne (C$_3$H$_4$),
    - C4: 1,3-Butadiene (C$_4$H$_6$),
    - C5: Cyclopentadiene (C$_5$H$_6$),
    - C8: Phenylacetylene (C$_6$H$_5$C$_2$H),

**New Set-Up: Direct connection between the HPST and the GC system**

*Average Carbon Recovery: 90% with the New Set-Up*
Species Specific to the Fuel

- **n-Propylbenzene**
  - Bibenzyl
  - Stilbene
  - Benzofuran

- **m-xylene**
  - 1,2-Di-p-tolylethane
  - 2,2’-Dimethylbiphenyl
  - Biphenylene

- **1,3,5-Trimethylbenzene**
  - 1-Ethynyl-4-methylbenzene
  - 1-Ethyl-3,5-dimethylbenzene
  - 1-Ethenyl-3,5-dimethylbenzene
  - 3,3’,5,5’-Tetramethylbibenzyl
  - 2,4,6-Trimethylbiphenyl

- **m-Ethylbenzaldehyde**
  - 3,5-Dimethylbenzaldehyde
  - m-Ethylbenzaldehyde
  - 1-Ethynyl-4-methylbenzene
  - 1-Ethyl-3,5-dimethylbenzene
  - 1-Ethenyl-3,5-dimethylbenzene
  - 3,3’,5,5’-Tetramethylbibenzyl
  - 2,4,6-Trimethylbiphenyl
Species Specific to the Fuel

1,3,5-Trimethylbenzene

1,3-Dimethylnaphthalene

Ethenylantracene

3,6-Dimethylphenanthrene

9-Phenylantracene

Cyclopentaphenantrene

Fluorantrene

1,2-Benzantracene

2,3-Benzofluorene

Methylfluorantrene

Chrysene
n-Propylbenzene Oxidation Modeling

- UIC n-Propylbenzene Oxidation Model (CNF submission, in press)
  - C0-C8 chemistry from Jet Fuel Surrogate Model\(^1\)
  - n-Propylbenzene oxidation chemistry
    - Rate constants of oxidation reactions based on analogous reactions of propane\(^2\)
      and toluene\(^3-7\)
    - 26 reactions
  - Polycyclic aromatic hydrocarbon chemistry (PAH)
    - Rate constants estimated for formation of indene from fuel radicals(8 reactions)
    - Reactions for formation of naphthalene, ethynynaphthalene and anthracene
      formation from Slavinskaya and Frank\(^8\) (61 reactions)
    - Reactions for formation of diphenylmethane, benzofuran and fluorene from Ranzi\(^9\)
      (13 reactions)

9. E. Ranzi, High temperature mechanism (C1-C16), http://www.chem.polimi.it/CRECKModeling
n-Propylbenzene Oxidation Model Results

Analysis of the Simulation

- Model shows good agreement for the decay of the fuel, O$_2$, CO and CO$_2$
- Model shows good agreement for the formation of other major intermediates such as toluene and styrene
n-Propylbenzene Oxidation Model Results

Analysis of the Simulation

- Model shows good agreement with indene and bibenzyl profiles.
- The model shows satisfactory agreement with the profiles of most of the other two ringed and three ringed compounds.

average P5 = 50 atm

[ Symbols ] Experimental Data  [ Lines] UIC n-Propylbenzene Oxidation Model
1,3,5-Trimethylbenzene Oxidation Modeling

UIC m-Xylene Oxidation Model

- Sequential oxidation reactions of 1,3,5-trimethylbenzene
- Methyl side chain abstraction reactions of 1,3,5-trimethylbenzene

UIC 1,3,5-Trimethylbenzene Model

- UIC 1,3,5-Trimethylbenzene Oxidation Model developed to predict single ring aromatic hydrocarbons and aliphatic compounds from fuel
- Rate constants of the oxidation reactions of 1,3,5-trimethylbenzene based on analogous reactions of m-xylene
  - 41 reactions
- Thermochemical data of 1,3,5-trimethylbenzene and its intermediates computed using group additivity and density functional theory (B3LYP/6-31G(d))
  - 12 species

1,3,5-Trimethylbenzene Oxidation Model Results

**Analysis of the Simulation**

- Models show satisfactory agreement for the decay of the fuel, $O_2$, CO and $CO_2$.
- Model shows formation of toluene and benzene at higher temperatures when compared to experiments.
- Possibility of other pathways for the fuel decay.
1st and 2nd Generation Surrogates versus Jet A POSF 4658

Temperature Range
904-1760 K

Pressure Range
18-35 atm

Mole Fraction (ppm)

Reflected Shock Temperature

Jet A 4658  1st Generation Surrogate  2nd Generation Surrogate
1\textsuperscript{st} and 2\textsuperscript{nd} Generation Surrogates versus Jet A POSF 4658

\begin{align*}
\text{Jet A 4658} & \quad \circ \quad \text{1st Generation Surrogate} \quad \Delta \quad \text{2nd Generation Surrogate}
\end{align*}
1st and 2nd Generation Surrogates Fuel Decay
Comparison with Single-Component Fuels

1st Generation Surrogate

\[ P = 21-33 \text{ atm} \]

- n-Decane
- iso-Octane
- Toluene

Reflected Shock Temperature /K

Carbon Balance

n-dodecane, n-decane, iso-octane, n-propylbenzene, and 1,3,5-trimethylbenzene oxidation data
n-Dodecane Experimental Data and Modeling

Additional species not shown for this experimental data set
- ethane, propene, propadiene, propyne, 1-butene, 1,3-butadiene, 1-pentene, 1,3-pentadiene, benzene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene

n-Decane Experimental Data and Modeling

- Additional species not shown for this experimental data set
  - ethane, propene, propadiene, propyne, 1-butene, 1,3-butadiene, 1-pentene, 1,3-pentadiene, benzene, 1-hexene, 1-heptene, 1-octene, 1-nonene

iso-Octane Experimental Data

![Graph showing the mole fraction of various compounds vs. reflected shock temperature (K).]

- CH₄
- C₂H₄
- C₂H₆
- C₂H₂
- C₃H₆
- aC₃H₄
- pC₃H₄
- C₄H₈

Mole Fraction / ppm vs. Reflected Shock Temperature / K

[ ] Line Connected Experimental Data

P5avg = 54 atm
iso-Octane Modeling

- **Original iso-Octane Sub-Model**
  - 1\textsuperscript{st} Generation Surrogate Model by Dooley et al.\textsuperscript{1} with n-decane\textsuperscript{2} reactions removed
    - C\textsubscript{0}-C\textsubscript{4} mechanism from Metcalfe et al.\textsuperscript{3}
    - iso-Octane (C\textsubscript{5}-iC\textsubscript{8}) reactions from Mehl et al.\textsuperscript{4}
    - Toluene reactions from Metcalfe et al.\textsuperscript{3}
- **Revised iso-Octane Sub-Model**
  - Additional C\textsubscript{1}-C\textsubscript{2} reactions from Gudiyella et al.\textsuperscript{5}
  - Replaced iC\textsubscript{7}H\textsubscript{14} reactions using Chaos et al.\textsuperscript{6}
  - Replaced key C\textsubscript{0}-C\textsubscript{4} reaction in the base mechanism

iso-Octane Pyrolysis Modeling

- Experimental Data
- Original Sub-Model
- Revised Sub-Model

**CH₄**

**C₂H₂**

**C₄H₈**

**C₆H₆**

**C₄H₆**

**C₇H₁₄**

**Reflected Shock Temperature /K**

[ ] Line Connected Modeling Data

P5avg = 60 atm
Extended Analytical Setup (GCxGC)
DURIP funded instrument

- Extended analytical setup
  - LECO GCxGC system
  - 2 x FID detectors
  - Agilent 7890A system
  - 1 x FID, 1 x TCD
Analytical Capabilities

- GCxGC 2-D chromatogram of JP-8 obtained at UIC

DURIP Funded GCxGC LECO System
## Experiments Summary

<table>
<thead>
<tr>
<th>Fuel</th>
<th>$\Phi$</th>
<th>Avg. Pressure /atm</th>
<th>Temperature /K</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-propylbenzene</td>
<td>0.5-2.0, $\infty$</td>
<td>25-50</td>
<td>910-1678</td>
</tr>
<tr>
<td>1,3,5-trimethylbenzene</td>
<td>0.5-2.0, $\infty$</td>
<td>25-50</td>
<td>845-1663</td>
</tr>
<tr>
<td>iso-octane</td>
<td>0.5-2.0, $\infty$</td>
<td>25-50</td>
<td>837-1672</td>
</tr>
<tr>
<td>n-decane</td>
<td>0.5-2.0, $\infty$</td>
<td>50</td>
<td>984-1718</td>
</tr>
<tr>
<td>n-dodecane</td>
<td>0.5-2.0, $\infty$</td>
<td>25-58</td>
<td>867-1739</td>
</tr>
<tr>
<td>1\textsuperscript{st} Gen. surrogate</td>
<td>1.0 &amp; $&gt;1$</td>
<td>25 &amp; 50</td>
<td>875-1749</td>
</tr>
<tr>
<td>2\textsuperscript{nd} Gen. surrogate</td>
<td>1.0</td>
<td>25 &amp; 50</td>
<td>910-1760</td>
</tr>
<tr>
<td>Jet A POSF 4658</td>
<td>$&lt;1.0$</td>
<td>25</td>
<td>901-1750</td>
</tr>
</tbody>
</table>
Experiments Summary

- Speciation data obtained for all the fuels
- Jet A 4658 and 1st and 2nd generation surrogates
  - Similar reactivity ($O_2$, $CO$, $CO_2$) between the surrogates and the real fuel
  - Similar small species ($C_1$-$C_3$) concentrations
- Polycyclic aromatic species up to 5 rings quantified in alkylaromatic experiments
  - Common two ringed and three ringed polycyclic aromatic hydrocarbons identified for all fuels
  - Formation of 4 ringed and 5 ringed aromatic hydrocarbons dependent on fuel structure
Modeling Summary

• Tested the published model against the
  – Oxidation data of decane and dodecane
• Revised the model for oxidation of iso-octane
• Importance of pyrolytic chemistry for n-alkane and iso-alkane components
• Developed chemical kinetic models for
  – Oxidation of n-propylbenzene and 1,3,5-trimethylbenzene
Future Work

- **Experiments**
  - Lean and rich oxidation experiments of the 1\textsuperscript{st} and 2\textsuperscript{nd} Generation Surrogate (n-dodecane/iso-octane/1,3,5-trimethylbenzene/n-propylbenzene) at 25 and 50 atm
  - Jet A POSF 4658, JP-8 oxidation experiments

- **Modeling**
  - 1,3,5-Trimethylbenzene Oxidation Model:
    - Additional steps: intermediate formation
    - Include the polycyclic aromatic hydrocarbon chemistry
  - Refinement and validation of the n-decane/n-dodecane sub-model and contribute to development of the 2\textsuperscript{nd} generation surrogate model
Acknowledgements

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