Detailed Studies on the Oxidation of Surrogate Fuel Components and Surrogates of JP-8

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2010 MURI AFOSR Annual Presentation
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
Princeton, NJ
September 22nd, 2010
High Pressure Single Pulse Shock Tube (HPST)

- HPST Operating Conditions
  - Temperatures: 800-2500 K
  - Pressures: 25 – 1000 bar
  - Reaction times: 1.0 – 3.0 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
1st Generation Surrogate versus POSF 4658

POSF 4658 [ ▀ ▄ ] 1st Gen. Surrogate [ ○ ○ ]
Comparison of 1st Gen. Surrogate and POSF 4658

Temperature /K

POSF 4658 [ ■ ■ ■ ]

1st Gen. Surrogate [ ○ ○ ○ ]
1st Generation Surrogate Experiments
Comparison with Model

- n-Decane
- Toluene
- iso-Octane

Temperature/K: 1000 1200 1400 1600
Oxygen: 0 25 50 75 100 125 150 175 200 225

Temperature/K: 1000 1200 1400 1600

- 1-Pentene
- 1-Hexene
- 1-Heptene
- 1-Octene
- 1-Nonene
- Measured Species
  - Carbon monoxide, carbon dioxide, methane, ethylene, ethane, acetylene, propylene, propadiene, propyne, 1-butene, 1,3-butadiene, 1-buten-3-yne, 1,3-butadiyne, 1-pentene, 1,3-pentadiene, 1-hexene, benzene, 1-heptene, 1-octene, 1-nonene
n-Decane Experiments and Modeling

- **UIC n-Decane/n-Dodecane Model**
  - C1-C4 base mechanism-MURI small species chemistry model
  - C5-C12 from Jet Fuel MechI (2007)
  - General reactions were added/changed to achieve better agreement with the pyrolysis experimental data
    - Additional reactions for 1-alkenes (C5-C9), n-decane → decyl, acetylene, 1,3-butadiyne, propylene decay, and benzene were added
    - Updated key reactions in the c1-c4 base mechanism

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n-Decane Experimental Data and Modeling

n-Dodecane Experimental Data and Modeling

- Additional species not shown
  - propadiene, propyne, 1,3-butadiene, 1-butene-3-yne, 1-pentene, 1,3-pentadiene, benzene, 1-heptene, 1-octene, 1-nonene, 1-undecene
The decay of n-propylbenzene and oxidizer

- independent of pressure
- dependent on $\Phi$
n-Propylbenzene Oxidation Modeling*

- UIC n-Propylbenzene Oxidation Model developed to predict single ring aromatics and aliphatics from fuel.
- Model sub-mechanisms
  - C0-C4 chemistry – MURI small species chemistry model\(^1\)
  - C5-C8 chemistry
    - High Pressure Toluene Oxidation Model\(^2\)
    - High Pressure Toluene Pyrolysis Model\(^3,4\)
  - n-Propylbenzene oxidation chemistry
    - Qi Chen and Froment n-propylbenzene pyrolysis mechanism\(^5\)
    - Rate constants of oxidation reactions based on analogous reactions of propane and toluene

*Manuscript in preparation
Analysis of the Simulation

- Models show good agreement for the decay of the fuel, \( O_2 \), CO and CO\(_2\).
- Shows satisfactory profiles for the formation of major intermediates for \( \Phi < 2 \).
- Polycyclic aromatic hydrocarbon chemistry should be included for complete predictions.
m-Xylene Oxidation Experiments

Experiments and modeling of m-xylene performed to assist development of 1,3,5-trimethylbenzene model

The decay of m-xylene and oxidizer

- independent of pressure
- dependent on $\Phi$
m-Xylene Oxidation Modeling*

- UIC m-Xylene Oxidation Model developed to predict single ring aromatic hydrocarbons and aliphatic compounds from fuel
- Rate constants of the oxidation reactions of m-xylene based on analogous reactions of toluene\(^2\)
- Rate constants of the important steps updated from
  - High pressure CO/H\(_2\) mechanism\(^6\)
  - High pressure ethane oxidation model\(^7\)
  - High pressure toluene pyrolysis model\(^3,4\)
- Thermochemistry of m-xylene and it’s oxygenated intermediates taken from Gail and Dagaut\(^8\) and Battin-Leclerc et al.\(^9\)
- Included reactions of methylcyclopentadiene, dimethylcyclopentadiene, p-xylylene and fulvenallene oxidation

*Manuscript submitted to Combustion and Flame

m-Xylene Oxidation Model Results

Analysis of the Simulation

- Models show good agreement for the decay of the fuel, \(O_2\), CO and CO\(_2\)
- Shows satisfactory profiles for the formation of major intermediates for \(\Phi < 4\)
- Large molecule and soot precursors formation steps should be included for better predictions
Carbon Balance

- Carbon Recovery > 92% for all datasets

- **Quantification of aliphatics (11 species)**
  - **Major intermediates:** CO, CO$_2$, methane (CH$_4$), ethene (C$_2$H$_4$), ethane (C$_2$H$_6$), acetylene (C$_2$H$_2$), diacetylene (C$_4$H$_2$) and vinylacetylene (C$_4$H$_4$)
  - **Minor intermediates:** allene (C$_3$H$_4$), propyne (C$_3$H$_4$), 1,3-butadiene (C$_4$H$_6$) 13

- **Quantification of aromatics (15 species)**
  - **Major intermediates:** benzene (C$_6$H$_6$), toluene (C$_8$H$_5$CH$_3$), benzofuran (C$_9$H$_6$O), 3, 3'-dimethylbibenzyl (C$_{16}$H$_{18}$), indene (C$_9$H$_8$), naphthalene (C$_{10}$H$_8$), 2-ethynlnaphthalene (C$_{12}$H$_{10}$), fluorene (C$_{13}$H$_{10}$), stilbene (C$_{14}$H$_{12}$), anthracene (C$_{14}$H$_{10}$)
  - **Minor intermediates:** styrene (C$_8$H$_5$C$_2$H$_3$), phenylacetylene (C$_8$H$_5$C$_2$H$_4$), p-xylene (C$_{8}$H$_{10}$), 1,2-propenylbenzene (C$_9$H$_{10}$), biphenylmethane (C$_{13}$H$_{12}$)

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  - **Minor intermediates:** allene (C$_3$H$_4$), propyne (C$_3$H$_4$), 1,3-butadiene (C$_4$H$_6$) 13 and triacetylene (C$_6$H$_2$)

- **Quantification of aromatics (26 species)**
  - **Major intermediates:** benzene (C$_6$H$_6$), toluene (C$_8$H$_5$CH$_3$), 3, 3'-dimethylbibenzyl (C$_{16}$H$_{18}$), indene (C$_9$H$_8$), naphthalene (C$_{10}$H$_8$), 2-ethynlnaphthalene (C$_{12}$H$_{10}$), fluorene (C$_{13}$H$_{10}$), acenaphthylene (C$_{13}$H$_{10}$) and anthracene (C$_{14}$H$_{10}$)
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**TSI vs. Sooting Tendency**

- **Threshold Sooting Index (TSI)** - measure of the sooting tendency.

<table>
<thead>
<tr>
<th>Species</th>
<th>TSI $^{10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Propylbenzene</td>
<td>52</td>
</tr>
<tr>
<td>m-Xylene</td>
<td>47</td>
</tr>
</tbody>
</table>

- n-Propylbenzene, m-xylene - similar sooting values, different sooting tendencies

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Extended Analytical Setup (GC x GC)

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

- GC x GC 2-D chromatogram of JP-8
Summary

- Experiments

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Temperature /K</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-propylbenzene</td>
<td>910-1678</td>
</tr>
<tr>
<td>m-xylene</td>
<td>1010-1742</td>
</tr>
<tr>
<td>n-decane</td>
<td>950-1602</td>
</tr>
<tr>
<td>n-dodecane</td>
<td>906-1483</td>
</tr>
<tr>
<td>1st Gen. surrogate</td>
<td>875-1565</td>
</tr>
<tr>
<td>PSOF 4658</td>
<td>841-1517</td>
</tr>
</tbody>
</table>

- Modeling
  - **UIC n-Propylbenzene Oxidation Model**: shows satisfactory agreement with the decay of the fuel, oxidizer and formation of the intermediates up to single ringed aromatic hydrocarbons
  - **UIC m-Xylene Oxidation Model**: shows satisfactory agreement with the decay of the fuel, oxidizer and formation of the intermediates up to single ringed aromatic hydrocarbons
  - **UIC n-Decane/n-Dodecane Model**: shows satisfactory agreement with the oxidizer and the formation of heavier intermediates
Future Work

- **Experiments**
  - 1,3,5-Trimethylbenzene oxidation experiments at 30 and 60 atm
  - iso-Octane and n-dodecane oxidation experiments at 30 and 60 atm
  - Oxidation experiments of the 1\(^{\text{st}}\) and 2\(^{\text{nd}}\) Generation Surrogate (n-dodecane/iso-octane/1,3,5-trimethylbenzene/n-propylbenzene) at 30 and 60 atm
  - POSF 4658, JP-8 oxidation

- **Modeling**
  - Development and validation of the 1,3,5-trimethylbenzene oxidation model
  - Include the polycyclic aromatic hydrocarbon chemistry in m-xylene and n-propylbenzene oxidation models
  - Further develop the n-Decane/n-Dodecane Oxidation Model
Acknowledgements

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