Oxidation of Potential Surrogate Fuel Components of JP-8

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

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Technical Approach

- Oxidation experiments of individual surrogate fuel components, m-xylene and n-propylbenzene in the High Pressure Single Pulse Shock Tube (HPST).
- Experimental regime:
  - Temperature: 900-1500K, pressure: 6-43 atm, equivalence ratios: 0.5-0.8.
- Validate currently available literature models against the experimental data.
- Develop chemical kinetic models for our experimental conditions.
Shock Tube Facility

HPST Facility

Sampling

Analytical: GC/MS, GC/FID-TCD

HPST Operating Conditions
Temperatures: 600-2500 K
Pressures: 5-1000 atm
Reaction Times: 0.5-3.0 ms
## Experimental Conditions

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Avg. Shock Pressure /atm</th>
<th>Fuel /ppm</th>
<th>O₂/ppm</th>
<th>Temperature Range /K</th>
<th>Φ</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Propylbenzene</td>
<td>19</td>
<td>63</td>
<td>1390</td>
<td>924-1587</td>
<td>0.55</td>
</tr>
<tr>
<td>m-Xylene</td>
<td>43</td>
<td>137</td>
<td>1885</td>
<td>1100-1350</td>
<td>0.75</td>
</tr>
<tr>
<td>m-Xylene</td>
<td>27</td>
<td>148</td>
<td>2996</td>
<td>1133-1500</td>
<td>0.52</td>
</tr>
<tr>
<td>m-Xylene</td>
<td>6</td>
<td>115</td>
<td>2162</td>
<td>1200-1318</td>
<td>0.65</td>
</tr>
</tbody>
</table>

**Analysis:** GC-TCD, FID, MS  
**Major Species:** CO, CO₂, C₂H₄, C₂H₂, C₆H₆, C₆H₅CH₃, C₂H₆  
**Trace Species:** 1,2-C₃H₄, C₃H₄, 1,3-C₄H₆, C₆H₅C₂H₃, C₇H₆O, C₆H₅C₂H₅
n-Propylbenzene Oxidation Modeling
P=19 atm, Φ=0.55

- Program: CHEMKIN version 3.6.2
- Subroutine: SENKIN
- Chemical kinetics model:
  - Dagaut model²
    - Validated for jet-stirred reactor data at P = 1atm, Φ = 0.5-1.5, 900-1250K

$P = 19 \text{ atm, } \Phi = 0.55$

**Graph:**

- **Experiments**
- **Dagaut Model**

**Axes:**
- **Temperature/K**
- **Mole fraction/ppm**

**Species:**
- $\text{C}_9\text{H}_{12}$
- $\text{O}_2$
- $\text{CO}$
- $\text{CO}_2$
- $\text{C}_2\text{H}_4$
- $\text{C}_6\text{H}_6$
- $\text{C}_6\text{H}_5\text{CH}_3$
- $\text{C}_2\text{H}_2$
- $\text{C}_6\text{H}_5\text{C}_2\text{H}_3$
- $\text{C}_2\text{H}_6$
- $\text{C}_6\text{H}_5\text{C}_2\text{H}_5$

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UIC n-Propylbenzene Oxidation Model

- Model submechanisms
  - High pressure CO/H₂ mechanism³
  - C1-C4 mechanism⁴
  - C5-C8 chemistry-UIC m-Xylene model
  - Dagaut et al. n-propylbenzene oxidation mechanism.


P = 19 atm, Φ = 0.55
Analysis of the Simulation

- Good agreement with the experimental data
  - $\text{C}_6\text{H}_5\text{C}_3\text{H}_7$, $\text{C}_6\text{H}_5\text{C}_2\text{H}_5$

- Species with very high concentration
  - $\text{O}_2$
  - $\text{C}_2\text{H}_2$, $\text{C}_2\text{H}_6$
  - $\text{C}_6\text{H}_5\text{C}_2\text{H}_3$

- Species with very low concentration
  - $\text{CO}$, $\text{CO}_2$
  - $\text{C}_2\text{H}_4$
  - $\text{C}_6\text{H}_6$, $\text{C}_6\text{H}_5\text{CH}_3$
$P = 19$ atm, $\Phi = 0.55$

![Graphs showing mole fraction vs. temperature for different compounds at 19 atm and $\Phi = 0.55$.](Image)

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Analysis of the Simulation Revised Model

- Good agreement with the experimental data
  - $\text{C}_6\text{H}_5\text{C}_3\text{H}_7$
  - $\text{C}_2\text{H}_4$
  - $\text{C}_6\text{H}_5\text{CH}_3$, $\text{C}_6\text{H}_5\text{C}_2\text{H}_3$, $\text{C}_6\text{H}_5\text{C}_2\text{H}_5$
- Species with very high concentration
  - $\text{O}_2$
  - $\text{C}_2\text{H}_2$
- Species with very low concentration
  - $\text{CO}$, $\text{CO}_2$
  - $\text{C}_6\text{H}_6$
- Trends very good
m-Xylene Oxidation Modeling

- Program: CHEMKIN version 3.6.2
- Subroutine: SENKIN

Models

- **Battin-Leclerc Model**
  - Modeling of ortho-, meta- and para-xylenes.
  - Validated for ignition delay times in shock tube, $P = 6.7$ to $9$ bar, $\Phi = 0.5-2$, $1330$-$1800K$.

- **Dagaut Model**
  - Validated for jet-stirred reactor data at $P = 1$ atm, $\Phi = 0.5-1.5$, $900$-$1400K$.


m-Xylene Oxidation Modeling

m-Xylene

P = 43 atm, \( \Phi = 0.75 \)

Normalized Molefraction vs. Temperature/K

P = 27 atm, \( \Phi = 0.52 \)

P = 6 atm, \( \Phi = 0.65 \)

O_2

P = 43 atm, \( \Phi = 0.75 \)

P = 27 atm, \( \Phi = 0.52 \)

P = 6 atm, \( \Phi = 0.65 \)

Normalized Molefraction vs. Temperature/K

Experiment ▢ Battin-Leclerc Model ▲ Dagaut Model

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UIC m-Xylene Model

- Analogous reactions of m-xylene based on High Pressure Toluene Oxidation Model.

- Model -submechanisms
  - High pressure toluene oxidation model
  - High pressure CO/H\(_2\) mechanism
  - High pressure toluene pyrolysis model
  - High pressure ethane oxidation model\(^{10}\)

- Thermochemistry taken from Dagaut and Battin-Leclerc m-xylene mechanisms.

- Added reactions
  - \(\text{OC}_6\text{H}_3(\text{CH}_3)_2=\text{CO}+\text{C}_5\text{H}_3(\text{CH}_3)_2\)
  - \(\text{OC}_6\text{H}_4\text{CH}_3=\text{CO}+\text{C}_5\text{H}_4-1\text{CH}_3\)
  - Reactions of methylcylopentadiene\(^{11}\) and dimethyl cyclopentadiene decay.


$P = 27 \text{ atm}, \Phi = 0.52$

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Carbon Balance, $P = 27$ atm, $\Phi = 0.52$
Analysis of the Simulation UIC Model

- Good agreement with the experimental data
  - m-Xylene
  - CO, CH₄
  - C₂H₂
- Correct trends and lower quantification
  - CO₂, O₂
  - C₂H₄
  - C₆H₆, C₆H₅CH₃
- No displaced trends
Summary

- **HPST:**
  - Oxidation experiments of m-xylene and n-propylbenzene.
  - Experimental conditions:
    - Temperature: 900-1500K, pressure: 6-43 atm, equivalence ratios: 0.5-0.8.
- **Modeling:**
  - Oxidation model of m-xylene shows good agreement with the experimental data.
  - Preliminary oxidation model developed for n-propylbenzene based on m-xylene model.
Future Work

Experiments

- Oxidation experiments of n-propylbenzene and m-xylene at fuel rich conditions.
- Oxidation and pyrolysis experiments on 1,3,5- and 1,2,4-trimethylbenzene.
- Improve carbon balance

Modeling

- Refinement of n-propylbenzene oxidation model.
- Validate the dominant pathways of m-xylene decay by theoretical methods.
Acknowledgements

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