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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Purpose of Study

- Simulate combustion behavior of JP-8 for improved combustor designs.
- Inadequate thermochemical, kinetic and transport data for JP-8 surrogate components.
- Selection of surrogate components, C8-C16 based on TSI, H/C and CN numbers.
- Potential surrogate compounds – m-xylene, 1,3,5-trimethylbenzene, n-propylbenzene, 1,2,4-trimethylbenzene, n-decane, n-dodecane and methylcyclohexane

Technical Approach

- Ignition delay studies, pyrolysis and oxidation experiments of individual surrogate fuel components, their mixtures and real fuels in the High Pressure Single Pulse Shock Tube (HPST).

- Experimental regime:
  - Temperature: 800-2500K, pressure: 10-40atm, equivalence ratios: 0.5-4.0, time: 0.5-3ms.

- Validate the experimental data against currently available literature models.

- Develop chemical kinetic models for our experimental conditions.
Shock Wave x-t Schematic

- Shock front
- Contact surface
- Reflected shock
- Rarefaction fan
- Reflected rarefaction

Driver Driven

Diaphragm

Head Tail

Distance x

Time t
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
Analysis of diesel fuel; LECO CORPORATION, Separation Science Technical Note.
m-Xylene Oxidation Modeling
P=22 bar, Φ=0.35

Program: CHEMKIN version 3.6.2
Subroutine: SENKIN

- Time evolution of homogeneous reacting gas mixtures in closed vessel.
- First order kinetic sensitivity analysis with respect to reaction rates.

Chemical kinetics models:

- Dagaut et al. (2007) model
  - Validated for jet-stirred reactor data at P = 1 atm, Φ = 0.5-1.5, 900-1400K.

- Battin-Leclerc et al. (2005) model
  - Modeling of ortho-, meta- and para-xylenes.
  - Validated for ignition delay times in shock tube, P = 6.7 to 9 bar, Φ = 0.5-2, 1330-1800K.

m-Xylene Oxidation, P=22 bar, Φ=0.35

Preliminary data-subject to revision

- m-C₆H₁₀
- C₆H₅CH₃
- O₂
- C₆H₆
- CO
- C₂H₂

Reflected Shock Temperature/K

Mole fraction/ppm

■ Experiment ▲ Battin-Leclerc Model △ Dagaut Model
UIC m-Xylene Model:

- A hierarchical structure based on High Pressure Toluene Oxidation Model$^4$.
- Elementary reactions of sequential oxidation and methyl side chains abstraction of m-xylene added to the High Pressure Oxidation Model.
- Thermochemistry of the species taken from Dagaut Model.

Sensitivity Analysis

Oxidation of m-Xylene, P=22 bar, $\phi=0.35$

Sensitivity Analysis of CO, $t = 2.1$ ms

Rxn # Reaction in ‘UIC m-Xylene Model’

- **G2.** $\text{H} + \text{O}_2 = \text{OH} + \text{O}$
- **G5.** $\text{H} + \text{O}_2 (+\text{M}) = \text{HO}_2 (+\text{M})$
- **G14.** $\text{O} + \text{HO}_2 = \text{O}_2 + \text{OH}$
- **G127.** $\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$
- **G456.** $\text{C}_6\text{H}_5\text{O} = \text{CO} + \text{C}_5\text{H}_5$
- **G527.** $\text{C}_6\text{H}_5\text{O} + \text{O} = \text{C}_6\text{H}_4\text{O}_2 + \text{H}$
- **G534.** $\text{MXYLEL} + \text{H} = \text{MXYLENE}$
- **G535.** $\text{MXYLENE} + \text{H} = \text{C}_6\text{H}_5\text{CH}_3 + \text{CH}_3$
- **G536.** $\text{MXYLENE} + \text{H} = \text{MXYLEYL} + \text{H}_2$
- **G544.** $\text{MXYLEYL} + \text{O} = \text{C}_8\text{H}_8\text{O} + \text{H}$
- **G571.** $\text{OC}_2\text{H}_7 = \text{CO} + \text{OC}_6\text{H}_7$
- **G577.** $\text{OC}_2\text{H}_7 + \text{H} = \text{CH}_3\text{C}_6\text{H}_4\text{OH}$

Normalized Sensitivity Coefficient

- $T = 1342K$
- $T = 1283K$
- $T = 1170K$
m-Xylene Oxidation, $P=22$ bar, $\Phi=0.35$

Preliminary data—subject to revision

- **m-C$_8$H$_{10}$**
- **C$_2$H$_2$**
- **C$_6$H$_6$**
- **O$_2$**
- **C$_6$H$_5$CH$_3$**

**Experiment**, UIC m-Xylene Model, Battin-Leclerc Model
1,3,5-Trimethylbenzene Oxidation Modeling

P=24 bar, \( \Phi=1.26 \)

**UIC m-Xylene Model**

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

**Chemical kinetics Mechanism:**
- Based on m-xylene oxidation mechanism\(^5\).

**UIC 135TMB Model:**
- Detailed chemical kinetic model unavailable in literature.
- 13 species and 41 reactions added to the UIC m-Xylene Model.
- Arrhenius parameters taken from analogous toluene reactions from High Pressure Toluene Oxidation Model.

Thermochemistry

- $\Delta H^0_{298K}$ of stable compounds determined using Group Additivity based Estimates$^6$.

- DFT calculation done for radicals using Gaussian 03, Scheme: B3LYP/6-31G(d).

- $\Delta H^0_{0K}$ of radicals determined using Ring Conserved Isodesmic Reaction Scheme$^7$ and DFT energies.

- $\Delta H^0_{298K}$ estimated using DFT energies and statistical mechanics.

- NASA polynomials obtained through FITDAT utility in CHEMKIN 3.7.

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1,3,5-Trimethylbenzene Oxidation

P=24 bar, $\Phi=1.26$

Preliminary data-subject to revision

- **$C_9H_{12}$**
- **$O_2$**
- **$CO$**
- **$CO_2$**
- **$C_2H_4$**
- **$C_2H_2$**

Experiment  UIC 135TMB Model
n-Propylbenzene Oxidation Modeling
P=17 bar, Φ=0.55

- Program: CHEMKIN version 3.6.2
- Subroutine: SENKIN
- Chemical kinetics model:
  - Dagaut et al. (2002)\(^8\) model
    - Validated for jet-stirred reactor data at P = 1atm, Φ = 0.5-1.5, 900-1250K

n-Propylbenzene Oxidation, P=17 bar, Φ=0.55

Preliminary data subject to revision

- **C<sub>9</sub>H<sub>12** (n-Propylbenzene)
- **O<sub>2**
- **CO**
- **C<sub>2</sub>H<sub>4** (Ethylene)
- **CO<sub>2**
- **C<sub>7</sub>H<sub>8** (Methylbenzene)

**Graphs:**
- Mole Fraction (ppm) vs. Reflected Shock Temperature (K)

**Legends:**
- ■ Experiments
- ○ Dagaut’s Model
1,3,5-Trimethylbenzene and n-Propylbenzene Mixture (1.5:1)

Decay of 1,3,5-Trimethylbenzene with and without n-Propylbenzene

Decay of n-Propylbenzene with and without 1,3,5-Trimethylbenzene

Reflected Shock Temperature /K

Preliminary data-subject to revision
HPST:

- Oxidation experiments of m-xylene, 1,3,5-trimethylbenzene and n-propylbenzene and a mixture of 1,3,5-trimethylbenzene and n-propylbenzene.
- Experimental conditions:
  - Temperature: 924-1587K, pressure: 17-24bar, equivalence ratio: 0.35-1.4, residence time: 0.5-3ms.

Modeling:

- Preliminary oxidation models developed for m-xylene and 1,3,5-trimethylbenzene
- Validated n-propylbenzene experimental data using Dagaut’s model.
Future Work

- Oxidation and pyrolytic experiments on surrogate fuel mixtures and real fuels.
- Development of m-xylene and 1,3,5-trimethylbenzene models by inclusion of more comprehensive fuel decay pathways.
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