Development of Detailed and Reduced Kinetic Mechanisms
for Surrogates of Petroleum-Derived and Synthetic Jet Fuels

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T. Lu (University of Connecticut)
D.L. Miller (Drexel University)
H. Pitsch (Stanford University)
H. Wang (University of Southern California)

In Collaboration with:
R.P. Lindstedt (Imperial College)
W. Tsang & J. Manion (NIST)
A. Violi (University of Michigan)

AFOSR Grant: FA9550-08-1-0040 (AFRL Energy-IPT)
Period of performance: 3/1/08 – 11/30/10
Technical Monitor: Dr. Julian M. Tishkoff
**Objectives**

- To contribute towards the development of surrogate (jet) fuels through detailed and quantitative characterization of combustion properties and kinetics for:
  - Single-component hydrocarbons
  - Mixtures of chosen hydrocarbons
  - Selected jet fuels

- To develop detailed *kinetic* and *transport* models that predict accurately the experimentally observed behavior of the surrogate fuel components and their blends.

- To reduce the size and stiffness of detailed kinetic models and to determine the associated uncertainty propagation so that can be used in large-scale simulations.
Approach: Experiments

- **Flow reactors** *(Bowman, Cernansky, Miller)*
  - Studies of low, intermediate, and high temperature kinetics
  - 650-1250 K, 1-25 atm

- **Stanford shock tube** *(Hanson)*
  - Studies of low, intermediate, and high temperature kinetics
  - Ignition delays and species time evolution
  - 600-3000 K, <1 to 600 atm

- **NIST shock tube** *(Tsang)*
  - Studies of decomposition and isomerization of alkyl, 1-olefinyl, and cyclo-alkyl radicals

- **Laminar flames** *(Egolfopoulos, Law)*
  - Laminar flame speeds
  - Ignition/extinction limits (premixed & non-premixed)
  - Up to 30 atm

- **Transport coefficients** *(Manion)*
**Approach: Theory**

- **Detailed kinetic models** *(Bowman, Cernansky, Hanson, Lindstedt, Miller, Tsang, Violi, Wang)*
  - Application of quantum chemistry and reaction rate theories
  - Kinetics foundation model (C₀⁻C₄)
  - Surrogate component models
    - Low-to-intermediate temperature chemistry
    - High temperature chemistry
  - Model optimization and validation

- **Transport models for H atoms and long-chain aliphatics** *(Manion, Violi, Wang)*

- **Model reduction and uncertainty propagation** *(Law, Lu, Wang)*
  - Skeletal reduction
  - Isomer lumping
  - Stiffness removal
  - Reduction of diffusion model
  - Error propagation

- **Direct numerical simulations of experimental configurations** *(Pitsch)*
## Jet Fuels Composition (courtesy of Tim Edwards)

<table>
<thead>
<tr>
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## Surrogate Component Palette (courtesy of Med Colket)

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<th>Current Understanding of Properties</th>
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<td>n-tetradecane</td>
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<td>B</td>
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<td>n-cetane (n-hexadecane)</td>
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<td>2-methylundecane</td>
<td>A</td>
<td>D</td>
<td>D+</td>
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<tr>
<td>iso-cetane (2,2,4,4,6,8,8-heptamethylnonane)</td>
<td>B</td>
<td>B</td>
<td>B-</td>
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<td>B+</td>
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<td>decalin</td>
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<td><strong>Single-ring Aromatics</strong></td>
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<tr>
<td>toluene</td>
<td>C</td>
<td>C</td>
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<td>tetralin</td>
<td>C+</td>
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<td>C</td>
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<td>1-methynaphthalene</td>
<td>B</td>
<td>C</td>
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</tbody>
</table>

### Legend

- **A**: Very important
- **B**: Important
- **C**: Possible surrogate, but not crucial
- **D**: Mechanism, but with major discrepancies
- **F**: No mechanism

### Relevance to Practical Systems
- **A**: Detailed mechanism that has been verified
- **B**: Mechanism, but not fully verified
- **C**: Possible surrogate, but not crucial
- **D**: Mechanism, but with major discrepancies
- **F**: No mechanism

### Thermodynamic Properties
- **Data available (density to 0.3 %)**
- **Sufficient data for model (density to 3 %)**
- **Limited data only**
- **Extremely limited/no experimental data, predictive model feasible.**
- **No data or predictive model available**

### Transport Properties
- **Correlations available for viscosity, diffusivity, thermal conductivity (5%)**
- **Data available for models (5-10%)**
- **Limited viscosity and/or thermal conductivity data**
- **Extremely limited/no experimental data; predictive model possible.**
- **No data or predictive model available**
Parameter Space (1)

- Fuels:
  - Reference Jet-A and JP-8 samples, including low and high aromatic contents;
  - Fischer-Tropsch and bio-derived jet fuels constituted entirely of \textit{n}- and \textit{iso}-alkanes;
  - A reference coal-derived jet fuel constituted entirely of cycloalkanes;
  - C_{10-12} \textit{n}- and \textit{iso}-alkanes;
  - C_{7-12} cycloalkanes;
  - Aromatics;
  - Binary and tertiary mixtures of the selected single-component fuels.
  - (Surrogate selection will be done by considering the findings of the parallel MURI effort and the recommendations of the Surrogate Working Group)
Parameter Space (2)

• Thermodynamic conditions:
  • Pressures: 0.25 to 30 atm;
  • Unburned reactant temperatures: 300 to 1250 K;
  • Shock tube experimental temperature range: 650 to 2000 K;
  • Reactant composition: equivalence ratio bracketed by lean and rich flammability limits, typically ranging from 0.5 to 1.5;
  • Inert dilution: zero to high.

• Reaction configurations:
  • Homogeneous systems: flow reactors and shock tubes;
  • Non-homogeneous systems: non-premixed and premixed flames.
Roadmap: Years 1-3 and Beyond

- **Years 1-2:** Development of JetSurf 1.0 (working model)
  - High-temperature kinetics for:
    - \( n \)-alkanes up to \( C_{12} \)

- **Years 2-3:** Development of JetSurf 1.1 (preliminary model)
  - Addition of high-temperature kinetics for:
    - \( n \)-butyl-cyclohexane

- **Year 3:** Development of JetSurf 2.0 (working model)
  - High-temperature kinetics for:
    - \( n \)-alkanes up to \( C_{12} \)
    - \( n \)-butyl-cyclohexane

- **Year 3:** Development of JetSurf 2.1 (preliminary model)
  - Addition of high-temperature kinetics for:
    - *iso*-alkanes (~\( C_8 \)-\( C_{12} \), slightly branched, symmetric)

- **2011:** Development of JetSurf 3.0 (working model)
  - High-temperature kinetics for:
    - \( n \)-alkanes up to \( C_{12} \)
    - \( n \)-butyl-cyclohexane
    - *iso*-alkanes

- **2011:** Development of JetSurf 3.1 (preliminary model)
  - Addition of high-temperature kinetics for:
    - \( n \)-propyl-benzene
| 3-Year Progress | C₄-C₁₂  
n-alkanes | iso-alkanes | cyclo-alkanes | n-alkenes  
iso-alkenes | aromatics | fuel mixtures | jet fuels |
|-----------------|-----------------|-------------|--------------|--------------|-----------|-------------|----------|
| Shock tube:  
Ignition delay, species concentrations | C₅, C₆, C₇, C₈, C₉, C₁₂  
0.35 to 34 atm | 2.4-DMP  
2.5-DMH  
iso-octane  
1-3 atm | cyclo-hexane  
(CHX)  
methyl-CHX  
n-butyl-CHX  
1-3 atm | reaction rate  
measurements of OH+alkenes | toluene  
1-50 atm  
(ARO) | JP-8, Jet-A,  
20 atm  
(ARO) | JP-7, RP-1  
4-40 atm  
(AFOSR) |
| Flow reactor at 8 atm:  
Low-intermediate T;  
reactivity sweeps and species concentrations | C₇, C₁₀, C₁₂  
iso-cetane  
(no reactivity) | n-propyl-CHX  
n-butyl-CHX | decalin | o-, m-, p-xylene  
(partially funded by ARO-STIR) | o-, m-, p-xylene+n-C₁₂  
iso-cetane+n-C₁₀ | Jet-A  
JP-8  
S-8  
DCL |
| Flow reactor:  
Intermediate-high T; species concentrations | C₇, C₁₂  
up to 8 atm | iso-butane  
iso-octane  
1-10 atm | CHX  
methyl-CHX  
ethyl-CHX  
n-propyl-CHX  
n-butyl-CHX  
1-20 atm | 1-butene  
2-butene  
iso-butene  
1-10 atm | benzene  
(B)  
toluene  
n-propyl-B  
1,2,4-TMB  
1,3,5-TMB  
o-, m-, p-xylene  
at 1 atm | methyl-CHX+n-C₁₂  
toluene+n-C₁₂  
at 1 atm | JP-7  
JP-8  
S-8  
Shell-GTL  
R-8  
at 1 atm |
| Laminar flame speeds | C₄, C₅, C₆, C₇,  
C₈, C₉, C₁₀, C₁₂  
1-20 atm | iso-butane  
iso-octane  
1-10 atm | CHX  
methyl-CHX  
ethyl-CHX  
n-propyl-CHX  
n-butyl-CHX  
1-20 atm | 1-butene  
2-butene  
iso-butene  
1-10 atm | benzene  
(B)  
toluene  
n-propyl-B  
1,2,4-TMB  
1,3,5-TMB  
o-, m-, p-xylene  
at 1 atm | methyl-CHX+n-C₁₂  
toluene+n-C₁₂  
at 1 atm | JP-7  
JP-8  
S-8  
Shell-GTL  
R-8  
at 1 atm |
| Flame ignition | C₅, C₆, C₇, C₈,  
C₉, C₁₀, C₁₂  
1-3 atm | CHX  
methyl-CHX  
ethyl-CHX  
n-propyl-CHX  
n-butyl-CHX  
at 1 atm | benzene  
(B)  
toluene  
n-propyl-B  
1,2,4-TMB  
1,3,5-TMB  
o-, m-, p-xylene  
at 1 atm |  | | | |
| Flame extinction (at 1 atm) | C₅, C₆, C₇, C₈,  
C₉, C₁₀, C₁₂  | CHX  
methyl-CHX  
ethyl-CHX  
n-propyl-CHX  
n-butyl-CHX  
at 1 atm | benzene  
(B)  
toluene  
n-propyl-B  
1,2,4-TMB  
1,3,5-TMB  
o-, m-, p-xylene  
at 1 atm |  | | | |
| Detailed kinetic models | JetSurf 1.0, 2.0 | JetSurf 2.0 | JetSurf 2.0  
(n-alkenes) | JetSurf 2.0  
(benzene & toluene) |  | semi-empirical  
with USC Mech II (STTR) |
| Transport properties | C₂-C₈  exp. & MD  
empirical estimates | empirical estimates | empirical estimates | empirical estimates | empirical estimates | empirical estimates |
| Model reduction | lumped+skeletal  
(USC Mech II)  
iso-octane  
(JetSurf 1.1) | skeletal  
n-butyl-CHX  
(JetSurf 1.1) | skeletal  
toluene  
(JetSurf 1.1) | skeletal  
n-C₁₂+n-butyl-CHX+toluene  
(JetSurf 1.1) |  |  |
Iso-Alkanes

- **Target compounds**
  - Slightly branched
  - Symmetric
    - *e.g.* 2,9 *dimethyl decane*

- **Recently quoted prices per 100 ml**
  - One methyl group
    - 2-*methyl-butane*................................. $57
    - 2-*methyl-hexane*................................. $912
  - Two methyl groups and symmetric
    - 2,4-*dimethyl-pentane*............................ $570
    - 2,5-*dimethyl-hexane*............................ $1000
    - 2,7-*dimethyl-octane*............................ $1960
  - Three or more methyl groups
    - 2,2,4-*trimethyl-pentane (iso-octane)*........ $4.2
    - 2,2,4,6,6 *pentamethyl-heptane (iso-decane)*... $5.1
JetSurF – A Jet Surrogate Fuel Model

JetSurF is a detailed chemical reaction model for the combustion of jet-fuel surrogate. The model is being developed through a multi-university research collaboration and is funded by the Air Force Office of Scientific Research. Project participants include:

- F. N. Egolfopoulos, Hal Wang
- R. K. Hanson, D. F. Davidson, C. T. Bowman, H. Pitsch
- C. K. Law
- N. P. Cemansky, D. L. Miller
- W. Tsang
- R. P. Lindstedt
- A. Violi

University of Southern California
Stanford University
Princeton University
Drexel University
National Institute of Standards and Technology
Imperial College, London
University of Michigan

New Release: JetSurF Version 2.0 – A working model for the combustion of n-alkane up to n-dodecane, cyclohexane, and mono-alkylated cyclohexane up to n-butyl-cyclohexane
(Release Date: September 19, 2010)

Old Releases:
- JetSurF Version 1.1 – A Interim model for the combustion of n-butyl-, n-propyl-, ethyl-, and methyl-cyclohexane and cyclohexane
  (Release Date: September 15, 2009)
- JetSurF Version 1.0 – A working model for n-alkane combustion
  (Release Date: September 15, 2009)
- JetSurF Version 0.2 (Release Date: September 8, 2009)
JetSurfF (Version 2.0)

Release date: September 17, 2010

Main page  JetSurf 2.0 download  Performance  How to cite

Download: Mechanism, Thermochemical, and Transport Databases in ChemKin format.

How to cite JetSurf 2.0

Performance that we know

Release notes:

JetSurfF 2.0 consists of 348 species and 2163 reactions. The development effort centers on n-dodecane and n-butyl-cyclohexane, but the model includes also the high-temperature chemistry of all n-alkanes up to n-dodecane, and mono-alkylated cyclohexanes, including n-propylcyclohexane, ethylcyclohexane, methylcyclohexane and cyclohexane.

The model is “un-tuned” and work-in-progress. The development effort centers on achieving consistent kinetic parameter assignment and predictions for a wide range of hydrocarbon compounds. This effort is reflected in the validation tests documented in the Performance that we know page.

JetSurf 2.0 is an extension to JetSurf 1.1 released in September 2009.

Some Model Details

The base model is USC-Mech II (111 species, 764 reactions) that describes the oxidation of H₂ and CO and the high-temperature chemistry of C₁-C₄ hydrocarbons. The base model considers the pressure dependence for unimolecular and bimolecular chemically activated reactions, and was validated against experimental data ranging from laminar flame speeds, ignition delay times behind shock waves, to species profiles in flow reactors and burner stabilized flames.

JetSurf 2.0 was developed in two steps. In the first step, USC Mech II was appended by a set of reactions describing the high-temperature pyrolysis and oxidation of n-alkanes from n-pentane to n-dodecane, leading to the release of JetSurfF1.0. In the second step, the high-temperature chemistry of cyclohexane and mono-alkylated cyclohexane was added, leading to the release of JetSurfF1.1.

The current version also includes limited low-temperature chemistry for cyclohexane and the alkylated cyclohexane compounds, though this part of the model remains weak and requires further work.

Additional model details may be found on the JetSurfF1.0 and JetSurfF1.1 web sites.
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<th>Presentation</th>
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<td>1:00-1:15</td>
<td>Program Overview (Egolfopoulos; University of Southern California)</td>
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<tr>
<td>1:15-1:45</td>
<td>Low/Intermediate Temperature Flow Reactor Studies (Cermansky &amp; Miller; Drexel University)</td>
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<tr>
<td>1:45-2:30</td>
<td>Intermediate/High Temperature Flow Reactor and Shock Tube Studies (Bowman &amp; Hanson; Stanford University)</td>
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<td>2:30-3:00</td>
<td>Flame Studies of Jet Fuels and Surrogate-Related Neat Hydrocarbons (Egolfopoulos; University of Southern California)</td>
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<td>3:00-3:30</td>
<td>Break</td>
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<td>3:30-4:15</td>
<td>Laminar Flame Studies in Counterflow and Spherically Expanding Configurations, Mechanism Reduction, and Chemical Explosive Mode Analysis for Computational Flame Diagnostics (Law; Princeton University &amp; Lu; University of Connecticut)</td>
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<td>(Wang; University of Southern California)</td>
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<td>5:00-5:30</td>
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