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

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Period of performance: 3/1/08 – **11/30/10**

Phase II: AFOSR Grant: FA9550-11-1-0217 (AFRL Energy-IPT)
Period of performance: 9/1/11 – 8/31/14

Objectives

1. **To contribute towards the development of surrogate (jet) fuels through detailed and quantitative characterization elementary kinetics and of combustion properties for:**
   - » **Single-component hydrocarbons**
   - » **Mixtures of chosen hydrocarbons**
   - » **Selected jet fuels**
2. **To develop detailed *kinetic* and *transport* models that predict accurately the experimentally observed behavior of the surrogate fuel components and their blends.**
3. **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.**
4. **In summary: *To produce the best possible "targeted science" for large MW hydrocarbons, by advancing further current state of the art experimental and theoretical approaches in reacting flows.***

Approach: Experiments

- **Flow reactors** *(Bowman, Cernansky, Miller)*
  - **Studies of low, intermediate, and high temperature kinetics**

- **Stanford shock tube** *(Hanson)*
  - **Studies of low, intermediate, and high temperature kinetics**
  - **Ignition delays and species time evolution**

- **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)**

- **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 (C_0-C_4)**
  - **Surrogate component models**
    - » **Low-to-intermediate temperature chemistry**
    - » **High temperature chemistry**
  - **Kinetic model uncertainty quantification and minimization**
- **Transport models with emphasis on 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**
- **Computational flame diagnostics** *(Lu, Law)*

Jet Fuels Composition (courtesy of Tim Edwards)

	4658	3327	4734	4572	4765	3773	World survey
	Jet A composite blend	JP-7	F-T Jet	RP-1	Coal-based jet fuel DCL	JP-8	Jet A, Jet A-1, JP-8, JP-5, TS-1
Paraffins (*n*- + *i*-)	55.2	67.9	99.7	57.6	0.6	57.2	58.8
Cycloparaffins	17.2	21.2	<0.2	24.8	46.4	17.4	10.9
Dicycloparaffins	7.8	9.4	0.3	12.4	47.0	6.1	9.3
Tricycloparaffins	0.6	0.6	<0.2	1.9	4.6	0.6	1.1
Alkylbenzenes	12.7	0.7	<0.2	2.1	0.3	13.5	13.4
Indanes/Tetralins	4.9	<0.2	<0.2	0.3	1.1	3.4	4.9
Indenes	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Naphthalene	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	0.13
Naphthalenes	1.3	<0.2	<0.2	0.3	<0.2	1.7	1.55
Acenaphthenes	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Acenaphthylenes	<0.2	<0.2	<0.2	0.4	<0.2	<0.2	<0.2
Tricyclic Aromatics	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2

	3638	3602	3642
	Jet A	Jet A	RP-1
Aromatics (ASTM D1319)	12	24	2.9

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 *n*- and *iso*-alkanes;**
  - **A reference coal-derived jet fuel constituted entirely of cycloalkanes;**
  - **$C_{5\text{-}12}$ *n*- and *iso*-alkanes;**
  - **$C_{7\text{-}12}$ *cyclo*-alkanes;**
  - **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)**

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.**

Roadmap: Phase I (completed) and Phase II (just started)

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

- **Years 4-6: Further development of JetSurf**
  - **High-temperature kinetics with emphasis also on pressure effects for:**
    - ***n*-alkanes up to C_{12}**
    - **cyclohexanes up to *n*-butyl-cyclohexane**
    - ***iso*-alkanes**
    - **aromatics up to *n*-propyl-benzene**

Up to date progress	C_4-C_{12} *n*-alkanes	*iso*-alkanes	cyclo-alkanes	*n*-alkenes *iso*-alkenes	aromatics	fuel mixtures	jet fuels
Shock tube: Ignition delay, species concentrations	C_5, C_6, C_7, C_8, C_9, C_{12} 0.35 to 34 atm	2,4-DMP 2,5-DMH 2,5-dimethyl-hexane 2,7-dimethyl-octane iso-octane 1-20 atm	cyclo-hexane (CHX) methyl-CHX *n*-butyl-CHX decalin 1-20 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	C_7, C_{10}, C_{12}	*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-C_{12} *iso*-cetane+*n*-C_{10}	Jet-A JP-8 S-8 DCL
Flow reactor: Intermediate-high T; species concentrations	C_7, C_{12} up to 8 atm						
Laminar flame speeds	C_4, C_5, C_6, C_7, C_8, C_9, C_{10}, C_{12} 1-20 atm	*iso*-butane 2- & 3-methyl-heptane 2,5-dimethyl-hexane *iso*-octane 1-10 atm	CHX methyl-CHX ethyl-CHX *n*-propyl-CHX *n*-butyl-CHX CPD 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 1 atm	methyl-CHX +*n*-C_{12} toluene+*n*-C_{12} 1 atm	JP-7 JP-8 S-8 Shell-GTL R-8 1 atm
Flame ignition	C_3,C_4, C_5, C_6, C_7, C_8, C_9, C_{10}, C_{12} 1-3 atm	*iso*-butane 2- & 3-methyl-heptane 2,5-dimethyl-hexane 2,7-dimethyl-octane *iso*-octane, 1 atm	CHX methyl-CHX ethyl-CHX *n*-propyl-CHX *n*-butyl-CHX 1 atm				
Flame extinction (at 1 atm)	C_5, C_6, C_7, C_8, C_9, C_{10}, C_{12}		CHX methyl-CHX *n*-butyl-CHX CPD		benzene, toluene *n*-propyl-B 1,2,4-TMB 1,3,5-TMB *o*-, m-, p-xylene		JP-7 JP-8 S-8 Shell-GTL R-8
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	C_3-C_8 exp. & MD	empirical estimates	empirical estimates	empirical estimates	empirical estimates	empirical estimates	empirical estimates
Model reduction	lumped +skeletal (USC Mech II)	*iso*-octane (LLNL)	skeletal *n*-butyl-CHX (JetSurf 1.1)		skeletal toluene (JetSurf 1.1)	skeletal *n*-C_{12}+*n*-butyl-CHX+toluene (JetSurf 1.1)	

Iso-Alkanes

- **Target compounds**
  - **Slightly branched**
  - **Symmetric**
    - ***e.g. 2,7 dimethyl-octane; 2,9 dimethyl-decane***
- **Typical 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 - Windows Internet Explorer

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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, Hai Wang	*University of Southern California*
R. K. Hanson, D. F. Davidson, C. T. Bowman, H. Pitsch	*Stanford University*
C. K. Law	*Princeton University*
N. P. Cernansky, D. L. Miller	*Drexel University*
W. Tsang	*National Institute of Standards and Technology*
R. P. Lindstedt	*Imperial College, London*
A. Violi	*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)*

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: JetSurF (Version 2.0)

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JetSurF (Version 2.0)

Release date: September 17, 2010

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How to cite JetSurF 2.0

Performance that we know

Release notes:

JetSurF2.0 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, 784 reactions) that describes the oxidation of H_2 and CO and the high-temperature chemistry of C_1-C_4 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 **JetSurF1.0**. In the second step, the high-temperature chemistry of cyclohexane and mono-alkylated cyclohexane was added, leading to the release of **JetSurF1.1**.

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 **JetSurF1.0** and **JetSurF1.1** web sites.

Energy-IPT Presentation Schedule

8:00-8:15	Program Overview (Egolfopoulos; University of Southern California)
8:15-8:45	Low/Intermediate Temperature Flow Reactor Studies (Cernansky & Miller; Drexel University)
8:45-9:30	Intermediate/High Temperature Flow Reactor and Shock Tube Studies (Bowman & Hanson; Stanford University)
9:30-10:00	Flame Studies of Jet Fuels and Surrogate-Related Neat Hydrocarbons (Egolfopoulos; University of Southern California)
10:00-10:30	Break
10:30-11:15	Laminar Flame Studies in Counterflow and Spherically Expanding Configurations, Mechanism Reduction, and Chemical Explosive Mode Analysis for Computational Flame Diagnostics (Law; Princeton University & Lu; University of Connecticut)
11:15-11:45	Detailed Kinetic Model Development Transport Coefficients Uncertainty Propagation (Wang; University of Southern California)
11:45-12:15	Discussion