

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



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**Technical Monitor:** Dr. Julian M. Tishkoff

## *Objectives*

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- **To contribute towards the development of surrogate (jet) fuels through detailed and quantitative characterization of kinetics and combustion properties for:**
  - **Selected jet fuels**
  - **Single-component hydrocarbons**
  - **Mixtures of chosen hydrocarbons**
- **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 error 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, Golden, Hanson, Lindstedt, Miller, Tsang, Violi, Wang*)
  - Application of quantum chemistry and reaction rate theories
  - Kinetics foundation model (C<sub>0</sub>-C<sub>4</sub>)
  - 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, Lindstedt, 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)

	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 ( <i>n- + i-</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

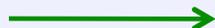
	3638	3602	3642
	Jet A	Jet A	RP-1
Aromatics (ASTM D1319)	12	24	2.9

# Surrogate Component Palette (courtesy of Med Colket)

	Relevance to Practical Systems	Current Understanding of Mechanism		Current Understanding of Properties	
	Jet	Low & Intermediate Temperatures	High Temperatures	Thermo-dynamics	Transport
<b>Straight-chain Alkanes</b>					
n-decane	A	B	A-	A	A
n-dodecane	A	B	A-	A	A
n-tetradecane	A	B	B	B+	B
n-cetane (n-hexadecane)	B	B	B	B+	B
<b>Branched-chain Alkanes</b>					
iso-octane (2,2,4-trimethylpentane)	B	A-	A	B+	B
2-methylundecane	A	D	D	D	D
iso-cetane (2,2,4,4,6,8,8-heptamethylnonane)	B	B	B	B-	C+
<b>Cycloalkanes</b>					
methylcyclohexane	B	C	B+	B+	B
decalin	B	D	D	B	B-
<b>Single-ring Aromatics</b>					
toluene	C	C	C	A	B+
propyl benzene	A	C	C	B	B
o-xylene	C+	C	B	B	B
p-xylene	C+	C	B	B	B
m-xylene	C+	C	B	B	B
trimethylbenzene	B	D	D	D	D
<b>Multi-ring Aromatics</b>					
tetralin	C+	D	C	B+	B-
1-methylnaphthalene	B	C	C	B	C

	Legend				
	A	B	C	D	F
Relevance to Practical Systems	Very important	Important	Possible surrogate, but not crucial		No relevance
Understanding of Mechanism	Detailed mechanism that has been verified	Mechanism, but not fully verified	Mechanism, but with major discrepancies	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;**
  - **A reference Fischer-Tropsch jet fuel constituted entirely of *n*- and *iso*-alkanes;**
  - **A reference coal-derived jet fuel constituted entirely of cycloalkanes;**
  - **C<sub>10-12</sub> *n*- and *iso*-alkanes (e.g., *n*-decane, *n*-dodecane);**
  - **C<sub>7-12</sub> cycloalkanes (e.g., *n*-butyl-cyclohexane);**
  - **Aromatics (e.g., *propyl*-benzene);**
  - **Binary and tertiary mixtures of the selected single-component fuels.**
  - **(Eventual selection will be done by considering the findings of the parallel MURI effort and the recommendations of the Surrogate Working Group)**

## *Parameter Space (2)*

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- **Thermodynamic conditions:**
  - **Pressures: 1 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.**

## ***Parameter Space (3)***

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- **Global and detailed properties:**
  - **Ignition delays and temperature and species concentration-time evolutions in shock tubes;**
  - **Species concentration-time evolutions in flow reactors;**
  - **Laminar flame speeds;**
  - **Ignition limits of non-premixed and premixed flames;**
  - **Extinction limits of 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<sub>12</sub>
  - **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<sub>12</sub>
      - *n*-butyl-cyclohexane
  - **Year 3: Development of JetSurf 2.1 (preliminary model)**
    - **Addition of high-temperature kinetics for:**
      - *iso*-alkanes (~C<sub>8</sub>-C<sub>12</sub>, slightly branched, symmetric)
- 
- **2011: Development of JetSurf 3.0 (working model)**
    - **High-temperature kinetics for:**
      - *n*-alkanes up to C<sub>12</sub>
      - *n*-butyl-cyclohexane
      - *iso*-alkanes
  - **2011: Development of JetSurf 3.1 (preliminary model)**
    - **Addition of high-temperature kinetics for:**
      - *propyl*-benzene

## ***Accomplishments of Years 1-2***

- **Experiments have been completed for C<sub>4</sub>-C<sub>12</sub> *n*-alkane and various cyclohexane fuels and for a wide range of conditions in:**
  - **Flow reactors**
  - **Shock tubes**
  - **Flames**
- **A transport formula has been advanced and will be tested for straight-chain molecules**
- **An uncertainty quantification and minimization method has been proposed on the basis of spectral chaos expansion**
- **JetSurF1.0 has been released for *n*-alkane combustion up to *n*-dodecane on the web as of 9/15/09: (<http://melchior.usc.edu/JetSurF1.0>)**
- **JetSurF1.1 – an interim version for the combustion of *n*-butyl-cyclohexane has been released on the web as of 9/15/09 (also including cyclohexane, methyl-, ethyl-, and *n*-propyl-cyclohexane) : (<http://melchior.usc.edu/JetSurF1.1>)**

JetSurF - A Jet Surrogate Fuel Model - Windows Internet Explorer

http://melchior.usc.edu/JetSurF/

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JetSurF - A Jet Surrogate Fuel Model



## 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

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

Current Release: **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)

Current Release: **JetSurF Version 1.0 – A working model for n-alkane combustion**  
(Release Date: September 15, 2009)

Old Release: **JetSurF Version 0.2** (Release Date: September 8, 2009)

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JetSurF (Version 1.0) - Windows Internet Explorer

http://melchior.usc.edu/JetSurF/JetSurF1.0/Index.htm

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JetSurF (Version 1.0)

## JetSurF (Version 1.0)

Release date: September 15, 2009

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**Performance that we know**

**Reduced Model**

**Release notes:**

JetSurF 1.0 consists of 194 species and 1459 reactions. The model describes the pyrolysis and oxidation kinetics of normal alkanes up to *n*-dodecane at high temperatures.

JetSurF 1.0 is capable of reproducing a large number of data sets, but it 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 1.0 release features a preliminary determination of the model uncertainty and its quantitative impact on predicted combustion properties, as shown for a selected set of validation tests.

**Some Model Details**

The base model is USC-Mech II (111 species, 784 reactions) that describes the oxidation of H<sub>2</sub> and CO and the high-temperature chemistry of C<sub>1</sub>-C<sub>4</sub> 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.

The base model is appended with a set of reactions (83 species and 675 reactions) to describe high-temperature pyrolysis and oxidation of normal alkanes (C<sub>k</sub>H<sub>2k+2</sub>, 5 ≤ k ≤ 12). The bulk of work is discussed initially in [1]. The following class of major reactions of *n*-alkanes have been considered:

Reaction type	Source and Method of Rate Estimation	Pressure fall-off
C-C bond fission in <i>n</i> -alkane	Back rate constant from 2C <sub>2</sub> H <sub>5</sub> → <i>n</i> -C <sub>4</sub> H <sub>10</sub> ( <i>k</i> <sub>∞</sub> )	No
H-abstraction by H, O, OH, O <sub>2</sub> , O <sub>3</sub>	Cohen's method using the rate constants of	N/A

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## JetSurF (Version 1.1)

Release date: September 15, 2009

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**Performance that we know**

**Release notes:**

This interim version of JetSurF (version 1.1) consists of 352 species and 2083 reactions. JetSurF 1.1 adds the pyrolysis and oxidation kinetics of *n*-butylcyclohexane at high temperatures into JetSurF 1.0. The development effort centers on *n*-butyl-cyclohexane, but the model includes also the high-temperature chemistry of *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 1.1 is an extension to JetSurF version 1.0 – a detailed model that describes the pyrolysis and oxidation kinetics of normal alkanes up to *n*-dodecane at high temperatures. JetSurF 1.0 consists of 194 species and 1459 reactions and has been validated against experimental data ranging from laminar flame speeds, ignition delay times behind shock waves, to species profiles in flow reactors.

JetSurF 1.0 is appended here with a set of reactions (158 species and 624 reactions) to describe high-temperature pyrolysis and oxidation of cyclohexane and its derivatives. The following class of major reactions of cyclic-alkanes have been considered:

Reaction type	Source and Method of Rate Estimation	Pressure fall-off
C-C bond fission on the lateral alkyl group (conserving the ring)	Back rate constant from 2C <sub>2</sub> H <sub>5</sub> → <i>n</i> -C <sub>4</sub> H <sub>10</sub> ( <i>k</i> <sub>∞</sub> )	No
C-C bond fission on the cyclic structure (opening the ring)		
H-abstraction by H, O, O <sub>2</sub> , HO <sub>2</sub> and CH <sub>3</sub>	Cohen's method. Used the rate constants of C <sub>3</sub> H <sub>8</sub> + X → <i>n</i> -C <sub>3</sub> H <sub>7</sub> or <i>i</i> -C <sub>3</sub> H <sub>7</sub> + HX	N/A

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## ***Team Presentation Schedule***

- 8:15-8:30 Program Overview  
(Egolfopoulos; University of Southern California)
- 8:30-9:00 Low/Intermediate Temperature Flow Reactor Studies  
(Cernansky & Miller; Drexel University)
- 9:00-9:45 Intermediate/High Temperature Flow Reactor and Shock Tube Studies  
(Bowman & Hanson; Stanford University)
- 9:45-10:15 Laminar Flame Studies in Counterflow Configurations  
(Egolfopoulos; University of Southern California)
- 10:15-10:45 Break
- 10:45-11:15 Laminar Flame Studies in Counterflow and Spherically Expanding Configurations  
Detailed Mechanism Reduction  
(Law; Princeton University)
- 11:15-11:35 Direct Numerical Simulations of Opposed Jet Reacting Flows  
(Pitsch; Stanford University)
- 11:35-12:15 Detailed Mechanism Development  
Transport Coefficients  
Uncertainty Propagation  
(Wang; University of Southern California)