Reaction Kinetics of Jet Fuels

Hai Wang

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The JetSurF Experience

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:

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R. K. Hanson, D. F. Davidson, C. T. Bowman, H. Pitsch
C. K. Law
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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-buty1-, 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)
The JetSurF Experience

• **JetSurF 2.0**: 2163 reactions and 348 species;
• *n*-alkane series: *n*-pentane to *n*-dodecane.
• Cyclohexane series: cyclohexane and its monoalkylated derivatives up to *n*-butylcyclohexane.
• Benzene and toluene chemistry.
• H$_2$/CO/C$_1$-C$_4$ chemistry.
• Validation tests for >170 separate sets of data (documented on the web – additional tests from IPT PIs’ publications).
• Web releases only.
• The JetSurF experience: our approach will not lead to a closure to a quantitative description of jet fuel chemistry.
Challenges in Reaction Mechanism Development

• Methodology extends from Dixon-Lewis’ s work some 50 years ago.
  • Write down every reaction step and find its rate coefficient.
  • $\text{H}_2$, $\text{H}_2$/CO etc with $\sim 2$ dozen reactions.
  • Can have a closure because of a limited number of rate parameters.
  • Allowed us to understand the detailed laminar flame structure.

• Later work focused on small hydrocarbons – $\text{O}(100)$ reactions – many of which have been probed by experiments and rate theory calculations.

• Recent effort for large hydrocarbons – $\text{O}(10^3\text{-}10^4)$ reactions – largely based on empirical knowledge.
  • Group additivity
  • Analogous reactions – reaction class
  • Guesses
  • Sensitivity analysis – you get information from what you put in.
  • Uncertainty analysis – try to assess and constrain uncertainty in our kinetic knowledge
Challenges in Reaction Mechanism Development

- The number of species/reactions increases exponentially as the fuel size increases, reaching $O(10^4)$ for practical fuels.

- The approach of detailed kinetic modeling is based on the notion that each and every rate parameters can be probed experimentally and/or theoretically. Hence, all model parameters and assumptions can be verified.

- The problem is a practical one – how do we verify the accuracy of the large number of assumptions/pathways/parameters?

An updated version of Lu & Law (2009)
The JetSurF Experience

Objective 1 – **Qualitative Insights**
- What chemistry causes faster ignition delay?
- Why a certain fuel propagates a flame faster than another?
- What does blending do to various combustion behaviors?
- What chemistry leads to increased low-T reactivity and why?
- ......

Objective 2 – **Quantitative Predictions**
- > 95% reaction pathways/rates have are assumed.
- Lumping/reaction class assumption falls apart for unimolecular and chemically activated reactions.
- Uncertainties in $k(T,p)$ are too large to pin the predictions.
- Fundamentally an ill-defined mathematic problem – ab initio theories and uncertainty quantification can’t address all of the issues at this time.
- Kinetic coupling – a large thermodynamic condition space: can we test it all?
The JetSurF Experience

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The JetSurF Experience

Symbols:
- experimental
- data
- (Hanson 2009);

Lines:
- JetSurF1.1

0.381% methylcyclohexane - 4% O_2 in Ar
\( \phi = 1, p_5 = 1.5 \text{ atm} \)

1.96% methylcyclohexane - 20.60% O_2 in N_2
\( \phi = 1, p_5 = 20 \text{ atm} \)

Symbols: experimental data (Hanson 2009); Lines: JetSurF1.1
The JetSurF Experience

$1.154\% c\text{C}_6\text{H}_{12} - 20.77\% \text{O}_2 \text{ in N}_2$

$\phi = 0.5, \ p_5 = 50 \ \text{atm}$

Other models have the same problem!
The JetSurF Experience

• Rate coefficients often show non-Arrhenius behaviors – lumping/class assignments are inaccurate.
The JetSurF Experience

- For many fuels, a detailed treatment of the reaction kinetics is challenging, if not impossible.

<table>
<thead>
<tr>
<th>MCHX dehydrogenation reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>-H (by H, OH, O, CH3)</td>
</tr>
<tr>
<td>H-elimination (P-dependent)</td>
</tr>
</tbody>
</table>

Reactions not shown:
- H₂ eliminations
- H-shifting
- β-scission ring-openings

Total Submechanism:
- ~40 species
- ~150 reactions

Many intermediates with nearly identical reaction paths and thermochemical properties.

Dames (2012)
The JetSurF Experience

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Objective 2 – **Quantitative Predictions**
- > 95% reaction pathways/rates have are assumed.
- Lumping/reaction class assumption falls apart for unimolecular and chemically activated reactions.
- Uncertainties in \( k(T,p) \) are too large to pin the predictions.
- Fundamentally an ill-defined mathematic problem – ab initio theories and uncertainty quantification can’t address all of the issues at this time.
- Kinetic coupling – a large thermodynamic condition space: can we test it all?
The JetSurF Experience

- A severely under-defined mathematical problem.
  - unknown pathways/rates, inaccurate rate coefficients

- Even if reaction pathways are known and the problem can be treated as an inverse problem, we are still facing large uncertainties.

Sheen & Wang (2012)
The JetSurF Experience

Objective 1 – Qualitative Insights
- What chemistry causes faster ignition delay?
- Why a certain fuel propagates a flame faster than another?
- What does blending do to various combustion behaviors?
- What chemistry leads to increased low-T reactivity and why?
- ......

Objective 2 – Quantitative Predictions – in a surrogate approach
- > 95% reaction pathways/rates are assumed.
- Lumping/reaction class assumption falls apart for unimolecular and chemically activated reactions.
- Uncertainties in $k(T,p)$ are too large to pin predictions without tuning.
- Fundamentally an ill-defined mathematic problem – ab initio theories and uncertainty quantification can’t address all of the issues at this time.
- Kinetic coupling – a large thermodynamic condition space: can we test it all?

Development of reaction kinetic model for large fuels is not an exact science. If we must rely on empiricism, what is the most logical path to predictability?
The Current Surrogate Approach

- **Key Assumptions:**
  - A mixture of several neat hydrocarbons can mimic the chemical and physical behaviors of a real jet fuel – **lumping** at the fuel level.
    - *n*-dodecane, *n*-butylcyclohexane, dimethyloctane, *n*-propylbenzene, etc.

A real fuel – thousands of compounds – combustion chemistry not tractable at a fundamental level.

A surrogate fuel – mimics a real fuel
- Physical properties
- Chemical properties
  - Enthalpy, C/H, chemical functionalities, combustion behaviors, …
- Combustion chemistry models, in principle, tractable at a fundamental level
The Current Surrogate Approach

• **Key Assumptions:**

  – A mixture of several neat hydrocarbons can mimic the chemical and physical behaviors of a real jet fuel – **lumping** at the fuel level.
    • *n*-dodecane, *n*-butylcyclohexane, dimethyloctane, *n*-propylbenzene, etc.

  – Detailed models for individual surrogate components can be developed and validated, rationally and thoroughly. It requires
    • An examination of assumptions involving all reaction pathways/rate coefficients;
    • Validation against a wide range of conditions encountered in turbulent flames, premixed and non-premixed.

  – Kinetic coupling of components and their reaction intermediates can be verified experimentally in an efficient manner.

• **For tools available, the current approach is semi-empirical in at least two aspects – the many assumptions made in the kinetic models and the approach to lumping itself.**
An Alternative Surrogate Approach

A real fuel – thousands of compounds – combustion chemistry not tractable at a fundamental level.

Map out flame preheat zone cracking kinetics

\[ x(T(t), \rho) \]

Detailed Model

- \( C_2H_4, H_2, CH_4, C_3H_6, 1-C_4H_8 (+soot precursors) \)
- \( CO, CO_2, H_2, H_2O \) etc
An Alternative Surrogate Approach

• Key assumptions:
  – Large fuels do not enter into the flame sheet directly. They must undergo cracking before oxidation;
  – In the presence of a flame, the cracking kinetics is fast and may be decoupled from the oxidation kinetics of cracking products;
  – The oxidation of the cracked products determine ultimately the rates of radical pool build-up and heat release.

• Approach:
  – Seek to identify low-dimensional kinetic manifold(s) that describe(s) the kinetics of real fuel cracking directly, leading to a very limited number of smaller molecular fragments (H₂, CH₄, C₂H₄, C₃H₆, 1-C₄H₈, C₆H₆ etc.). *The rates don’t matter as much as the composition of the cracking products.*
  – Detailed kinetic description of H₂/C₁-C₄ pyrolysis and oxidation reaction kinetics.
• Large fuel molecules cracks into small fragments (H₂, CH₄, C₂H₄, C₃H₆ etc) initially over a substantially short time period before oxidation dominated by radical-chain branching.

Davidson, Hong, Pilla, Farooq, Cook & Hanson, *Combustion and Flame* (2010)
Laminar Flame Structure and Fuel Kinetics

- Fuel takes a nose-dive before oxygen is depleted.
- The temperature at which dodecane is depleted is 1400 K.
Laminar Flame Structure and Fuel Kinetics

- Fuel takes a nose-dive before oxygen is depleted.
- The temperature at which dodecane is depleted is 1400 K.
- Flame is established after the parent fuel is gone.

![Diagram showing mole fraction and temperature profiles for an \( n-C_{12}H_{26}\)-air flame (\( \phi = 1, T_0 = 298 \text{ K}, p = 1 \text{ atm} \))](image)
Laminar Flame Structure and Fuel Kinetics

- Fuel takes a nose-dive before oxygen is depleted.
- The temperature at which dodecane is depleted is 1400 K.
- Flame is established after the parent fuel is gone.
- The parent fuel cracks to C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>6</sub>, CH<sub>4</sub> and H<sub>2</sub> which enter into the flame, is oxidized and release heat.
- The pyrolysis zone is separated from the flame.
- Pyrolysis occurs in the ~1000-1450 K window and is facilitated by H and OH (10<sup>-4</sup> to 10<sup>-3</sup> in mole fractions).
- Pyrolysis took ~100 μs.
Laminar Flame Structure and Fuel Kinetics

- Fuel takes a nose-dive before oxygen is depleted.
- The temperature at which dodecane is depleted is 1400 K.
- Flame is established after the parent fuel is gone.
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- The pyrolysis zone is separated from the flame.
- Pyrolysis occurs in the 1050-1450 K window and is facilitated by $\text{H}$ and $\text{OH}$ (10^-4 to 10^-3 in mole fractions).
- Pyrolysis took $\sim$100 μs.
- Other fuels do not behave differently (except for aromatics).
Chemistry in Fuel Rich Flames

- In laminar flames, large fuel molecules cracks into small fragments in the preheat zone;
- Heat conducted from the flame is partitioned into sensible heat and reaction enthalpy (endothermicity due to fuel cracking);

![Graph showing mole fraction and temperature as functions of distance](image)

Lightly stretched burner-stabilized dodecane-O\textsubscript{2}-Ar flame ($\phi = 2.0$, 1 atm)

Abid et al. (2009)
Why Large Fuel Molecules and Flame Do Not Mix?

- Disparity in molecular diffusion rates
  - w/o cracking to smaller molecular fragments, the fuel would never have caught up with $O_2$. 

![Graph showing temperature, mole fraction, and diffusion rates for $n$-C$_{12}$H$_{26}$-air flame ($\phi = 1$, $T_0 = 298$ K, $p = 1$ atm).](image-url)

\[ D_{O_2} \sim 4 D_{C_{12}H_{26}} \]
Why Large Fuel Molecules and Flame Do Not Mix?

• Disparity in molecular diffusion rate
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• If the fuel and flame mix, cracking endothermicity would lower the local temperature, reduce heat conduction, and weaken the flame. Flame must move downstream to separate it from the fuel cracking zone.
Why Large Fuel Molecules and Flame Do Not Mix?

• Disparity in molecular diffusion rate
  – w/o cracking to smaller molecular fragments, the fuel would never have caught up with \( \text{O}_2 \).

• If the fuel and flame mix, cracking endothermicity would lower the local temperature, reduce heat conduction, and weaken the flame. Flame must move downstream to separate it from the fuel cracking zone.

• Large hydrocarbon fuels cracks faster than small hydrocarbons.

• Composition of cracked products insensitive to the size of the fuel (with the class)
Homogeneous Cracking Kinetics

- Fuel cracking is endothermic and driven by entropy.
- For time scales relevant to flames
  - fuel cracking is kinetically controlled far from chemical equilibrium.
- For *n*-alkanes, dominant products are \( \text{C}_2\text{H}_4 \), \( \text{H}_2 \), \( \text{C}_3\text{H}_6 \), \( \text{CH}_4 \) \( \text{C}_2\text{H}_6 \) and 1-\( \text{C}_4\text{H}_8 \) (true for all *n*-alkanes).
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- At the upper end of flame pyrolysis zone (~1400 K), pyrolysis reaches the “plateau” region within 100 \( \mu \)s without initial \( \text{H} \) and \( \text{OH} \) presence.
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- At the upper end of flame pyrolysis zone (~1400 K), pyrolysis reaches the “plateau” region within 100 \( \mu \)s without initial H and OH presence.
- Cracking goes faster isothermally.
Homogeneous Cracking Kinetics

- Fuel cracking is endothermic and driven by entropy.
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  - fuel cracking is kinetically controlled far from chemical equilibrium.
  - For n-alkanes, dominant products are $\text{C}_2\text{H}_4$, $\text{H}_2$, $\text{C}_3\text{H}_6$, $\text{CH}_4$, $\text{C}_2\text{H}_6$ and 1-$\text{C}_4\text{H}_8$ (true for all n-alkanes).
- At the upper end of flame pyrolysis zone (~1400 K), pyrolysis reaches the “plateau” region within 100 $\mu$s without initial H and OH presence.
- Cracking goes faster isothermally.
- It goes blazingly faster when radicals are brought in (100 PPM H atom) – reaching the plateau within < 100 $\mu$s at 1300 K.
Turbulence Can Enhance Fuel Cracking Rates

An Alternative Surrogate Approach

• Key assumptions:
  – Large fuels do not enter into the flame sheet directly. They must undergo cracking before oxidation;
  – In the presence of a flame, the cracking kinetics is fast and may be decoupled from the oxidation kinetics of cracking products;
  – The oxidation of the cracked products determine ultimately the rates of radical pool build-up and heat release.

• Approach:
  – Seek to identify low-dimensional kinetic manifold(s) that describe(s) the kinetics of real fuel cracking directly, leading to a very limited number of smaller molecular fragments (H\textsubscript{2}, CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{4}, C\textsubscript{3}H\textsubscript{6}, 1-C\textsubscript{4}H\textsubscript{8}, C\textsubscript{6}H\textsubscript{6} etc.). The rates don’t matter as much as the composition of the cracking products.
  – Detailed kinetic description of H\textsubscript{2}/C\textsubscript{1}–C\textsubscript{4} pyrolysis and oxidation reaction kinetics.
1. Test the concept on \( n \)-dodecane – develop a lumped model for \( n \)-dodecane pyrolysis.

2. Develop an empirical jet fuel cracking kinetic model from experiments.
(1) Test the Idea Against *n*-Dodecane

### Lumped Model of *n*-Dodecane

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>(A)</th>
<th>(n)</th>
<th>(E_a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(n-C_{12}H_{26} \rightarrow 3C_2H_4 + 2n-C_3H_7)</td>
<td>(5.6 \times 10^{26})</td>
<td>-2.7</td>
<td>88171</td>
</tr>
<tr>
<td>2</td>
<td>(n-C_{12}H_{26} \rightarrow 2C_2H_4 + 2p-C_4H_9)</td>
<td>(5.1 \times 10^{25})</td>
<td>-2.5</td>
<td>88117</td>
</tr>
<tr>
<td>3</td>
<td>(n-C_{12}H_{26} + H \rightarrow 4C_2H_4 + p-C_4H_9 + H_2)</td>
<td>(1.3 \times 10^6)</td>
<td>2.5</td>
<td>6756</td>
</tr>
<tr>
<td>4</td>
<td>(n-C_{12}H_{26} + H \rightarrow 1.2C_2H_4 + 0.2C_3H_6 + 0.4n-C_3H_7 + 0.2C_4H_8 - 1 + 0.6) (p-C_4H_9 + 0.2C_5H_{10} + 0.6C_6H_{12} + H_2)</td>
<td>(1.3 \times 10^6)</td>
<td>2.4</td>
<td>4471</td>
</tr>
<tr>
<td>5</td>
<td>(n-C_{12}H_{26} + O \rightarrow 4C_2H_4 + 2p-C_4H_9 + OH)</td>
<td>(1.9 \times 10^5)</td>
<td>2.7</td>
<td>3716</td>
</tr>
<tr>
<td>6</td>
<td>(n-C_{12}H_{26} + O \rightarrow 1.2C_2H_4 + 0.2C_3H_6 + 0.4n-C_3H_7 + 0.2C_4H_8 - 1 + 0.6) (p-C_4H_9 + 0.2C_5H_{10} + 0.6C_6H_{12} + OH)</td>
<td>(4.8 \times 10^4)</td>
<td>2.7</td>
<td>2106</td>
</tr>
<tr>
<td>7</td>
<td>(n-C_{12}H_{26} + OH \rightarrow 4C_2H_4 + 2p-C_4H_9 + H_2O)</td>
<td>(1.4 \times 10^3)</td>
<td>2.7</td>
<td>527</td>
</tr>
<tr>
<td>8</td>
<td>(n-C_{12}H_{26} + OH \rightarrow 1.2C_2H_4 + 0.2C_3H_6 + 0.4n-C_3H_7 + 0.2C_4H_8 - 1 + 0.6) (p-C_4H_9 + 0.2C_5H_{10} + 0.6C_6H_{12} + H_2O)</td>
<td>(2.7 \times 10^4)</td>
<td>2.4</td>
<td>393</td>
</tr>
<tr>
<td>9</td>
<td>(n-C_{12}H_{26} + CH_3 \rightarrow 4C_2H_4 + 2p-C_4H_9 + CH_4)</td>
<td>1.8</td>
<td>3.7</td>
<td>7153</td>
</tr>
<tr>
<td>10</td>
<td>(n-C_{12}H_{26} + CH_3 \rightarrow 1.2C_2H_4 + 0.2C_3H_6 + 0.4n-C_3H_7 + 0.2C_4H_8 - 1 + 0.6) (p-C_4H_9 + 0.2C_5H_{10} + 0.6C_6H_{12} + CH_4)</td>
<td>3.0</td>
<td>3.5</td>
<td>5480</td>
</tr>
</tbody>
</table>

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Units are mol, cm, sec, Cal, and K. You et al. 2009

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**C-C fissions**

*H-abstraction* +

**β-scissions**
(1) Test the Idea Against $n$-Dodecane

**Lumped Model of $n$-Dodecane**

For example:

\[ n\text{-}C_{12}H_{26} + H \rightarrow s\text{-}C_{12}H_{25} + H_2 \rightarrow \ldots \rightarrow C_3H_6 + n\text{-}C_3H_7 + C_6H_{12} + H_2 \]

(secondary)  \hspace{1cm} (R4a)

\[ \rightarrow s2\text{-}C_{12}H_{25} + H_2 \rightarrow \ldots \rightarrow C_4H_8 + 2C_2H_4 + p\text{-}C_4H_9 + H_2 \]

(tertiary)  \hspace{1cm} (R4b)

\[ \rightarrow s3\text{-}C_{12}H_{25} + H_2 \rightarrow \ldots \rightarrow C_5H_{10} + 2C_2H_4 + n\text{-}C_3H_7 + H_2 \]

(quaternary) \hspace{1cm} (R4c)

\[ \rightarrow s4\text{-}C_{12}H_{25} + H_2 \rightarrow \ldots \rightarrow C_6H_{12} + C_2H_4 + p\text{-}C_4H_9 + H_2 \]

(quinary) \hspace{1cm} (R4d)

\[ \rightarrow s5\text{-}C_{12}H_{25} + H_2 \rightarrow \ldots \rightarrow C_6H_{12} + C_2H_4 + p\text{-}C_4H_9 + H_2 \]

(senary) \hspace{1cm} (R4e)

A lumped step by assuming the rates of H-abstraction to be identical

\[ n\text{-}C_{12}H_{26} + H \rightarrow 1.2C_2H_4 + 0.2C_3H_6 + 0.4n\text{-}C_3H_7 + 0.2C_4H_8 + 0.6p\text{-}C_4H_9 + 0.2C_5H_{10} + 0.6C_6H_{12} + H_2 \]

(R4)

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You et al. 2009
(1) Test the Idea Against $n$-Dodecane – Selected Results

$n$-$C_{12}H_{26}$ pyrolysis in a plug flow reactor (0.336% $n$-$C_{12}H_{26}$-$N_2$, $p = 1$ atm)

![Conversion plot](image)

Experimental data: Dahm et al.; Solid lines: detailed model; dashed line: lumped $C_{12}$ model + USC Mech II

You et al. 2009
(1) Test the Idea Against n-Dodecane – Selected Results

2% \( n-C_{12}H_{26} \) pyrolysis in He in a jet-stirred reactor \((p = 1 \text{ atm})\)

Conversion of \( n-C_{12}H_{26} \) (\( n \)%)

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Residence Time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>873</td>
<td>0</td>
</tr>
<tr>
<td>973</td>
<td>0</td>
</tr>
<tr>
<td>1073</td>
<td>0</td>
</tr>
</tbody>
</table>

Experimental data: Herbinet et al.; Solid lines: detailed model; dashed line: lumped \( C_{12} \) model + USC Mech II

You et al. 2009
(1) Test the Idea Against $n$-Dodecane – Selected Results

$n$-$\text{C}_{10}\text{H}_{22}$ oxidation behind reflected shock waves

Experimental data: Herbinet et al.; Solid lines: detailed model; dashed line: lumped $\text{C}_5$-$\text{C}_{12}$ model + USC Mech II

You et al. 2009
Laminar Flame Speed of $n$-Dodecane-Air Mixtures

$p = 1 \text{ atm}$

470 K

403 K

Solid lines: detailed model; dashed line: lumped $C_{12}$ model + USC Mech II

You et al. 2009
(1) Test the Idea Against $n$-Dodecane – Conclusions

• Fuel cracking and oxidation of cracked products ($C_1$-$C_4$) are decoupled during high-temperature oxidation of $n$-dodecane.

• The same decoupling is expected to work for JP7, i.e., the reaction model may be approximated by a semi-empirical description of the cracking kinetics + a foundational fuel ($H_2/CO/C_1$-$C_4$) model.
(2) Test the Idea Against JP7 – Cracking Model

The cracking model tuned against turbulent flow reactor experiments at 1 atm (residence time = 0.75 sec)

Figure 2. Experimental (symbols) and computed (lines) concentrations of species during JP7 pyrolysis in a turbulent flow reactor (0.1%-mol JP7 in N₂) at a residence time of 0.75 sec and a constant pressure of 1 atm, as a function of temperature. The experimental data of JP7 were derived from carbon balance. Simulations used the semiempirical JP7 model developed in the present work.

Wang & Egolfopoulos, unpublished
(2) Test the Idea Against JP7 – Cracking Model

Table 1. An Empirical JP7 Cracking Model

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>( k = A T^n e^{-E/RT} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( A )</td>
</tr>
<tr>
<td>1</td>
<td>JP7 + M → CH₄ + 2C₂H₄ + C₃H₆ + C₄H₇ + M</td>
<td>1.0×10^{11}</td>
</tr>
<tr>
<td>2</td>
<td>JP7 + H → CH₃ + 2C₂H₄ + C₃H₆ + sC₄H₉</td>
<td>4.6×10^{5}</td>
</tr>
<tr>
<td>3</td>
<td>JP7 + H → CH₃ + 1-C₄H₈ + C₃H₆ + sC₄H₉</td>
<td>4.6×10^{5}</td>
</tr>
<tr>
<td>4</td>
<td>JP7 + OH → CH₃ + 2C₂H₄ + C₃H₆ + C₄H₇ + H₂O</td>
<td>3.0×10^{4}</td>
</tr>
<tr>
<td>5</td>
<td>JP7 + O₂ → CH₃ + 2C₂H₄ + C₃H₆ + C₄H₇ + HO₂</td>
<td>8.0×10^{11}</td>
</tr>
<tr>
<td>6</td>
<td>JP7 + HO₂ → CH₃ + 2C₂H₄ + C₃H₆ + C₄H₇ + H₂O₂</td>
<td>1.0×10^{4}</td>
</tr>
<tr>
<td>7</td>
<td>JP7 + CH₃ → CH₃ + 2C₂H₄ + C₃H₆ + C₄H₇ + CH₄</td>
<td>4.0×10^{0}</td>
</tr>
</tbody>
</table>

The units of the rate parameters are cm, s, and cal. The empirical JP7 model was fitted to (a) the species concentration profiles after thermal cracking of JP7 in a turbulent flow reactor; (b) the laminar flame speeds of JP7, and (c) the ignition delay times of JP7-oxygen-argon mixture behind reflected shock waves. The model should be used with USC Mech II to provide detailed oxidation and pyrolytic kinetics for the cracking products.

Wang & Egolfopoulos, unpublished
(2) Test the Idea Against JP7 – Selected Results

Data: Davidson, Haylett & Hanson, Combust. Flame (2008).

Wang & Egolfopoulos, unpublished
(2) Test the Idea Against JP7 – Selected Results

Laminar Flame Speed of JP7-Air Mixtures
($p = 1$ atm, $T_0 = 403$ K)

Flame Speed, $S_U^o$ (cm/s)

Equivalence Ratio, $\phi$

Wang & Egolfopoulos, unpublished
(2) Test the Idea Against JP7 – Selected Results

Flame speeds of cracked JP7 (1 atm, $T_0 = 403$ K): coupled JP7 cracking in a TFR and partially decomposed products burned in a Bunsen flame.

Wang & Egolfopoulos, unpublished
(2) Test the Idea Against JP8 and Jet-A – Selected Results

Data: Vasu, Davidson & Hanson, Combust. Flame (2008).

Wang & Egolfopoulos, unpublished
Conclusion

- An alternative surrogate method and approach is defined and demonstrated for a rather narrow range of conditions.
- The fundamental validity of the alternative approach is examined and justified.
- For flame phenomena fuel cracking is not rate limiting and may be decoupled from the oxidation kinetics of the cracked products.
- The composition of cracking products is critical to flame phenomena; the mathematical description of the low-D manifold(s) will be defined through experimentation.