Reaction Models of Fundamental Combustion Properties

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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

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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
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)
JetSurF Status

• Version 1.0+1.1 → **JetSurF 2.0**
  
  *$n$*-butyl-, *$n$*-propyl-, ethyl- and methyl- cyclohexanes* and cyclohexane.

  *$n$*-pentane to *$n$*-dodecane

  Some branched chain HCs + aromatics

• **Key Revisions from version 1.0+1.1**
  
  • Low temperature chemistry of cyclohexane and methylcyclohexane added
  
  • H-abstraction rates from Violi
  
  • ......

• **Validation test sets > 200** (documented online)
  
  http://melchior.use.edu/JetSurF
Multispecies Time-History Data

Davidson, Hong, Pilla, Farooq, Cook & Hanson, *Combustion and Flame* (2010)

[Diagram showing mole fraction of various species over time with labels for C2H4, CO2, H2O, OH.]

Solid lines: experiments; dashed lines: JetSurF 1.0
Multispecies Time Histories

300 ppm $n$-$C_7H_{16}$ - 3300 ppm O$_2$ in Ar, $T_5 = 1365$ K, $p_5 = 2.35$ atm

Solid lines: experiments; dashed lines: JetSurF 1.0
Multispecies Time Histories

What can we learn from the multispecies time-histories?

• The model is accurate, but is it precise?

• Given the ~±5% experimental accuracy, can the data be utilized to improve model precision?

• To what extent the data improve model precision?
Propagation of Uncertainty

\[ x_i = x_i^{(0)} + \sum_{j=1}^{m} \alpha_{ij} \xi_j + \sum_{k=1}^{m} \sum_{j=k}^{m} \beta_{ijk} \xi_j \xi_k + \ldots \]

Data structure that describes a chemical model + associated uncertainty

\[ \eta_r(\mathbf{x}) \approx \eta_{r,0} + \sum_{i=1}^{N} a_{r,i} x_i + \sum_{i=1}^{N} \sum_{j \geq i}^{N} b_{r,ij} x_i x_j \]

Represents some physics model, e.g. PREMIX

\[ \eta_r(\mathbf{x}, \xi) = \eta_r(\mathbf{x}^{(0)}) + \sum_{i=1}^{m} \hat{\alpha}_{r,i} \xi_i + \sum_{i=1}^{m} \sum_{j=i}^{m} \hat{\beta}_{r,ij} \xi_i \xi_j \]

Predictions of a chemical model (e.g. laminar flame speed) + associated uncertainty

Sheen et al. (2009)
Multispecies Time Histories
(Model Uncertainties)

300 ppm \( nC_7H_{16} \) / 3300 ppm \( O_2 \) / Ar (\( T_5 = 1494 \text{ K}, p_5 = 2.15 \text{ atm} \))

JetSurF 1.0 is quite accurate
**Multispecies Time Histories**
*(Model Uncertainties)*

300 ppm $nC_7H_{16}$ / 3300 ppm O$_2$ / Ar ($T_5 = 1494$ K, $p_5 = 2.15$ atm)

JetSurF 1.0 is quite accurate... but aren’t we lucky!
Multispecies Time Histories
(Model Uncertainties)

300 ppm $nC_7H_{16}$ / 3300 ppm O$_2$ / Ar ($T_5 = 1365$ K, $p_5 = 2.35$ atm)

Even less precise towards lower $T_5$. 

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Multispecies Time Histories
Analyses of Experimental Uncertainties

300 ppm \( nC_7H_{16} / 3300 \text{ ppm } O_2 / \text{ Ar} \)
\( T_5 = 1494 \text{ K}, p_5 = 2.15 \text{ atm} \)

300 ppm \( nC_7H_{16} / 3300 \text{ ppm } O_2 / \text{ Ar} \)
\( T_5 = 1365 \text{ K}, p_5 = 2.35 \text{ atm} \)

Dashed lines: \( \pm 10 \text{K} \) \( T_5 \) uncertainty; dotted lines: \( \pm 20\% \) uncertainty on species concentration
Method of Uncertainty Minimization (MUM-PCE)

\[ \Phi \left( x^{(0)*} \right) = \min_{x^{(0)}} \sum_{r=1}^{M} \left[ \eta_{r,0}^{\text{obs}} - \eta_r \left( x^{(0)} \right) \right]^2 \left( \sigma_r^{\text{obs}} \right)^2 \]

\[ \eta_r^{\text{obs}} (\xi) = \eta_{r,0}^{\text{obs}} + \sigma_r^{\text{obs}} \xi_r \]

\[ x_i = x_i^{(0)} + \sum_{j=1}^{m} \alpha_{ij} \xi_j \]

\[ \eta_r (x, \xi) = \eta_r \left( x^{(0)} \right) + \sum_{i=1}^{m} \hat{\alpha}_{r,i} \xi_i + \sum_{i=1}^{m} \sum_{j=1}^{m} \hat{\beta}_{r,ij} \xi_i \xi_j \]

\[ \Phi_{\alpha} \left( \alpha^* \right) \approx \min_{\{\alpha\}} \sum_{r=1}^{M} \frac{1}{\left( \sigma_r^{\text{obs}} \right)^2} \left\{ \sum_{i=1}^{M} \left[ \sigma_r^{\text{obs}} \delta_{ir} - \hat{\alpha}_{r,i} \right]^2 + \sum_{i=1}^{M} \sum_{j=1}^{M} \hat{\beta}_{r,ij} \right\} \]

Sheen, et al. (2009)
Method of Uncertainty Minimization (MUM-PCE)

\[ \Phi\left( x^{(0)*} \right) = \min_{x^{(0)}} \sum_{r=1}^{M} \left[ \eta_{r,0}^{\text{obs}} - \eta_r \left( x^{(0)} \right) \right]^2 \]

\[ \eta_{r}^{\text{obs}} (\xi) = \eta_{r,0}^{\text{obs}} + \sigma_{r}^{\text{obs}} \xi_r \]

\[ x_i = x_i^{(0)} + \sum_{j=1}^{m} \alpha_{ij} \xi_j + \sum_{k=1}^{m} \sum_{j=k}^{m} \beta_{ijk} \xi_j \xi_k + \ldots \]

\[ \eta_r \left( x, \xi \right) = \eta_r \left( x^{(0)} \right) + \sum_{i=1}^{m} \hat{\alpha}_{r,i} \xi_i + \sum_{i=1}^{m} \sum_{j=i}^{m} \hat{\beta}_{r,ij} \xi_i \xi_j \]

\[ \Phi_{\alpha\beta} \left( \alpha^*, \beta^*, \ldots \right) = \min_{\{\alpha, \beta, \ldots\}} \sum_{r=1}^{M} \frac{1}{\sigma_r^{\text{obs}}} \left\{ \sum_{i=1}^{M} \left[ \sigma_{r}^{\text{obs}} \delta_{ir} - \hat{\alpha}_{r,i} \right]^2 + \sum_{i=1}^{M} \sum_{j=i}^{M} \hat{\beta}_{r,ij} + \ldots \right\} \]

1-atm C₂H₄-air mixtures

Egolfopoulos & Law (1990)
Faeth & co-workers (1998)
Law & co-workers (2005)

Sheen, et al. (2009)
Multispecies Time Histories
Model Precision Improved by the data

300 ppm $n\text{C}_7\text{H}_{16}$ / 3300 ppm O$_2$ / Ar ($T_5 = 1494$ K, $p_5 = 2.15$ atm)
Multispecies Time Histories

Impact on Flame Speed Predictions

$n$-heptane-air mixtures ($p = 1$ atm, $T_0 = 353$ K)
Multispecies Time Histories
Effect of Experimental Uncertainties

\( n \)-heptane-air mixtures \((p = 1 \text{ atm}, T_0 = 353 \text{ K})\)

![Graph showing uncertainty in species value, \(2\sigma^{\text{obs}}\)]

- \(\phi = 1.0\)
- \(\phi = 1.4\)

![Graph showing uncertainty in species value, \(2\sigma^{\text{obs}}\)]

- CH\(_3\) (Series 2) only
- OH (Series 1) only
- All multi-species (Series 1 & 2)
Multispecies Time Histories

Effect of Experimental Uncertainties

$n$-heptane-air mixtures ($p = 1$ atm, $T_0 = 353$ K)

(a) unconstrained – prior model

(b) posterior model (±20%)

(c) posterior model (±5% - hypothetical)
Model is Accurate, and (Looks) Precise (Too) with constrained joint parameter uncertainties

\[ n\text{-heptane-air mixtures (} p = 1 \text{ atm, } T_0 = 353 \text{ K)} \]

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Diagram showing:
- (a) Unconstrained – prior model
- (b) 2 sets of OH, H₂O, CO₂ profiles
- (d) 2 sets of OH, H₂O, CO₂ profiles

Graphs plot:
- Flame Speed (cm/s) vs. Equivalence Ratio, \( \phi \)
Model is Accurate, and *(Looks) Precise *(Too)* with constrained joint parameter uncertainties* 

Open diamond: Smith et al. (2005); filled circles: Davidson et. al. (2010)
Joint Parameter Uncertainties

Multispecies Global properties Multispecies+ Global properties

\[ \text{H}_2 + \text{O}_2 \leftrightarrow \text{O} + \text{OH} \]

\[ \text{H}_2 \text{O} + \text{H}_2 \leftrightarrow \text{H}_2 \text{O}_2 + \text{H}_2 \]

\[ \text{C}_2\text{H}_5 + \text{O}_2 \leftrightarrow \text{CH}_2\text{CHO} + \text{O} \]
Onset of OH emission. Lines: JetSurF v1.1 predictions.

Onset of OH emission. Lines: JetSurF v1.1 predictions
Onset of OH* emission. Lines: JetSurF v1.1 predictions.
Cyclohexane Low-Temperature Chemistry

Miller, Taatjes (2009)

Onset of OH⁺ emission. Lines: JetSurf v2.0 predictions.
Onset of OH emission. Lines: JetSurF v2.0 predictions.
Cyclohexane Ring-Opening Reaction

\[ k \ (s^{-1}) = 5 \times 10^{16} \exp\left[ -\frac{88 \text{ kcal/mol}}{RT} \right] \] (Tsang 1978)
Methylcyclohexane Ring-Opening Reaction

\[
\begin{align*}
\text{CH}_3 & \quad \rightarrow \quad \text{CH}_3 \\
\text{H}_3\text{C} & \quad \text{CH} = \text{CH}_2 \\
\text{H}_3\text{C} & \quad \text{CH}_3
\end{align*}
\]
Ring-Opening Reactions

CBS-QB3 energy

\[ \Delta H_0 = 89.8 \text{ kcal/mol} \]

\[ \Delta H_0 = 79.0 \text{ kcal/mol} \]
$E_a = 71 \text{ kcal/mol}$

$E_a = 88 \text{ kcal/mol}$
• JetSurF 2.0 is available online (still needs work).

• Major improvement from version 1.1
  • Added low temperature of cyclohexane

• Unresolved problems
  • Low-temperature chemistry for \textit{n}-butylcyclohexane not yet implemented
  • Kinetics of alkylated cyclohexane thermal decomposition (ring opening through the carbene mechanism) currently unavailable)