Surrogate Fuel Modeling and Uncertainty Quantification

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• Component Library Approach for transportation fuel surrogates
  – Chemistry reduction techniques
  – Component library approach
  – Application: Jet fuel surrogate
• Chemical mechanism for aliphatic species
• Uncertainty quantification in chemical systems
Reduction Strategies

**DRGEP**\(^1\): Directed Relation Graph with Error Propagation

- Removes as many species and reactions as possible while retaining the accuracy of detailed mechanism
- Automatic, fast and efficient
- Generates skeletal mechanisms with consistent chemical pathways

**Chemical Lumping**\(^2\)

- Replaces chemical isomers by one single representative species
- Very efficient for large hydrocarbons oxidation
- Rate coefficients of the lumped reactions estimated accurately through statistical analysis of the detailed results

**Quasi-steady state assumptions**

- Replaces differential equations by algebraic expressions

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Integrated Approach

- Highest reduction ratio obtained by combining all techniques
- Example: Iso-octane oxidation mechanism
  - Initial size: 850 species, 7212 reactions
  - Reduced size: 57 species, 504 reactions

Plug Flow Reactor
Very lean I-C₈H₁₈/air
T₀ = 945K

Atmospheric laminar burning velocities
T₀ = 298K

I-C₈H₁₈/air ignition delay times
Component Library Approach

Transportation fuel: kerosene, diesel, gasoline...

Applications

Surrogate composition

Existing detailed kinetic mechanisms for pure components

First stage of reduction

DRGEP, Lumping

Skeletal mechanisms for pure components

Component library

Combination: Skeletal mechanism for mixture

Interaction modules, Feature modules

Incremental modules

Second stage of reduction

QSSA

Reduced chemical model
# Individual Components and Detailed Kinetic Models

<table>
<thead>
<tr>
<th>Class</th>
<th>Molecule</th>
<th>Formula</th>
<th>Structure</th>
<th>Comments</th>
</tr>
</thead>
</table>
| Paraffins     | Dodecane          | C<sub>12</sub>H<sub>26</sub> | ![Structure](image) | Mech: 174 species, Wang et al., 2008  
Exp: ST, flames |
|               | Iso-octane        | C<sub>8</sub>H<sub>18</sub> | ![Structure](image) | Mech: 850 species, LLNL, 2002  
Exp: ST, PFR, flames |
| Naphthenes    | Methyl-cyclohexane| C<sub>7</sub>H<sub>14</sub> | ![Structure](image) | Mech: 998 species, LLNL, 2005  
Exp: ST, PFR |
| Aromatics     | Toluene           | C<sub>7</sub>H<sub>8</sub>  | ![Structure](image) | Mech: Blanquart et al., 2008  
Exp: ST, PFR, flames |
|               | Benzene           | C<sub>6</sub>H<sub>6</sub>  | ![Structure](image) |                                  |

Base chemistry (C<sub>0</sub>-C<sub>4</sub>) developed for PAH and soot formation
- Extensively validated
- 151 species, Blanquart et al., 2008.
Possible Jet Fuel Surrogate Compositions

- Automatic composition optimization for any given targets based on group additivity theory

<table>
<thead>
<tr>
<th>Composition [%mol]</th>
<th>Average Jet Fuel**</th>
<th>Neat Dodecane</th>
<th>Surrogate 1*</th>
<th>Surrogate 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dodecane</td>
<td>N/A</td>
<td>100</td>
<td>73.5</td>
<td>45</td>
</tr>
<tr>
<td>Iso-octane</td>
<td></td>
<td></td>
<td>5.5</td>
<td></td>
</tr>
<tr>
<td>MCH</td>
<td></td>
<td></td>
<td>10</td>
<td>26.1</td>
</tr>
<tr>
<td>Toluene</td>
<td></td>
<td></td>
<td>10</td>
<td>28.9</td>
</tr>
<tr>
<td>Benzene</td>
<td></td>
<td></td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>H/C ratio</td>
<td>1.91</td>
<td>2.17</td>
<td>2.09</td>
<td>1.91</td>
</tr>
<tr>
<td>Formula</td>
<td>C_{11}H_{21}</td>
<td>C_{12}H_{26}</td>
<td>C_{10.7}H_{22.3}</td>
<td>C_{9.3}H_{17.7}</td>
</tr>
<tr>
<td>Hydrocarbon composition [%vol]</td>
<td>Paraffins</td>
<td>~60</td>
<td>100</td>
<td>88</td>
</tr>
<tr>
<td></td>
<td>Naphthenes</td>
<td>~20</td>
<td>0</td>
<td>6.4</td>
</tr>
<tr>
<td></td>
<td>Aromatics</td>
<td>~18</td>
<td>0</td>
<td>5.6</td>
</tr>
<tr>
<td>Cetane Number</td>
<td>~42.7</td>
<td>80</td>
<td>73.4</td>
<td>58</td>
</tr>
<tr>
<td>Treshold Sooting Index</td>
<td>~15</td>
<td>5.2</td>
<td>9.3</td>
<td>16.3</td>
</tr>
</tbody>
</table>

*Violi et al., Comb. Sci. Tech. 174:11, 2002
Validation Procedure

- Reduction done for various configurations and over a wide range of pressures, equivalence ratios, and temperatures > 900 K
- Validation performed at each stage of reduction and combination, for each fuel component

![Pyrolysis of MCH in plug flow reactor]

<table>
<thead>
<tr>
<th>Mechanisms</th>
<th>$N_S$</th>
<th>$N_R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Components</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Base Chemistry</td>
<td>151</td>
<td>1658</td>
</tr>
<tr>
<td>Dodecane</td>
<td>174</td>
<td>2625</td>
</tr>
<tr>
<td>Iso-octane</td>
<td>850</td>
<td>7212</td>
</tr>
<tr>
<td>Methyl-cyclohexane</td>
<td>998</td>
<td>8820</td>
</tr>
<tr>
<td>Multi-component surrogate</td>
<td>90 + 91 QSS</td>
<td>1197</td>
</tr>
</tbody>
</table>
Comparison with Jet Fuel Experiments

Kerosene Premixed Flame\textsuperscript{2}

- Experiments
- 5 components
- 3 components

Jet fuel auto-ignition\textsuperscript{1}

- $P = 20$ bar
- $P = 50$ bar

Jet fuel laminar burning velocity\textsuperscript{3}

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\textsuperscript{1} S. S. Vasu, D. F. Davidson, R. K. Hanson - Combust. Flame, 2008
\textsuperscript{2} Doute et al, Combust. Sci. Tech. 106, 1995
\textsuperscript{3} Eberius et al., 2001
Component Library Infrastructure

- Fully automatic, multi-stage reduction strategy
- Development of an **interactive framework** for chemical modeling of transportation fuel surrogates
  - Modular and flexible
- Future:
  - Incorporate JetSurF into Component Library
  - Validate multi-component surrogates with experimental data
Chemical Mechanism Development

- Objective:
  - Integrate our recent developments for PAH chemical mechanism into JetSurF mechanism
PAH Thermodynamics

• Thermodynamic Properties
  – Describe how stable each species are
  – Required for accurate modeling of combustion
    • Heat capacity
    • Entropy
    • Heat of formation

• Polycyclic Aromatic Hydrocarbons (PAH)
  – Formed in rich premixed and diffusion flames
  – Intermediates to soot formation

• New Database of Thermodynamic Properties
  – Ab-initio quantum calculations
    • G3MP2/B3
  – Internal degree of rotation
    • Hindered rotors
  – Group Corrections (GC)

Chemical Mechanism

• Based Blanquart et al. mechanism
• PAH part starts from Wang, Frenklach mechanism
• Updated with new rates and pathways

⇒ Blanquart, G., Pepiot-Desjardins, P., Pitsch, H. « Chemical mechanism for high temperature combustion of engine relevant fuels with emphasis on soot precursors » Combustion and Flame (2008) submitted
PAH Growth
Results

- 1 Detailed chemical mechanism
- 13 fuels
- 149 species
- 1651 reactions

⇒ Blanquart, G., Pepiot-Desjardins, P., Pitsch, H. « Chemical mechanism for high temperature combustion of engine relevant fuels with emphasis on soot precursors » Combustion and Flame (2008) submitted
Validation Results

• Entire mechanism validated with large database of experimental data
  – Ignition delay times
    • Lean
    • Stoichiometric
    • Rich
  – Laminar **Burning Velocities**
    • Atmospheric
    • Moderate pressure (3bar - 5bar)
    • *High* pressure (up to 25bar)

• Soot precursors in flames
  – Premixed flames
    • n-heptane
    • iso-octane
  – Counterflow **diffusion** flames
    • acetylene
    • n-heptane
Soot Precursors

Laminar Premixed Flames

Iso-Octane / Air flame
Rich mixture (φ=1.9)
Atmospheric

Laminar Diffusion Flames

Acetylene counterflow flame
Partially premixed (φ=0.63)
Atmospheric
Results Analysis
- Accurate prediction of soot concentration in premixed flames
- Soot volume fraction increases with equivalence ratio ($\phi$)
Uncertainty Quantification for Reactive Flow Simulations

• Uncertainty in numerical solution can be classified into
  • Aleatory: Uncertainty due to randomness in system, e.g. uncertainty in operating conditions of system or physical properties
  • Epistemic: Uncertainty due to lack of knowledge
• Monte Carlo (MC) simulations can be used for propagation of parametric uncertainty
  • MC simulations for complex models are very inefficient
  • No information about sensitivity of model to parametric uncertainty
• Polynomial chaos (PC) expansions can be used for stochastic representation of uncertainty
Polynomial Chaos Expansion Approach

- Uncertain model parameter ($\alpha$) can be represented as spectral expansion given its PDF.
- Spectral expansions called Polynomial Chaos expansions can be constructed using
  - Orthogonal polynomials (Hermite, Legendre, Laguerre etc.)
  - Weights associated with PDF

\[
\alpha = \sum_{k=0}^{\infty} \alpha_k \Psi_k
\]

- If Hermite polynomials are used then $\Psi_0 = 1$, $\Psi_1 = \xi$, $\Psi_2 = \xi^2 - 1$ etc.
Non-Intrusive Polynomial Chaos

- MC sampling of stochastic parameters is done to compute deterministic solution
- Coefficients of PC expansion are computed by projecting solutions onto PC basis

- **Advantage:** No need to modify trusted deterministic codes
- **Disadvantage:** Expensive for computationally intensive problem

- Intrusive method can be used for efficient solution
Intrusive Polynomial Chaos

- Variable $u(x,t,\xi)$ is expressed in form of PC expansion

$$u(x, t, \xi) = \sum_{k=0}^{N} u_k(x, t) \psi_k$$

- The expansion is substituted in the deterministic equation
- Orthogonality is used to get $N+1$ equations for $u_k$’s
- Nonlinear models involve operations on multiple stochastic parameters
- Pseudospectral approach is used to simplify function evaluation of stochastic parameters
Uncertainty Quantification

• Objective:
  – Uncertainty propagation in LES
    • E.g.: Effect of uncertain rates on NOx emissions from aircraft engine
  – Intrusive PC too expensive and complicated
    ➞ New UQ method with greatly reduced cost based on direct solution of uncertainty PDF equation
    ➞ New method didn’t work!
  – Focus on
    – Intrusive PC in laminar chemistry code
    – Epistemic uncertainty
      – Uncertainty caused by chemistry reduction
Pseudospectral Approach

• Intrusive PC leads to high order polynomials in non-linear terms
  • Pseudospectral approach

Multiplication
• Product of two PC expansions having order P result in PC expansion of order 2P
• Expansion of order 2P is projected on PC expansion of order P
• Thus if \( w = u \times v \) then

\[
w = \sum_{k=0}^{P} w_k \psi_k \quad \text{where} \quad w_k = \sum_{i=0}^{P} \sum_{j=0}^{P} u_i v_j \frac{\langle \psi_i \psi_j \psi_k \rangle}{\langle \psi_k^2 \rangle}
\]
Implementation

• Overloaded mathematical operators and functions were implemented in a library
• Can be used in chemical kinetic calculations to propagate uncertainty in initial conditions, reaction rate parameters, thermodynamic properties etc.
• E.g. Knowing PC expansions of A, T, $E_a$, evaluation of reaction rate $k = AT^n \exp(-E_a/T)$ can be done as

$$k = A \star \exp(n \star \ln(T) - E_a \odot T)$$

Where $\star$ and $\odot$ are overloaded multiplication and division operators
Future Work

• Incorporation of JetSurF into Component Library
• Validate surrogates based on JetSurF
• Integration of PAH chemistry into JetSurF mechanism
• UQ
  – Intrusive PC in laminar chemistry code
  – Model uncertainty caused by chemistry reduction