Chemistry Modeling

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Acknowledgements: Gaetano Esposito, Brendyn Sarnacki, Mohammad Rahimi form UVa
David Caughey, Varun Hiremath from Cornell

AFSOR-NASA Hypersonics Fundamental Research Review

National Center for Hypersonic Combined Cycle Propulsion
Williamsburg, Virginia, June 16, 2011
Modeling and Simulation Roadmap

2009 2010 2011 2012 2013 2014

Gen I

RANS Application to TBCC, Turbulence Model, Grid Generation, ............

RANS and Hybrid LES-RANS Application to UVa Rig, wall and turbulence models, ....

Compressible Turbulence Models For RANS and LES

VULCAN Implement SFMDF in VULCAN
Simple Flow/Grid

VULCAN Implement SFMDF in VULCAN
Complex Structured Grid

VULCAN Simulations of UVa Experiment

Gen II

Scalar FMDF Improve SFMDF Submodels and Numerical Solver

Scalar FMDF LES-SFMDF of Mixing Layer, jet,.....

Scalar FMDF LES-SMDF of UVa Combustor

DNS Temporal and Spatial Mixing Layer

DNS Shock-homogeneous turbulence Mixing Layer, H₂ Reactions

DNS A priori and A Posteriori Testing of LES/FMDF Submodels

Gen III

Chemistry New Reduced Kinetics Mechanisms for Hydrocarbons
Efficient Chemistry Solver ISAT+Message Passing, Parallel Methods, ...

EPV-FMDF Formulate

EPFVS-FMDF Evaluate /Improve submodels

EPFVS-FMDF Mixing and Reaction

EPFVS-FMDF Applications

National Center for Hypersonic Combined Cycle Propulsion
### Goals

<table>
<thead>
<tr>
<th>Goals</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. NIST: Detailed kinetic data for hydrocarbon fuels for hypersonic propulsion</td>
</tr>
<tr>
<td>2. UVa: Detailed, skeletal and reduced reaction models for ethylene</td>
</tr>
<tr>
<td>3. Cornell: Computationally-efficient implementation of ethylene chemistry for LES/FMDF</td>
</tr>
</tbody>
</table>
NIST Status Update
## Goals/Approaches/Tasks (NIST)

<table>
<thead>
<tr>
<th>Goals</th>
<th>Approaches/Tasks</th>
</tr>
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</table>
| Detailed kinetic models    | • Identify representative cracked fuel components based on fuel pyrolysis studies  
                                • Develop and optimize detailed kinetic models for lower order hydrocarbons (C1-C4), including chemically activated rate constants |
| Experimental data          | • Shock tube fuel pyrolysis studies                                                                                                              |
Fuel Pyrolysis - Shock Tubes vs. Tube Reactors

- At high temperature conditions, the storable hydrocarbon molecules undergo fast thermal pyrolysis or “cracking” to form smaller fragments
- Ethylene is a significant fragment

Heptyl radical decomposition from NIST shock tube studies showing ethylene as the primary cracked fuel, for 1000-1200 K and 0.2-2.0 bar

n-Dodecane decomposition from UTRC heated tube reactor studies showing formation of hydrogen and C1-C4 species, for ~920K and ~40bar

- Need further studies to develop and validate fuel decomposition models for real fuels (or surrogate mixtures), temperature, pressures, and residence times.
Shock Tube Studies on Fuel Pyrolysis

MECHANISM AND BRANCHING RATIOS FOR THE DECOMPOSITION OF OCTYL RADICALS

4 isomers undergoing 6 beta bond scissions and 6 reversible isomerizations
Elementary Kinetic Rates

- Uncertainty of kinetic parameters:
  - Require systematic analysis to reduce the uncertainty levels of kinetic parameters
  - Need accurate experimental data with narrow uncertainty bounds
  - Need systematic optimization approaches

- From shock tube studies, elementary kinetic rates of H-atom attack on C1-C4 hydrocarbon molecules are being investigated to reduce the large uncertainties (Rosado-Reyes, Manion, Tsang, 2010)

H+O2 rate constant vs. 1/T from NIST Kinetics Database

Propene, propyne

H+Propene (add, t) *(Kerr et al. 1972) 19
H+Propene (add, nt) *(Kerr et al. 1972) 19
H+1-Butene (add, t) *(Kerr et al. 1972) 19
H+1-Butene (add, nt) *(Kerr et al. 1972) 19
H+Propene (Harris 1982) 3
H+Propene (Kurylo 1971) 4
H+Propene (Wagner 1972) 18
H+(E)-2-Butene (Kyogoku 1983) 21
H+(Z)-2-Butene (Kyogoku 1983) 21
H+Propyne (Rosado-Reyes 2010) 2
H+Propene (This Work)
UVa Status Update
## Goals/Approaches/Tasks (UVa)

<table>
<thead>
<tr>
<th>Goals</th>
<th>Approaches/Tasks</th>
</tr>
</thead>
</table>
| **Skeletal and reduced reaction models** | • Development of skeletal/reduced reaction models for the dominant C1-C4 components identified using (i) sensitivity based principal component analysis (PCAS) and (ii) quasi-steady state approximations (QSSA)  
• Implement reduced kinetic models in a representative high-speed reacting flow configuration (e.g. compressible shear flows) |
| **Experimental data** | • Counterflow extinction and ignition limit measurements |
Skeletal and Reduced Models

- PCAS based method was successfully implemented in reducing ethylene-air kinetic model developed by USC, identified USC Mech II (opt.)
  

- PCAS method is currently being extended to propene, 1-butene, 1,3 butadiene, etc.

- QSSA was applied to obtain a 20-step reduced reaction model for ethylene, based on previous work performed under NASA NRA (Zambon and Chelliah, Combust. and Flame, 2007)

- The models developed have been shared with Center members, NASA, AEDC, AFRL, GE, and others

- However, the accuracy of the parent detailed kinetic model used in above reductions has raised some concern (see next 2 slides)
Extinction Limits and Uncertainties

- Extinction limits of counterflow nonpremixed fuel-air mixtures and their uncertainties have been measured at UVa (Sarnacki, Esposito, Krauss, Chelliah, in review Combust. and Flame)

<table>
<thead>
<tr>
<th>Fuel-air system</th>
<th>Local Extinction Strain Rate (1/s)</th>
<th>Model Predict. (1/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>380±21</td>
<td>456-469</td>
</tr>
<tr>
<td>Ethylene</td>
<td>1284±48</td>
<td>1222-1231</td>
</tr>
<tr>
<td>Propylene</td>
<td>617±34</td>
<td>606-624</td>
</tr>
<tr>
<td>n-Butane</td>
<td>499±38</td>
<td>544-550</td>
</tr>
</tbody>
</table>

Comparison of UVa experiments and USC Mech II (opt.) of methane extinction

Comparison of UVa experiments and USC Mech II (opt.) of ethylene extinction
Ignition Delay Predictions

- For hypersonic applications, accurate prediction of ignition delay is **critical**!
- Ignoring pressure rise effects in shock tube experiments, the following figures show a comparison between the USC Mech II (opt.) model and experimental data reported in the literature (based on excited OH*/CH*, dp/dt, etc.)

Comparison between USC Mech II (opt.) and hydrogen ignition delay data from Bhaskaran et al. (1973). Also shown are the predictions using the model of Hong et al. (2011).

Comparison between USC Mech II (opt.) and methane ignition delay data from Spadaccini and Colket (1994).

Comparison between USC Mech II (opt.) and ethylene ignition delay data from Brown and Thomas (1999).
Uncertainty of Kinetic Parameters

- Uncertainty factors \( (f = \frac{k}{k_0}) \) of key kinetic parameters can range from 1.2-5.0!

- A better understanding of kinetic parameter uncertainty propagation, both forward and backward, is needed.

- Full Monte Carlo (MC) calculations over the entire parameter space is impossible, i.e. requires \( 2^p \) calculations with \( p=784 \)! However, MC calculations of a subset of dominant reactions is possible, e.g. \( p=14 \)

- This task was accomplished by using distributed computing facilities available at UVa. Note: on a single CPU, MC calculations of extinction limits \( (3 \times 2^{14}) \) can take about 3500 days but can be done in about 3 weeks on a 300 CPU cluster.

- Backward propagation requires accurate experimental data of combustion limits, e.g. ignition delay, extinction limits, species information, etc., which we are measuring at UVa.
# Uncertainty Factors of Rate Constants

- Uncertainty factors of the selected 14 reactions (from 784 reactions in USC Mech II) in our Global Sensitivity Analysis study is listed below:

<table>
<thead>
<tr>
<th>#</th>
<th>Reaction</th>
<th>Uncertainty factors</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H+O2 = O+OH</td>
<td>f = 1.2</td>
</tr>
<tr>
<td>2</td>
<td>CO2 + OH = CO2 + H</td>
<td>f = 1.2</td>
</tr>
<tr>
<td>3</td>
<td>CO2 + OH = CO2 + H</td>
<td>f = 1.2</td>
</tr>
<tr>
<td>4</td>
<td>C2H3 + H = C2H2 + H2</td>
<td>f = 5.0</td>
</tr>
<tr>
<td>5</td>
<td>O+H2 = H+OH</td>
<td>f = 1.3</td>
</tr>
<tr>
<td>6</td>
<td>HCO + M = CO + H + M</td>
<td>f = 2.0</td>
</tr>
<tr>
<td>7</td>
<td>C2H3 + O2 = HCO + CH2O</td>
<td>f = 2.0</td>
</tr>
<tr>
<td>8</td>
<td>OH + H2 = H + H2O</td>
<td>f = 1.3</td>
</tr>
<tr>
<td>9</td>
<td>C2H3 + H = H2CC +H2</td>
<td>f = 5.0</td>
</tr>
<tr>
<td>10</td>
<td>HCO + O2 = CO + HO2</td>
<td>f = 2.0</td>
</tr>
<tr>
<td>11</td>
<td>C2H4 + H = C2H3 + H2</td>
<td>f = 2.0</td>
</tr>
<tr>
<td>12</td>
<td>C2H2 + O = HCCO + H</td>
<td>f = 1.5</td>
</tr>
<tr>
<td>13</td>
<td>C2H4 + O = C2H3 + OH</td>
<td>f = 2.0</td>
</tr>
<tr>
<td>14</td>
<td>14 C2H4 + OH = C2H3 + H2O</td>
<td>f = 2.0</td>
</tr>
</tbody>
</table>
Outcome of Uncertainty Analysis

- Actual experimental uncertainty of $a_{\text{ext}}$
- $a_{\text{ext}}$ variation due to 14 rate constant uncertainties
- Most probable rate parameters

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National Center for Hypersonic Combined Cycle Propulsion
Outcome of Uncertainty Analysis

• MC analysis can also provide accurate information about interaction between reactions, which needs to be taken into account during optimizations.

First-order effect of $C_2H_3 + H = C_2H_2 + H_2$ reaction uncertainty on predicted extinction strain rate.

Second-order coupling effect of $C_2H_3 + H \leftrightarrow C_2H_2 + H_2$ and $HCO + M \leftrightarrow CO + H + M$ on extinction strain rate.

• Final Objective: better optimized detailed reaction models, and accurate reduced reaction models for reacting flow simulations!!!
Cornell Status Update
Goals/Approaches/Tasks (Cornell)

<table>
<thead>
<tr>
<th>Goals</th>
<th>Approaches/Tasks</th>
</tr>
</thead>
</table>
| **Computationally-efficient implementation** | • Computationally-efficient implementation of ethylene combustion for Generation II & III LES/FMDF studies  
• Dimension reduction: rate-controlled constrained equilibrium (RCCE)  
• Tabulation: *in situ* adaptive tabulation (ISAT)  
• Scalable parallel implementation  
• Test and demonstrate the above algorithms in LES/FMDF simulations of turbulent combustion |
LES/FMDF with Ethylene

- Develop computationally-efficient implementations of ethylene chemistry

- Demonstrate in Large-Eddy Simulation (LES) / Filtered Mass Density Function (FMDF) calculations of turbulent combustion

- Large-scale parallel computations: $10^7$-$10^8$ particles, $10^4$-$10^5$ time steps $\rightarrow 10^{12}$ chemistry queries

- Ethylene Chemistry:
  - USC Mech-II Detailed: 111 species
  - ODE Integration: 0.25 s CPU time per query
  - 70 M CPU hours for $10^{12}$ chemistry queries
Test Case: PaSR with Ethylene Combustion

Partially-Stirred Reactor (PaSR):

- Representative of real LES/FMDF calculations
- Ethylene/air premixed combustion
- Two streams:
  - premixed stream of stoichiometric ethylene/air at 600 K
  - pilot stream of equilibrium products

- Constant atmospheric pressure
- Residence time of 100 μs
- Mixing and Pairing time of 10 μs
- Number of particles = 100
Representation of Chemistry

Detailed Mechanism:
• USC Mech II (optimized in 2010)
• 5 elements: O, H, C, N, Ar
• 111 species and 784 reactions

Skeletal Mechanism (using PCA):
• Developed by Harsha Chelliah (UVa)
• 38 species and 212 reactions

Reduced Mechanism (using QSSA):
• Developed by Harsha Chelliah
• 24 species and 20-step reactions
Strategies: Direct Evaluation

- Direct evaluation of reaction mapping using ODE integrator
- Method currently used at Pitt. and MSU for H₂
ODE Integrators and Error Control

- ODE Integrators: DVODE, DASSL, DDASPK, DDASAC, EXP4, etc.

- 111 species ethylene mechanism, DDASAC: 0.25s CPU time per reaction mapping (relatively expensive)

(Sukheswalla & Pope 2011)

- Incurred error vs. error tolerance
- CPU time vs. incurred error
Strategies: Tabulation using ISAT

- Tabulation of reaction mapping using ISAT
- Reaction mapping computed using the detailed mechanism
- Average query time for 111 species is 400 μs
- 625x faster than Direct Evaluation
Strategies: Combined Dimension Reduction and Tabulation

- Dimension Reduction using RCCE (rate controlled constrained equilibrium)
- Full representation in terms of $n_s=111$ species: $z$
- Reduced representation in terms of $n_r$ specified represented variables: $r$
- e.g., $n_r=30$: 25 “represented species” plus 5 elements
- Species reduction: $r = B^T z$, where $B$ is a $n_s \times n_r$ matrix determined by the represented species
- Species reconstruction: $z = z^{CE}(r)$, maximum entropy composition
- In CFD, solve for $r$
Strategies: Combined Dimension Reduction and Tabulation

- Dimension Reduction using RCCE with user-specified constrained species
- Tabulation of the reduced mapping using ISAT
- Reaction mapping computed using the detailed mechanism
- Average query time reduced to 23 µs
- 17x faster than ISAT alone
Strategies: Selection of Represented Species

• GALI: Greedy Algorithm with Local Improvement

• Pre-Processing: Species selection using GALI with PaSR

• Choice of the represented species encapsulated in the constraint matrix $B$

GALI: species selection for methane combustion
Strategies: ISAT/RCCE/GALI

- GALI: Greedy Algorithm with Local Improvement
- Pre-Processing: Species selection using GALI with PaSR
- Choice of the represented species encapsulated in the constraint matrix $B$
Recent Work

• Test the combined ISAT-RCCE-GALI approach using the Partially-Stirred Reactor (PaSR) test case

• Compare the accuracy and performance of representing ethylene chemistry using the following approaches:
  – ISAT: using ISAT directly with ethylene detailed mechanism
  – ISAT+SKELETAL: using ISAT with ethylene skeletal mechanism
  – ISAT+REDUCED: using ISAT with ethylene reduced mechanism
  – ISAT+RCCE: using combined ISAT-RCCE with the detailed mechanism and represented species selected using GALI
Reduction-Tabulation Error

- ISAT tabulation error
  - < 1%
- ISAT+Skeletal
  - 38 species
  - 3% error
- ISAT+Reduced
  - 24 species
  - 7% error
- ISAT+RCCE:
  - 7% and 3% error with 18(+4) and 25(+5) variables, respectively.

Reduction-Tabulation error using (i) ISAT (with detailed mechanism); (ii) ISAT+SKELETAL; (iii) ISAT+REDUCED; and (iv) ISAT+RCCE with $n_{rs}$ represented species selected using GALI
ISAT Performance

- slope- ‘query-time’
- y-intercept – ‘build-time’

- ODE Integration $10^5 \mu s$
- Query time:
  - ISAT: 400 $\mu s$
  - ISAT+Skeletal: 21 $\mu s$
  - ISAT+Reduced: 17 $\mu s$
  - ISAT+RCCE: 23 $\mu s$

- LES/FMDF
  - $10^{12}$ queries at 23 $\mu s = 6,400$ hours
  - 10,000x speed-up relative to Direct Evaluation
  - Reduction in number of variables: 111 to 30 (70% reduction)

ISAT query-time using (i) ISAT (with detailed mechanism); (ii) ISAT+SKELETAL; (iii) ISAT+REDUCED; and (iv) ISAT+RCCE with $n_{rs}$ represented species selected using GALI
## Summary of Performance

<table>
<thead>
<tr>
<th>Method</th>
<th>No. of variables</th>
<th>Error (cf. detailed)</th>
<th>Query time (μs)</th>
<th>Time for $10^{12}$ queries (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detailed/DE</td>
<td>111</td>
<td>0%</td>
<td>250,000</td>
<td>70 M</td>
</tr>
<tr>
<td>Detailed/ISAT</td>
<td>111</td>
<td>1%</td>
<td>400</td>
<td>110 k</td>
</tr>
<tr>
<td>Skeletal/ISAT</td>
<td>38</td>
<td>3%</td>
<td>21</td>
<td>5.8 k</td>
</tr>
<tr>
<td>RCCE/ISAT</td>
<td>30</td>
<td>3%</td>
<td>23</td>
<td>6.4 k</td>
</tr>
<tr>
<td>Reduced/ISAT</td>
<td>24</td>
<td>7%</td>
<td>17</td>
<td>4.7 k</td>
</tr>
<tr>
<td>RCCE/ISAT</td>
<td>22</td>
<td>7%</td>
<td>23 (est.)</td>
<td>6.4 k</td>
</tr>
</tbody>
</table>
Parallel LES/FMDF Computations of Flame D

- Flame D:
  - Jet: CH$_4$/Air 294 K
  - Pilot: Hot equilibrium mixture at 1800 K
  - Coflow: Air at 294 K

- LES domain: 16D x 8D x 2Π
- 1024 processors (Ranger TACC)

- x2f_mpi/ISAT
- 4M particles
- 16-species ARM1 mechanism
- 10$^{10}$ ISAT queries
- No dimension-reduction (will be tested in the future)
Performance with Different Parallel Strategies

- \texttt{x2f_mpi} modes:
  - PLP: Purely Local Processing
  - URAN: Uniformly Random

- Simple Flamelet mode takes 1 hr

- Estimates:
  - Direct evaluation (DE) with load balancing: 19 h
  - ISAT w/ perfect load balancing and no MPI comm.: 1.9 h
  - ISAT w/ only retrieves: 1.7 h

- PLP takes about 4.5 h walltime

- URAN takes only 2.2 h walltime (50\% less than PLP)

- URAN performs within 30\% of the best estimates
Performance with Different Parallel Strategies

LES/FMDF of flame D; 16-species ARM1 for methane; 1024 processors; $10^{10}$ particle steps

<table>
<thead>
<tr>
<th>Method</th>
<th>Wall time (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct Evaluation, no communication</td>
<td>56</td>
</tr>
<tr>
<td>Direct Evaluation, perfect load balancing</td>
<td>19</td>
</tr>
<tr>
<td>ISAT/PLP (no communication)</td>
<td>4.5</td>
</tr>
<tr>
<td>ISAT/URAN (uniform random for ODE)</td>
<td>2.2</td>
</tr>
<tr>
<td>ISAT retrieve time</td>
<td>1.7</td>
</tr>
<tr>
<td>Flamelet (1 composition, no reaction)</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Conclusions
Conclusions (1/2)

NIST Work:
• Shock tube experiments are being performed to describe fuel pyrolysis pathways and kinetic rates of various fuel radicals

UVa Work:
• Extraction of **skeletal reaction models** using PCAS works well for C1-C4 fuels
  - need 38 species skeletal reaction model to predict the extinction limits of ethylene-air within 2-3% of the detailed model
  - can go as low as 31 species for ignition, with less than 1% error
• 20 species **reduced reaction model** can replicate 38 species skeletal model with same level error (<2-3%)
• Monte Carlo calculations with a subset of dominant rate parameters have been performed over their uncertainty space yielding valuable insight on first-order effects and second-order coupling effects
• Extinction limits were measured for key cracked fuel components and will be used in future model optimizations
Conclusions (2/2)

**Cornell Work:**

- GALI successfully used to select good represented species for dimension reduction with RCCE
- ISAT/RCCE/GALI approach tested for ethylene combustion using PaSR
- Combined approach shows good error control and performance relative to direct use of ISAT for representing combustion chemistry
- Preliminary study of parallel implementations of x2f_mpi has been performed using LES/FMDF computations of Flame D
- Significant speedup is obtained using the x2f_mpi’s inbuilt URAN strategy relative to direct use of ISAT (PLP)
Future Work

• Application of PCAS approach developed to C3-C4 species, i.e. propene, 1-butene, 1,3 butadiene

• Continue collecting experimental data on extinction limits of C1-C4 components and mixtures, with lowest possible uncertainties

• Implement extinction limit response functions in model optimization, together with higher-order interaction information from MC simulations

• Implementation in LES/FMDF

• Parallel strategies (x2f_mpi) with dimension reduction
Publications (1/2)

Publications (2/2)


Gen II and Gen III Modeling Efforts

LES-RANS and RANS for UVa Dual-Mode Experimental setup
Edwards and Jaberi

Improved Turbulence Models for High Speed Non-Reacting and Reacting Flows
Ristorcelli, Edwards, Jaberi

Formulations of EPFVS-FDF for High Speed Reacting Flows
Givi, Pope, Jaberi

Experimental Data for Model Validation – NASA Coannular Jet, AFRL Jet in Cross Flow, UVa Dual Mode, HYPULSE etc.
Goyne, MacDaniel, Cutler, Hanson, Carter

Improved Subgrid Models and Numerical Methods for Scalar FMDF
Jaberi, Givi

DNS Data for Model Development and Testing – Supersonic Mixing Layer, Shock-Isotropic Turbulence
Madnia, Jaberi

Implementation of scalar FMDF in VULCAN
Jaberi, Baurle, Drozda

Reliable and Efficient Chemical Kinetics Models for RANS, LES and FDF
Pope, Chelliah, Tsang

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