Computationally Efficient Modeling of Hydrocarbon Oxidation Chemistry

K. G. Harstad* and J. Bellan*,**

*Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 90019-8099

**Mechanical Engineering Dept., California Institute of Technology, Pasadena, CA 91125

MACCCCR 2009 Fuels Summit
September 15-17, 2009
Los Angeles, CA

Sponsored by the Army Research Office under the direction of Dr. Ralph Anthenien
Outline

• Background
• Our previous work
  • chemistry modeling consistent with turbulence modeling
  • concept finding of a self similarity for n-heptane oxidation
  • \textit{a priori} modeling
  • \textit{a posteriori} assessment
• Recent results
  • further evaluation of the concept finding of quasi-linear relationships for two major species for n-heptane oxidation
  • identification of model further simplification
  • identification of the process through which modeling can be further refined
• Summary and conclusions
• Future work
Background

• Necessity to reduce the computational cost of chemistry in simulations of turbulent combustion

• Some existing chemistry reduction schemes:
  – reduction of detailed mechanisms to a few reactions and species
  – reduction of detailed mechanisms to ‘representative’ reactions past C$_4$ hydrocarbons using species lumping
  – piecewise implementation of solution mapping (PRISM)
  – \textit{in-situ} adaptive tabulation (ISAT)
  – intrinsic low-dimensional manifold (ILDM)
  – computational singular perturbation (CSP)
  – directed relation graph (DRG) reduction
Making chemistry modeling framework consistent with turbulence modeling

**Turbulence modeling**

1. Exact solution computable: Direct Numerical Simulation (DNS), but it is too costly for practical computations
2. Reduced modeling: solve differential equations only for energetically important scales and model the other scales (Large Eddy Simulation (LES))
   - find models
   - test to see how they fit the neglected scales (*a priori* analysis)
3. Conduct LES using the model(s) for the neglected scales and see how well one recovers the exact solution (*a posteriori* analysis)

**Our chemistry modeling**

1. Start with exact set of elementary reactions, e.g. LLNL database, which is too costly for practical computations
2. Reduced modeling: solve differential equations only for energetically important (and pollutant, if of concern) species and model other species
   - find models
   - test to see how they fit the modeled species (*a priori* analysis)
3. Conduct simulations using the model(s) for the approximated species and see how well one recovers the set of elementary reactions (*a posteriori* analysis)
Further similarities between turbulence and chemical reduction

- In the reduction process
  - The scales containing most motion-related energy are retained in LES and the other scales are modeled in turbulence
  - The scales containing most thermodynamic/kinetic-related energy are retained as progress variables in the kinetic reduction and the other scales are modeled

- The modeling consists in providing mathematical forms to fit the approximated-scale behavior. This is a major departure from current reduction schemes.
**A priori model: The concept of a base**

- **Species list**
  - **Light (we do not decompose)**
    - Air, final combustion products
  - **Light radicals/molecules** (e.g. CH₃, CH₄, H₂O₂)
  - **Heavy (we decompose)**
    - Radicals
    - Stable
    - Constituents

For general alkane or alkene with air:

The base = Light species + Constituents

(26) (13)

Remove NOx, C, C₂, N₂ and N at this preliminary stage, and then,

The base = Light species + Constituents

(20) (13)
**A priori model: Concept**

**Facts**

1. Plots of the heats of combustion for alkanes and for alkenes having a C double bond at the molecular chain end have a linear variation with the C number, $n$.

2. At fixed $T$, the species $C_p$ vary linearly with $n$.

**Implications**

Heats of combustion and $C_p$’s may be considered obtainable by summing those of constituent radicals CH$_2$, CH$_3$ and C$_2$H$_3$ that form these hydrocarbons.

For $n \geq 3$, species may be decomposed into constituent radicals. This is consistent with group additivity theory.
Group additivity and constituents

- Starting point akin to, but different from, typical chemical group additivity
  
  **Group additivity**
  - interactions with adjacent groups
  - interactions with non-adjacent groups
  - accounts for steric effects

  **Constituents**
  - only interactions with adjacent groups
  - only first order (compositional) effects

- Focus is on
  - comprehensiveness
  - accuracy
  - relative simplicity

- Our process is different from lumping
  - we are decomposing ALL heavy species
  - a constituent may span the entire species set of heavy species
  - we can recover the individual constituent molar fraction in the ensemble of constituents
1. Inspection of the LLNL kinetics shows that a subset of the light species is quasi-steady (i.e. gain and loss balance within 5% or less). These species are: O, CH, CH₂, CH₃, HO, HCO, HO₂, HC₂, C₂H₃.

2. Examination of the global constituent mole fraction, $N_c$, shows that, appropriately multiplied/divided by other variables/parameters and plotted against a non-dimensionalized temperature, it has a self-similar behavior (will show).

3. Conclusion: the final base is
   - $N_c$
   - molar densities of unsteady light species: H₂O, CO₂, O₂, H, CO, H₂, CH₄, H₂O₂, C₂H₂, C₂H₄, CH₂O
1. Examined data from LLNL: 160 species and 1540 reaction rates with the goal of forming non-dimensional groups of variables.

2. Systematic tests performed for $p_0$ from 1 to 60 bar and for equivalence ratios $\phi\in[1/8,8]$. Very time-consuming iterative process.

3. Try to reduce the problem to its essence by defining

$$N_c \equiv \sum_{k=1}^{13} N_k \quad \quad K_c \equiv -\frac{d(\ln N_c)}{dt}$$

4. Non-dimensional groups of variables

$$N^* \equiv \frac{N_{N2}}{N_{ref}} \quad \quad N_{ref} = 31.5 \text{ mol/m}^3$$

$$\theta \equiv \frac{T-T_s}{T_r(\phi,N^*)}, \quad T_r = 2065(N^*)^{0.06} w(\phi), \quad w(\phi) = \phi \frac{1.5+1.31\phi}{1+0.71\phi+1.1\phi^2}$$
Identification of self-similar behavior

\[ N_c/(\phi \times N^*) \text{ in mol}/(\text{m}^3), \; p_0 \text{ in bar}, \; T_s \text{ in K} \]
Meaning of the $N_c$ self-similarity

• Reduction in the dimensionality of the problem. Found a lower-dimensional manifold.

• Not to be confused with ILDM which is for species, whereas the present model is for $N_c$.

• The fact that the constituents rather than the heavy species are important can be directly traced to the fact that the heavy species decompose and it is the reaction of these products of decomposition that matters for the energetics.
The energetics

Energy equation:

\[
\left( N_c C_{p,h} + \sum_{i \in \text{lights}} C_{p,i} N_i \right) \frac{dT}{dt} = -\sum_{i \in \text{lights}} h_i R_i + N_c (R_u T_{ref}) K_h
\]

where \( N_i \) is the light species mole fraction and

\[
R_i = (dN_i/dt)_{\text{reac}}
\]

\[
C_{p,h} = (\sum_{l \in \text{heavies}} C_{p,l} N_l)/N_c
\]

\[
K_h = -\left( \sum_{l \in \text{heavies}} h_l R_l \right) \frac{1}{R_u T_{ref} N_c}
\]

\[
\left( \frac{dN_i}{dt} \right)_{\text{reac}} = \frac{dN_i}{dt} \bigg|_{\text{lights}} + \frac{dN_i}{dt} \bigg|_{\text{heavies}}
\]

\[
\frac{dN_i}{dt} \bigg|_{\text{heavies}} = N_c (KG_i - X_i KL_i)
\]
The light species

Light species ensemble partitioned into two categories:

1. Species that require rate equations and are part of the base set: H₂O, CO₂, O₂, H, CO, H₂, CH₄, H₂O₂, C₂H₂, C₂H₄, CH₂O

   ➡ 11 species (10 for a constant-volume PSR, as H is quasi-steady)

   \[
   \left( \frac{dN_i}{dt} \right)_{\text{react}} = \frac{dN_i}{dt} \bigg|_{\text{lights}} + \frac{dN_i}{dt} \bigg|_{\text{heavies}}
   \]

2. Species having a quasi-steady behavior that will be reproduced with curve fits for mole fractions: O, CH, CH₂, CH₃, HO, HCO, HO₂, HC₂, C₂H₃

   ➡ 9 species
Performed \textit{a priori} modeling

- \( K_c \)
- \( K_h \)
- \( KG_i \)
- \( RL_i \equiv KL_i/KG_i \)
- \( X_i \) (molar fraction of light quasi-steady species)
- All are very complex functions having two extrema over the \( \theta \) regime
  - Have three distinct regimes: \( \theta \ll 1; 10^{-2} \leq \theta \leq 10^{-1}; \theta \geq 10^{-1} \)
  - Need several types of functions to model over the entire \( \theta \) regime
  - Quantities \( K_c, K_h, KG_i \) and \( RL_i \) vary over seven orders of magnitude in a four-parameter space \( (T_0, N^*, \phi, T) \) small inaccuracies in a logarithmic plot may lead to large ‘local’ inaccuracies
A posteriori assessment of refined a priori model: T evolution

- $p_0 = 20, T_0 = 680, \phi = 1$
- $p_0 = 10, T_0 = 680, \phi = 1$
- $p_0 = 20, T_0 = 820, \phi = 1$
- $p_0 = 20, T_0 = 820, \phi = 1$
- $p_0 = 40, T_0 = 680, \phi = 3$
- $p_0 = 40, T_0 = 680, \phi = 1$
- $p_0 = 40, T_0 = 820, \phi = 1$
- $p_0 = 60, T_0 = 820, \phi = 1$
A posteriori results of the refined a priori model: $t_{\text{ign}}$

$p_0 = 40, \phi = 1$

$p_0 = 40, T_0 = 700$

$T_0 = 700, \phi = 1$
Questions!

• What determines the accuracy of the reduced model?
  – The concept? Use the concept with the functional forms provided by the LLNL template (in form of tables)!
  – The functional modeling in the \textit{a priori} stage?
  – Both concept and functional fits?

• Where should one concentrate effort to improve the model without sacrificing the computational efficiency?
  – Important for higher order hydrocarbons, e.g iso-octane
Concept assessment with ‘exact’ functions from the LLNL template

\[ \theta \equiv \frac{T - T_0}{T_r(\phi, N^*)} \]

LLNL with Chemkin II:

- ○ ○ $p_0 = 40$ atm; □ □ $p_0 = 10$ atm

Our concept with LLNL extracted functional forms:

- — $p_0 = 40$ atm; - - - - $p_0 = 10$ atm
Self-similar behavior persists

\[ \frac{N_c}{(\phi \times N^*)} \text{ (mol/m}^3\text{)}, \ p_0 \text{ in bar, } T_0 \text{ in K} \]
Additional benefit of concept assessment

- No2 (mol/m³)
- N_{H2O} (mol/m³)

- T₀ = 800 K, p₀ = 40 bar
- T₀ = 700 K, p₀ = 5
- T₀ = 700, p₀ = 10
- T₀ = 700, p₀ = 20
- T₀ = 700, p₀ = 40
- T₀ = 600, p₀ = 40

- φ = 1/4
- φ = 1/2
- φ = 1
- φ = 2
- φ = 4

- T₀ = 800 K, p₀ = 40
- T₀ = 700, p₀ = 5
- T₀ = 700, p₀ = 10
- T₀ = 700, p₀ = 20
- T₀ = 700, p₀ = 40
- T₀ = 600, p₀ = 40

φ = 1
Revised reduced model

- Fit $N_c$ rather than fitting $K_c$
- Revised model for $K_h$
  - Refined functional fit for $\theta \ll 10^{-2}$ (curve fitting improvement)
  - Modification of the initial slope w.r.t. $T$ to capture the lost information due to mechanism reduction (modeling improvement)
- Modeling of $N_{O_2}$ and $N_{H_2O}$ as quasi-linear functions of $\theta$
- Refined functional fit of $KG_i$ for $\theta \ll 10^{-2}$ (curve fitting improvement)
A priori modeling: functional fits for \( \text{N}_\text{O}_2 \) and \( \text{N}_\text{H}_2\text{O} \)
A posteriori results with revised model: T evolution
Prediction of ignition time

$p_0 = 40, \phi = 1$

$t_{\text{ign}}$ (ms) vs. $T_0$ (K)

$p_0 = 40, T_0 = 700$

$t_{\text{ign}}$ (ms) vs. $p_0$ (bar)

$T_0 = 700, \phi = 1$
Prediction of $N_{\text{OH}}$
Summary and conclusions

1. Explained how our reduced kinetics modeling parallels turbulence modeling within the concept of LES: *a priori* and *a posteriori* studies.

2. Conducted decoupled concept and *a priori* model (i.e. functional fits) assessments using the LLNL template.

3. Revised our previous *a priori* model and simplified it. The revised final model has
   - 9 instead of 12 ultimate species progress variables (removed $N_c, N_{O2}$ and $N_{H2O}$)
   - 12 instead of 17 quasi-steady rate functions (removed $K_c, KG_{O2}, KG_{H2O}, KL_{O2}$ and $KL_{H2O}$)
   - 3 added fits as function of $\theta$ ($N_c, N_{O2}$ and $N_{H2O}$)
   - 9 curve fits for light species quasi-steady mole fractions, as in the original model
   - 1 curve fit for $C_{p,h}$, as in the original model

4. Conducted an *a posteriori* assessment of the revised model study and found very good to excellent quantitative agreement for $t_{ign}$, $T(t)$ and species mole fractions.
Future work

1. Enlargement to higher C alkanes is conceptually straightforward if the quasi-steady aspect is preserved because additional species do not lead to additional progress variables due to the $N_c$ grouping.

   Extend the model to iso-octane (Remains to be seen if the present curve fits are valid for higher C alkanes or must be modified)

2. Model mixtures of hydrocarbons

3. Model flames