Modeling for Jet Fuel Surrogate Mixtures

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Generation of Comprehensive Surrogate Kinetic Models and Validation Databases for Simulating Large Molecular Weight Hydrocarbon Fuels

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Outline

• Some Modeling Issues already addressed in other talks
• Here we discuss:
  – Fundamental parameter assessments/data exchange
  – General modeling approaches
  – Modeling requirements
  – Identify specific areas where advances are needed
  – Briefly summarize initial modeling agenda
Fundamental Parameters and Process Informatics

• Sheer complexity of large carbon number mixtures leads to very large detailed models and numbers of estimated thermochemical and rate parameters

• Emerging Large Databases for
  – Thermochemistry, e.g. Argonne National Labs
    • Ruscic and co-workers, “Active Thermochemical Tables”
  – Physical Properties, e.g. NIST (Boulder)
    • Frenkel and co-workers, “ThermoData Engine”
  – Gas-phase reaction kinetics, e.g. Leeds, NASA/JPL, NIST, Argonne

• Global multi-dataset management - Process Informatics
  – (PrIMe for Process Informatics Model data integration, analyses,…and model generation)
    • data-centric approach to developing predictive models for complex chemical reaction systems
    • Both theory and experimental validation information (and inter-comparisons) are central to success
    • Eventual ability to construct models of reaction processes for any particular targets
  – PRIME sub-space specifically set aside for this MURI)
  – Validation experimental data, etc. to be database for MURI exchange and eventually part of overall data base (when published)
High Temperature Hydrocarbon Oxidation Kinetics
(Hierarchical Kinetic Character)

Surrogate Components

Detailed Kinetics < C₄

C₂H₅OH/O₂

CH₃CHO

C₂H₆

C₂H₄/O₂

CH₃OH/O₂

CH₂O/O₂

CO/H₂/H₂O/O₂

H₂/O₂

Autoignition
Heat Release Rate
Particulates
Toxics

CH₄

CH₃

CH₃OCH₃
Detailed Reaction Models Based on Hierarchical Approach
(since 2001)

• Small-species models (Dryer and Co-workers)
  – H₂/O₂ (Li et al., 2004)
  – CO/H₂/O₂ (Li, et al., 2004; Dryer and Chaos, 2007a, b)
  – CH₂O/CH₃OH (Li, et al., 2004; Li et al., 2007)
  – C₂H₄ (Carrière, et al., 2002)
  – C₃H₆ (Zheng, et al., 2003)
  – CH₃OCH₃ (Curran et al., 2001; Fischer et al., 2001; Zhao et al., 2005, 2006, 2007)

• Large fuel molecule (> C₆) models for practical applications (Dryer and Co-workers)
  – n-heptane/iso-octane at high temperatures only (Chaos et al., 2007)
  – n-heptane/iso-octane/toluene (Conley et al., 2003; Kazakov et al., 2003; Chaos et al. 2007; further publication fall 2007)
  – n-heptane/iso-octane/toluene at high temperatures only (available)
  – n-decane (Zeppieri et al., 2002; Zhao, et al., 2004)
  – n-hexadecane (Chaos, et al., 2005, 2006)
  – n-alkane mixtures: C₇ – C₁₆ (In progress)
More Reaction Modeling by Other Team Members
(since 2001)

- Small-species chemistry
  - H2/O2 (O’Conaire et al., 2004)
  - CO/H2/O2 (Sivaramakrishnan et al.)
  - CH4/C2H8 (Petersen et al., 2007)
  - CH3OCH3 (Curran et al., 2001; Fischer et al., 2001; Zheng et al., 2004)
  - Numerous publications on hydrocarbon radical thermochemistry
- Large fuel molecules (> C5) chemistry for practical applications (Curran and co-workers)
  - n-pentane (Ribaucour et al., 2001)
  - n-heptane (Seiser et al., 2001)
  - n-heptane isomers (Westbrook et al., 2001; Silke et al., 2005; Smith et al., 2007)
  - Iso-octane (Chen et al., 2001; Curran et al., 2002)
  - Methyl cyclo hexane (Orme et al., 2006; Pitz et al., 2007)
  - n-hexadecane (Chaos, et al., 2005, 2006)
  - n-alkane mixtures: C7 – C16 (In progress)
  - 1,2, dimethyl benzene (In Review, 2007)
  - Surrogate Fuels for Gasoline (Naik et al., 2005)
- Other Studies on Aromatics, including Benzene, toluene, toluene/n-butane blends, ethyl benzene, xylenes, and 1-methyl naphthalene (Brezinsky and co-workers, most recently, Toluene (Sivaramakrishnan et al., 2006, 2006)
- Area where we will depend heavily on other programs – soot kinetics models
  - Construct surrogate models to couple with soot modeling elsewhere
Modeling Approaches

• “Comprehensive” (Westbrook and Dryer, 1981) – originally referred to models developed and validated on the basis of validation against several sets of experimental observations across a wide range of parameters (frequently not overlapping)
  – There is at present no such thing as a kinetic model that fits all experimental observations and that will never need revisiting as “new validation data become available, mechanism knowledge increases, predicted parameters of interest change…
• The “Hierarchical” modeling approach does not assume sub-models are frozen as components are added of more complexity
  – Only emphasizes that changes in sub-models are always constrained first and foremost by sub model validation observations as new constraints are considered!
  – Each level must be constantly reviewed for improvements in parameters, and emergence of new validation target results
• Does every potential elementary reaction possible need to be considered?
  – Computational model construction is emerging and will eventually replace the “art” of model development, But…
  – “Completeness” not guaranteed (as new knowledge on mechanism emerges) and comes with increasing uncertainties in model and numbers of estimated parameters (even if minimization/optimization is applied)
  – Chemical kinetic purism – put everything in… Engineering interest – make model predictive for the targets pertinent to the application
• MURI will take advantage of both methodologies to yield validated models
Over-Arching Modeling Approach

• Detailed model assembly
  – Use mechanism evaluation, hierarchical, and computer generated detailed model generation methods

• Model “minimization”
  – Minimize model species and reactions to those necessary for reproducing targets in the parameter range of interest

• Model “optimization”
  – Use model analysis methodologies to identify controlling reactions/thermochemistry/transport phenomena and fundamental thermochemistry/rate parameter/transport selection achieve model prediction of experimental validation data

• Use minimized/optimized detailed model as basis for further dimensional reduction to CFD “utility”
Model Minimization

- Minimization emphasizes removing those species and reactions that do not contribute significantly to reproducing selected target predictions resulting from the original model.
- Brute force minimization, computational singular perturbation (CSP), directed relation graph (DRG), genetic algorithm (GA) methods all produce nearly the same minimized model numbers of reactions and species, if the same targets are used and the required predictive accuracies are constrained similarly.
- Without minimization, consideration of validation targets that couple transport with chemical kinetics are difficult to encompass in model verification and are frequently ignored.
Example: Laminar Flame Speeds of C$_7$/C$_8$ Mixtures

- Original LLNL PRF model (~1000 species, ~5000 reactions) based upon Curran’s C7/C8 models is too large to use flame codes such as Premix
- Minimized model (240 species, 603 reactions) while reproducing pure kinetic targets, poorly predicts laminar flame speed
- Similar results are obtained for the Curran et al C$_7$, C$_8$ model predictions compared against pure C$_7$, C$_8$ data.
- Part of difficulty relates to specified forward/reverse rate constants not always consistent with equilibrium constants
Surrogate Modeling for Real Fuels

• General problem: need data for real fuel and surrogate components and their mixtures in each of the fundamental experimental venues
  – The kinetic validation database becomes significantly more complex with the number of components to be used in the surrogate mixture
  – Few data over wide parameter ranges and venues for pure components
  – Even fewer data for mixtures to validate individual component interactions.

• Experimental difficulties become significantly greater with molecular carbon numbers above 12-14 (keep materials in the gas phase without decomposition)

• Both the model development and validation data requirements favor working with the least number of components.
  – Example - Gasoline Surrogate Model
Gasoline Example

- Combustion Property Targets:
  - Carbon/hydrogen ratio
  - Autoignition properties (low temperature reactivity, turnover T, and hot ignition),
  - Heat release rate
  - Laminar flame speeds
    - Few data to include premixed and non-premixed flame ignition and extinction characteristics as modeling targets for surrogate components and mixtures
    - Particulate modeling processes not relevant to application (but may be in the future)

- Need at least three components (vary C/H ratio) to encompass gasoline: n-heptane/iso-octane (PRF), components plus toluene
Toluene and PRF+1 Autoignition Properties

- Toluene oxidation exhibits no negative temperature coefficient (two-stage ignition) kinetic behavior itself.
  - The ignition behavior of a PRF+1 mix that replicates C/H ratio can be independently adjusted by changing the ratio of n-heptane and iso-octane without varying the toluene molar fraction.
  - Toluene coupling with PRF autoignition is through interactions of small species and radicals, *not* large radical species.
  - Toluene suppresses negative temperature coefficient behavior of a PRF+1 mixture relative to the PRF mixture without toluene by “competing for active radicals and having a much slower ability to regenerate active radicals (in comparison to alkanes)
  - *But* Toluene also affects hot ignition condition of PRF mixtures
Generic Large Carbon Number Oxidation Mechanisms

\[ \text{RH} + \text{O}_2 = \dot{\text{R}} + \text{HO}_2 \]
\[ \text{RH} = \dot{\text{R}}_1 + \dot{\text{R}}_2 \]
\[ \text{RH} + X = \dot{\text{R}} + \text{HX} \]

\( X = \text{OH}, \text{HO}_2, \text{CH}_3, \text{H}, \text{O} \)

Low Temperature Active Radical Generation

High Temperature Active Radical Generation

\[ \dot{\text{R}}_1 + \dot{\text{R}}_2 \]
\[ \dot{\text{R}} \]

\( \dot{\text{R}} \) propagation

\( \dot{\text{O}}\text{OOH} \) ketohydroperoxide + OH

\( \dot{\text{O}}_2\text{OOOH} \)

\( \text{H}_2\text{O}_2 + \text{M} = \text{OH} + \text{OH} \)

\( \dot{\text{R}}_s + 1 \)-olefin

isomerization & decomposition & H-abstraction

H\textsubscript{2}/O\textsubscript{2} & C\textsubscript{1}-C\textsubscript{4} kinetics
Procedure (Gasoline)

- A suitable combination of minimized versions for $iso$-octane and $n$-heptane was identified, hydrogen/oxygen kinetics, especially, were updated, inconsistencies in forward/reverse rate assignments were removed, and the combined model was tested and optimized to reproduce pure component (PRF=0 and PRF=100) and mixture autoignition and heat release rate targets, along with laminar burning rate characteristics.
- **But** no suitable literature toluene sub-mechanism could be found that predicted well new VPFR high pressure toluene oxidation data at high pressure.
Toluene Model Development and Integration

• Develop a revised sub-mechanism for toluene oxidation, based upon current (and, still, incomplete) understanding phenyl/benzyl ring oxidation.

• Redevelopment process included several steps:
  – Basic model structure (toluene, benzyl, benzaldehyde, benzene, and their derivatives based on Klotz (1998)
  – Appropriate reaction rate coefficients were assigned based on an extensive up-to-date literature review
  – Thermochemistry was taken from the Burcat and LLNL databases, where possible, otherwise estimated using available theoretical methods
  – Updated cyclopentadienyl radical thermochemistry from Roy et al. (2000) and Kiefer et al. (2000) were adopted.

• Integrated Toluene sub-model 22 species and 102 added reactions) with the PRF Min/Opt model (linking it to C3, C2, and C1 intermediates and final products) and validated against component and mixture experiments.

• **PRF+1 model has 469/1221 species/reactions.**
Flame speeds of toluene/air mixtures are reproduced well by the model at all equivalence ratios for data of [15] (Davis:1996).
• PRF+1 model predictions against \( n \)-heptane/toluene and \( iso \)-octane/toluene reactivity data collected in the VPFR.
  – Major species, the NTC region is properly reproduced
• Characteristic reaction time scales and dependences on equivalence ratio are properly captured by the model (not shown).
Model Validation
VPFR – PRF+1 Emulation of a Gasoline with ON of 87

Princeton VPFR (12.5 atm, $\phi = 1$, 740 ppm)
Model Validation
PRF+1 Emulation of Gasoline ON=87

- Shock Tube data appeared in the open literature after the development of the present model [16] (Gauthier: 2004).
- Flame data at Princeton in air at 1 atm, with noted EGR (by volume).
How to Match a Gasoline with Surrogate Mixture??

- Kalghatgi:2005 - Octane Index, OI = (1-K)RON + K(MON) where RON and MON are the Research and Motor Octane numbers and K is a constant depending only on the pressure and temperature variation in the engine.

- Our work has in parallel established that fundamentally (RON+MON/2; “Road Octane”, RON, or MON, are not appropriate matching parameters for matching a surrogate against a gasoline with the same C/H ratio. ON of surrogate is not equal to ON of the gasoline.
What if Low Temperature Autoignition is not Significantly Relevant to Application?

• Evidence presently remains unconvincing that low temperature and NTC behavior are relevant in gas turbine designs (perhaps just chemistry that includes that associated with hot ignition).
  – Temperature/residence times in mixing processes are too short in comparison to kinetic characteristics times for NTC behavior.

• Typical hierarchical approach in developing full detailed models addresses modeling for conditions above hot ignition condition.
  – Low Temperature kinetics are then coupled with the high temperature model.

• How to model high temperature kinetics sufficiently for jet applications now?
High Temperature Example – n-Heptane
Current Large Molecule High Temperature Models

n-Decane

Primary Reference Components

Primary Reference + 1 (Toluene)
Full range and High T models completed and in use by HONDA, others (Mechanisms Avlbl soon)

n-Nonane, n-Dodecane, n-Hexadecane
High T Model developments complete, some validation
Recent Flame Modeling

- Modeling of laminar flame speed data from CWRU using the high temperature models for n-decane and n-dodecane are encouraging.
Ciezki and Adomeit

$\phi = 1.0$, $P = 13.5$ bar

$n$-heptane

$log_{10} \tau \text{ / ms}$

$1000 \text{ K} / T$

-1.0 -0.5 0.0 0.5 1.0 1.5

-1.0 -0.5 0.0 0.5 1.0 1.5
Ciezki and Adomeit

$\phi = 1.0$, $P = 13.5$ bar

$n$-heptane

$n$-decane
Ciezki and Adomeit

φ = 1.0, P = 13.5 bar

- n-heptane
- n-decane
- nc8 simulation
- nc9 simulation

1000 K / T

log τ / ms