Multiscale Kinetic Knowledge Propagation - Combustion Chemistry of Small Hydrocarbons

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• Optimal utilization of alternative synthetic and biofuels requires advances in combustion science and engineering.

• Advances in combustion technology can substantially stretch the petroleum supply and reduce GHG emissions.
Combustion – a Multiscale, Multiphenomenon Challenge

Multi-Scale Tools

- Rapid deployment for combustion engine design.
- Rapid adaptation and utilization of emerging synthetic or biofuels.
- Science-based fuel design and blending strategies.
Combustion – a Multiscale, Multiphenomenon Challenge

- Highly nonlinear problems
- Large thermo-dynamic condition space
- Mathematically ill-defined
Combustion Reaction Model Hierarchy

Products
- $H_2O, CO_2$
- $H_2, CO$
- $C_2H_2, soot$
- $(NO_x)......$

- CH$_4$
- Alcohols
- Bio-Diesel
- CH$_xO_y, C_2-4H_x$ Oxidation
- CO-H$_2$ Oxidation
- H$_2$ Oxidation
Ab initio & reaction rate theory predictions of elementary reaction rate constants

Chemical reactions:

(i) \[ H + HO_2 \rightarrow H_2O + O^3P \]
(ii) \[ H_2O + O \rightarrow HOOH \]
(iii) \[ H_2O + O^{1D} \rightarrow H_2O + O \]
(iv-1) \[ OH + OH \rightleftharpoons H_2O + O \]
(iv-2) \[ OH + OH \rightarrow H_2O + O \]
(v) \[ H_2O + O^{3P} \rightarrow H + HO_2 \]
(vi) \[ HO...OH \rightarrow H_2O + O \]
(vii) \[ H + HO_2 \rightarrow H_2O + O \]

Graphical representation:

- Graph showing temperature vs. kinetics of reaction rates with different pathways indicated.

Klippenstein/ANL
Ethylene Pyrolysis
Rate Determination: $\text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_2 + \text{H}_2$

Ethylene Oxidation

Shock tube/laser absorption measurements:
Ethylene time-Histories
Measurement and model validation: laminar flame speeds

Symbols: experimental data
Lines: USC-Mech II predictions

Methane/Air

$n$-Butane/Air, $p=1$ atm

Egolfopoulos/USC
Measurement and model validation: mass burning rate of hydrogen

$H_2/O_2/Ar, \phi=2.5$

$T_f \sim 1600K$

Dryer & Ju/Princeton
Critical review of literature kinetic data
Model compilation
"Tuning"
Validation
Publish model

Combustion Reaction Model Development (the old approach)

proliferation of models
A New Approach

- **Review of literature**
  - kinetic data

- **Model compilation**

- **Sensitivity analysis**

- **Electronic structure calculations**

- **Reaction rate theory**

- **Validation**

- **New experiments**

- **Uncertainty minimization**

- **Response surface development**

**Take home messages:**

- Consistency is more critical than predictability!
- Need a comprehensive model to truly reflect the inherent model hierarchy.
Knowledge (Uncertainty) Quantification by Polynomial Chaos Expansions

\[ x = x_0 + \alpha \xi \]

Data structure that describes a chemical model + associated uncertainty

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

\[ x_i = \frac{\ln k_i/k_{i,0}}{\ln f_i} \]

Represents some physics model, e.g. a laminar flame

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

Predictions of a chemical model (e.g. mass burning rate) + associated uncertainty

Sheen, et al. (2009 & 2011)
$x = x_0 + \alpha \xi$

Data structure that describes a chemical model + associated uncertainty

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

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

Predictions of a chemical model (e.g. mass burning rate) + associated uncertainty

Sheen, et al. (2009 & 2011)
Uncertainty Minimization by Polynomial Chaos Expansions

\[ \mathbf{x} = \mathbf{x}_0 + \alpha \xi \]

**Chemical model + associated uncertainty**

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

**Physics model**

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

**Predictions + associated uncertainty**

\[ \Phi(\mathbf{x}_0^*) = \min_{\mathbf{x}_0} \left\{ \sum_{r=1}^{M} \frac{\left[ \eta_{r,0}^{\text{obs}} - \eta_r(\mathbf{x}_0) \right]^2}{\left( \sigma_r^{\text{obs}} \right)^2} + \sum_{n=1}^{N} \left( x_{0,n} \right)^2 \right\} \]

\[ \Sigma = \left[ \sum_{r=1}^{n} \frac{1}{\left( \sigma_r^{\text{obs}} \right)^2} \left( \mathbf{b} \mathbf{x}_0^* \mathbf{x}_0^T + \mathbf{a} \mathbf{x}_0^T + \mathbf{b} \mathbf{x}_0^* \mathbf{a}^T + \mathbf{a} \mathbf{a}^T \right) + 4 \mathbf{I} \right]^{-1} \]

\[ \alpha^* = \Sigma^{1/2} \]
Uncertainty Minimization by Polynomial Chaos Expansions – Measured Progress!

Considering no combustion experiments

Model constrained by knowledge prior to 2010

Model constrained by the latest knowledge
The Future

• Detailed reaction models with well defined uncertainties as the integral part of engine design tools

• Unified, consistent base model

• Active design of experiments

• Two-way knowledge propagation.