New Approaches to Reacting Flow Modeling for Endothermic Fuel Cracking and Combustion in High-Speed Combustion

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**Objectives**

**Intermediate term**

Mechanisms of early-stage homogeneous coking and methods to suppress PAH coalescence/reaction.

**Long term**

Enable new approaches to kinetic modeling.
The Problem

Endothermic cooling system
- Fuel pyrolysis to remove heat
- Cracked products give better combustion performance
- Coke formation is a problem
- May use catalysts

Combustor
- Burns cracked fuel – composition coupled to cooling system operation and design
- Shocks and wide range of $\phi$.
- Flame processes may be facilitated by the use of catalysts

JP7

- Fuel cracking in the cooling system gives heat sinking capability, but also promote coke formation.
  - Fuel cracking and coke formation driven by the same force – entropy!
Thermodynamic Driving Forces

\[ \frac{1}{3} C_3 H_8 \]

\[ \frac{1}{2} C_2 H_2 \]

\[ \frac{1}{6} C_6 H_6 \]

\[ \frac{1}{10} C_{10} H_8 \]

\[ \frac{1}{16} C_{16} H_{10} \]

\[ C_{(s)} \]

\[ \frac{1}{3} H_2 \]
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• Fuel cracking in cooling system gives heat sinking capability, but also promote coke formation.
  - Fuel cracking and coke formation driven by the same force – entropy!
  - The processes are kinetically controlled (and supercritical).

• Three types of coke deposits (Edwards 2003)
  - Filamentous – fluid/surface interactions in origin and controllable by surface materials engineering).
  - Amorphous and graphitic – PAHs formed in the fluid phase “coalesce” into particulates which deposit on walls – a key problem to be addressed.
PAHs as Intermediates to Coke

- Amorphous and graphitic wall deposits are presumably from particulate matters due to PAH-PAH coalescence/reaction.

- PAH binding mechanisms not well established: dispersion/electrostatic interactions, excited states, dynamic bonding etc.

Wornat (2007)
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- A highly coupled kinetic problem – how do we generate chemical reaction models directly from results of *ab initio* theory?
1. Fuel pyrolysis and PAH/coke formation share the same thermodynamic driving force. It is impossible to maximize fuel pyrolysis while suppress PAH formation at the same time.

2. Suppressing PAH-PAH coalescence/reaction is feasible, because such processes do not yield large Gibbs free energy drop.
   - Fundamental binding interactions among PAHs (purely dispersion/electrostatic forces or also involves other *unknown* interactions – electronically excited states, $\pi$ diradicals etc).
   - Dynamic effects under supercritical condition.
   - If these interactions/effects can be understood, is there an additive that can trick PAHs into disliking each other.
Working Hypotheses/Questions(2)

The Long-Term Combustion Chemistry Problem

1. Looking for an approach more robust and more “ab initio” than the current chemistry modeling approach.
   - Designs of endothermic cooling system and combustors are evolving;
   - New catalysts are being developed
   - Long lead-time to develop any predictive, coupled kinetic models
   - High pressure/supercritical kinetics – rate theory (and its application) falls apart.
   - ……

2. We have been using the approach of detailed kinetic modeling for more than 50 years.
   - Is this the only “fundamental” approach we can take?
   - Do we need to write out thousands of reactions before we can make a prediction about the kinetic and heat release rates?
Potential Energy Landscape and Associated Approaches

- A concept widely used in protein folding kinetics (Joseph Bryngelson)

Wales & Bogdan *JPCB* (2006)

- and in materials/fuel cell research.
Potential Energy Landscape and Associated Approaches

- Accuracy of kinetic prediction may be improved, as needed, by adapting the resolution of potential energy.
RCCE and Potential Energy Landscaping (RCCE-PEL)

0\textsuperscript{th} order potential energy landscape
- No reaction steps $\rightarrow$ Infinite rate kinetics
- The end state represents chemical equilibrium

Higher-order potential energy landscapes
- Slow(er) reaction steps added – equivalent to adding details (barriers and local minima) into the potential energy landscape
- Finite rate kinetics with accuracy improved by an adaptive approach to adding PES details
- Converging chemical time scale $\leftrightarrow$ physical time scale (flow, turbulence, transport)
The Team

Guillaume Blanquart
CalTech

• PEL-RCCE in turbulent reacting flow modeling

Ronald K. Hanson
Stanford

• Experimental method developments
  \( T(t), H(t), S(t), G(t) \)

William L. Hase
Texas Tech

• Chemical dynamics
  aromatic interactions and binding
  post-transition state dynamics

Keiji Morokuma
Emory/Kyoto U.

• Automated PES search methods

Hai Wang
USC

• PEL-RCCE theory and application
• PAH-PAH binding interactions/coalescence suppression
• Nanocatalysts
Rate-Controlled Constrained-Equilibrium (RCCE)

Keck & Gillespie (1971); Keck (1990); Beretta et al. (2012)

The method of Lagrange Multipliers as applied to chemical equilibrium

\[
L = \frac{G}{R_u T} + \sum_{m=1}^{M} \lambda_m \left( \sum_{k=1}^{K} a_{mk} n_k - e_m \right)
\]

The equilibrium composition is given as

\[
n_k = n_0 \exp \left[ -\frac{g_k^0 (T)}{R_u T} - \ln \frac{p}{p^0} - \sum_{m=1}^{M} \lambda_m a_{mk} \right]
\]

\[
= n_0 Q_k \exp \left[ -\sum_{m=1}^{M} \lambda_m a_{mk} \right]
\]

where the multipliers are solved by

\[
e_m = n_0 \sum_{k=1}^{K} a_{mk} Q_k \exp \left[ -\sum_{m=1}^{M} \lambda_m a_{mk} \right] \quad (m = 1, \ldots, M \text{ elements})
\]

\[1 = \sum_{k=1}^{K} Q_k \exp \left[ -\sum_{m=1}^{M} \lambda_m a_{mk} \right]\]
Rate-Controlled Constrained-Equilibrium (RCCE)

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For non-equilibrium problems, additional constraints are added as needed, preferably starting from rate limiting steps:

\[ e_l = \sum_{k=1}^{K} a_{lk} n_k \quad (l - m = 1, ... R) \]

\[
\frac{d \left( \frac{e_l}{V} \right)}{dt} = \sum_{k=1}^{K} a_{lk} \frac{d \left( \frac{n_k}{V} \right)}{dt} = \sum_{k=1}^{K} a_{lk} \left( \sum_{l=1}^{s_l} v_{kl} R_{lf} - \sum_{l=1}^{s_l} v'_{kl} R_{lb} \right)
\]

- Yields the exact solution when the number of constraining equations \( R = \) number of reactions \( I \) (Keck 1990).
- Good quality, converging solution achieved usually with \( R \ll I \).
- A mechanism reduction method – allowing for separation of time scales – still require a (detailed) reaction mechanism to be made available.
• Can a potential energy landscape (PEL) approach be developed from ab initio methods?

• Can the rate limiting steps on the PEL be identified in a robust manner?

• Can new experimental approaches be developed to interrogate parts of a PEL?

• What are the role of the better known $\text{H}_2/\text{C}_1-\text{C}_4$ chemistry in the RCCE-PEL approach?

• Can the RCCE-PEL approach be implemented in turbulent flame simulations?
• Methodology based on Dixon-Lewis’ s work in the 1960s’.  
  • Write down every reaction step and find its rate coefficient.  
  • \( H_2, H_2/CO \) etc with ~ 2 dozen reactions.  
  • Can have a closure because of a limited number of rate parameters.  
  • Allowed us to understand the detailed laminar flame structure.  

• Later work by many focused on combustion chemistry of small hydrocarbons – O(100) reactions – many of which have been probed directly by experiments and rate theory calculations.

• Recent effort for large hydrocarbons largely based on empirical knowledge  
  • group additivity  
  • analogous reactions – reaction class  
  • guesses
• The number of species/reactions increases exponentially as the fuel size increases.
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![Graph showing the increase in number of reactions and species with fuel size increasing.]

• A solar system model built on the position and velocity of each and every planet is a triumph of science.

• A milky-way galaxy model built on the position and velocity of each plant and star is probably a terrible model.
Combustion Reaction Mechanism Development

• Methods of mechanism reduction becomes mature.
  • Still require detailed reaction models to be made available
  • The number of scalars remain large, perhaps too large to incorporate in CFD codes (high-speed combustion) for years to come

• Rethink our strategy for treating chemistry.
  • Adaptive resolution/accuracy
  • Key property to follow: time evolution of energy and entropy

• Throw away the concept of reaction mechanism for the moment
• Focus on the potential energy surface
  some initial thoughts in the context of Keck’s RCCE