



Mechanism Reduction and Advanced Chemistry Solvers

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2017 Princeton-Combustion Institute
Summer School on Combustion
June 25-30, 2017

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Outline

- Background
- Mechanism reduction
 - Reaction state sampling
 - Skeletal reduction
 - Timescale based reduction
 - Reduced HyChem models for real fuels
 - Reduced molecular diffusion models
 - Sample reduced mechanisms and applications
- Advanced chemistry solvers
 - Limitation of splitting schemes in combustion simulations
 - Chemical stiffness removal for explicit time integration
 - Implicit solvers with analytic and sparse Jacobian, dynamic adaptive hybrid integration

Background



Need for detailed Kinetics: Example: H_2 - O_2 Chemistry

Species: H_2 , O_2 , H_2O , (Major species); H , O , OH , HO_2 , H_2O_2 (Radicals)

No. Reactions

H_2 - O_2 Chain Reactions

- (1) $H + O_2 = O + OH$
- (2) $O + H_2 = H + OH$
- (3) $OH + H_2 = H + H_2O$
- (4) $O + H_2O = OH + OH$

H_2 - O_2 Dissociation/Recombination

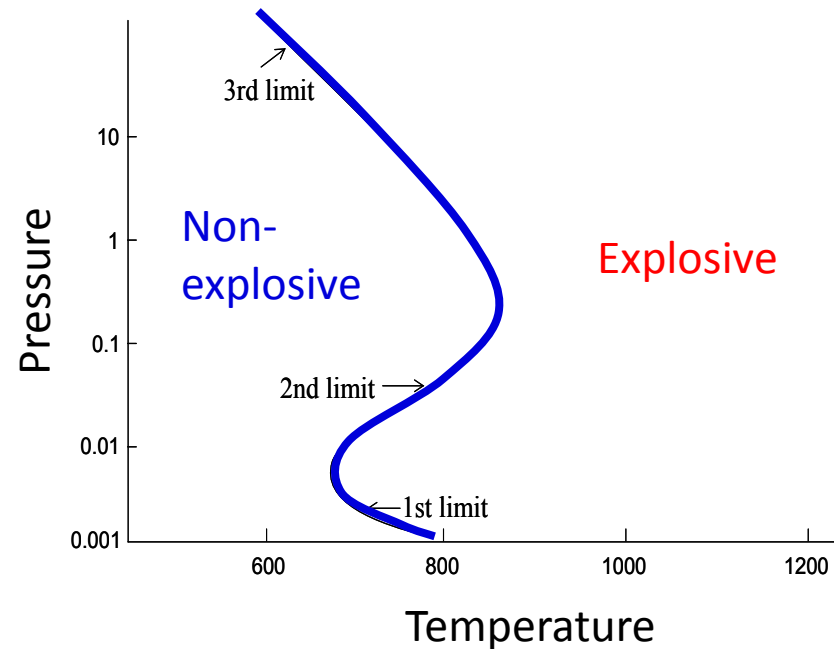
- (5) $H_2 + M = H + H + M$
- (6) $O + O + M = O_2 + M$
- (7) $O + H + M = OH + M$
- (8) $H + OH + M = H_2O + M$

Formation and Consumption of HO_2

- (9) $H + O_2 + M = HO_2 + M$
- (10) $HO_2 + H = H_2 + O_2$
- (11) $HO_2 + H = OH + OH$
- (12) $HO_2 + O = OH + O_2$
- (13) $HO_2 + OH = H_2O + O_2$

Formation and Consumption of H_2O_2

- (14) $HO_2 + HO_2 = H_2O_2 + O_2$
- (15) $H_2O_2 + M = OH + OH + M$
- (16) $H_2O_2 + H = H_2O + OH$
- (17) $H_2O_2 + H = H_2 + HO_2$
- (18) $H_2O_2 + O = OH + HO_2$
- (19) $H_2O_2 + OH = H_2O + HO_2$



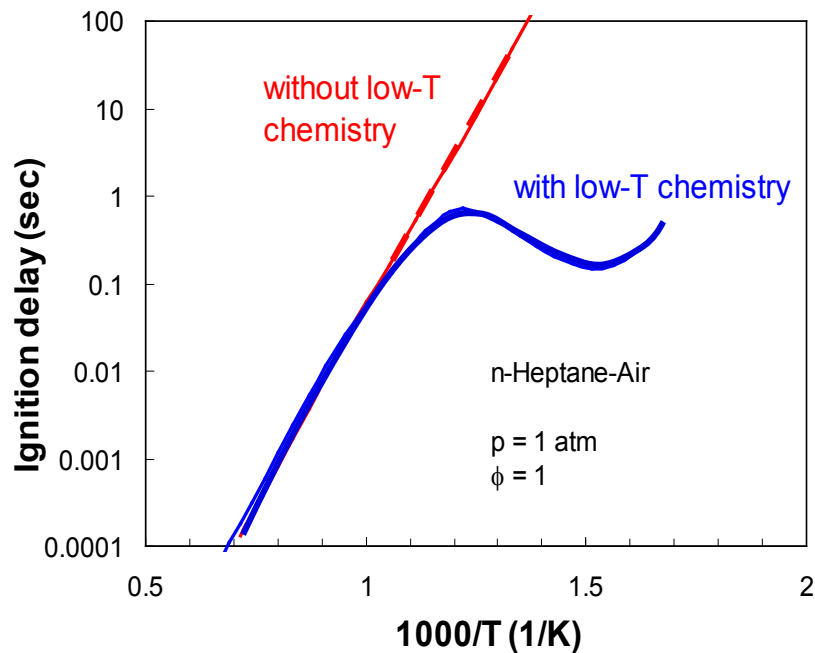
Detailed chemistry are crucial for:
Ignition, extinction, instabilities ...



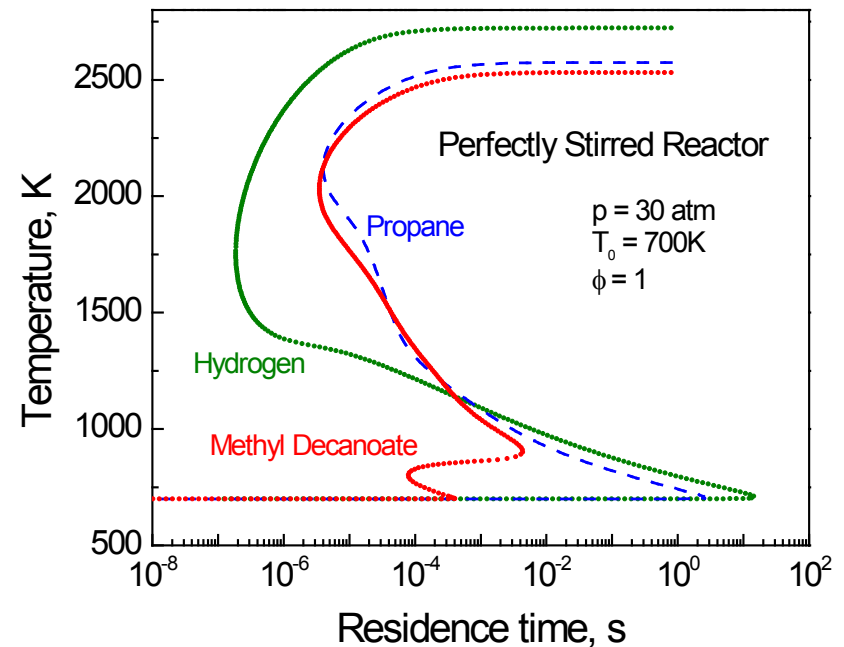
Need of Realistic Chemistry

- Fuel chemistry substantially affects flame dynamics
- Accurate chemical kinetics needed to **predict** flame behaviors

Ex1: Negative Temperature Coefficients (NTC)



Ex2: Combustion “S”-curves



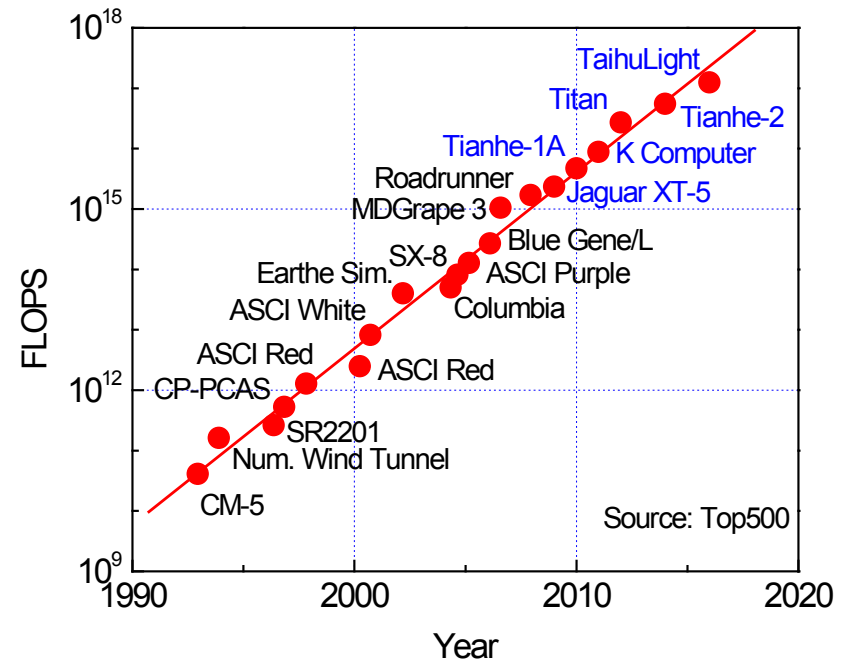


Computers and Numerical Combustion



ENIAC, 1946

<https://en.wikipedia.org/wiki/ENIAC>

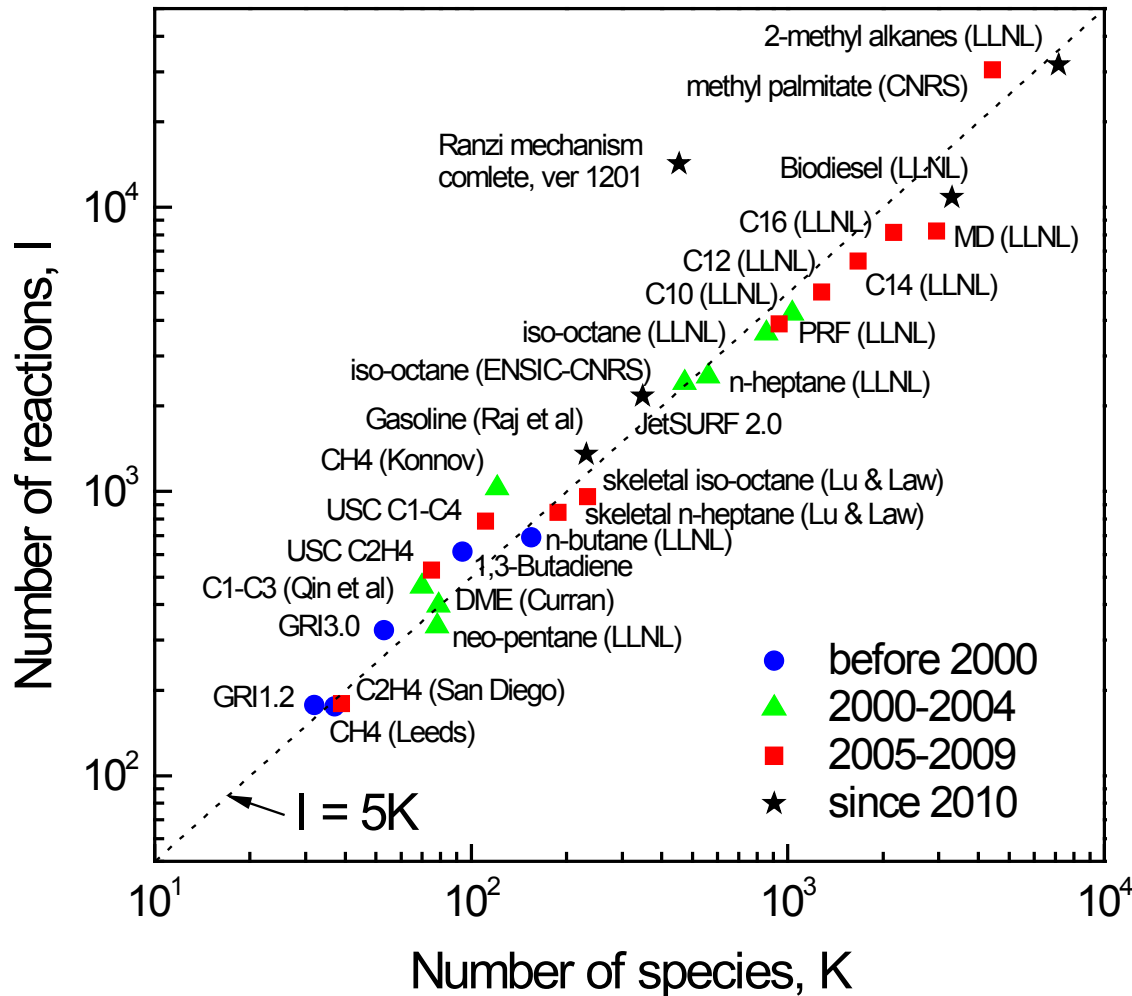


<https://www.top500.org/news/china-tops-supercomputer-rankings-with-new-93-petaflop-machine/>

Sunway TaihuLight,
>10 million cores, 125 PetaFLOPS (Peak)



Scaling of Detailed Chemistry



(Lu & Law, PECS 2009)

- Detailed mechanisms are large
- Transportation fuels:
~ 10^3 species
~ 10^4 reactions
- Flame simulations with detailed chemistry are time-consuming or unaffordable
- The excessive output data renders it difficult to identify the controlling physicochemical processes



Numerical Solution of Multi-Dimensional Flows

- Transport equations of reactive scalars

$$\frac{DY}{Dt} = \frac{\partial Y}{\partial t} + \mathbf{V} \cdot \nabla Y = \dot{\omega} + \nabla \cdot (\rho \mathbf{D} \nabla Y) + \dots$$

Y : vector of dependent variables, e.g. T and species concentrations

\mathbf{V} : velocity, $\dot{\omega}_\phi$: chemical source term, D_ϕ : diffusivity

- Discretization

- Time derivative is typically approximated by finite difference involving the current and future values
- The gradient and divergence operators are typically approximated with linear functions involving multiple neighboring cells
- Subgrid modeling is needed if nontrivial structures are present within a single grid/cell, e.g. in large eddy simulations (LES)
- No subgrid models are needed if the structure of ϕ is fully resolved by the mesh grid, e.g. in direct numerical simulations (DNS)



Starting Point of Mechanism Reduction: CPU Cost Analysis

- Considering the time integration of a stiff reacting system

$$\frac{d\mathbf{Y}}{dt} = \mathbf{g}(\mathbf{Y}) \quad \mathbf{y}: \text{vector of dependent variables, e.g. T and species concentrations}$$

$$\frac{\mathbf{Y}^{n+1} - \mathbf{Y}^n}{h} \approx \mathbf{g}(\mathbf{Y}^{n+1})$$

$$\mathbf{F}(\mathbf{Y}^{n+1}) = \mathbf{Y}^{n+1} - h\mathbf{g}(\mathbf{Y}^{n+1}) - \mathbf{Y}^n = 0$$

$$0 = \mathbf{F}(\mathbf{Y}^{n+1}) \approx \frac{\partial \mathbf{F}}{\partial \mathbf{Y}} (\mathbf{Y}^{n+1} - \mathbf{Y}^n) + \mathbf{F}(\bar{\mathbf{Y}})$$

$$\mathbf{J}(\mathbf{Y}^{n+1} - \mathbf{Y}^n) + \mathbf{F}(\mathbf{Y}^n) = 0$$

- Each implicit integration step involves
 - Evaluation of chemical source term
 - Evaluation of diffusion and other non-chemical source terms
 - Jacobian evaluation and factorization, solving linear equations



The Time Complexity

- Time complexity of major components:
 - **Chemistry**: $\sim I \sim 5K$ (I: # of reactions, K: # of species)
 - **Jacobian** (brute force): $\sim KI \sim 5K^2$
 - **Diffusion** (mixture average): $\sim K^2/2$
- Reducing K and I is an obvious approach to accelerate combustion simulations – mechanism reduction
- Implicit solvers (Jacobian, chemistry, diffusion)
 - Time steps typically limited by the CFL condition
 - $t_{\text{imp}} \sim KI + I + K^2/2 \sim 10K^2 + 10K + K^2$
 - Most effective acceleration approaches: analytic Jacobian, sparse Jacobian techniques, reduced diffusion models
- Explicit solvers (chemistry, diffusion)
 - Time steps limited by the shortest chemical timescale
 - $t_{\text{exp}} \sim I + K^2/2 \sim 10K + K^2$
 - Most effective acceleration approaches: chemical stiffness removal, reduced diffusion models



The Jacobian

- Needed in Newton solvers for steady state systems (e.g. PREMIX), and implicit integration solvers
- **Jacobian evaluation and factorization is the most expensive step in many combustion simulations**

$$\frac{dy}{dt} = \mathbf{g}(\mathbf{y})$$

\mathbf{y} : vector of variables, e.g. species concentration

$$\frac{d\mathbf{g}}{dt} = \mathbf{J} \cdot \mathbf{g}(\mathbf{y}),$$

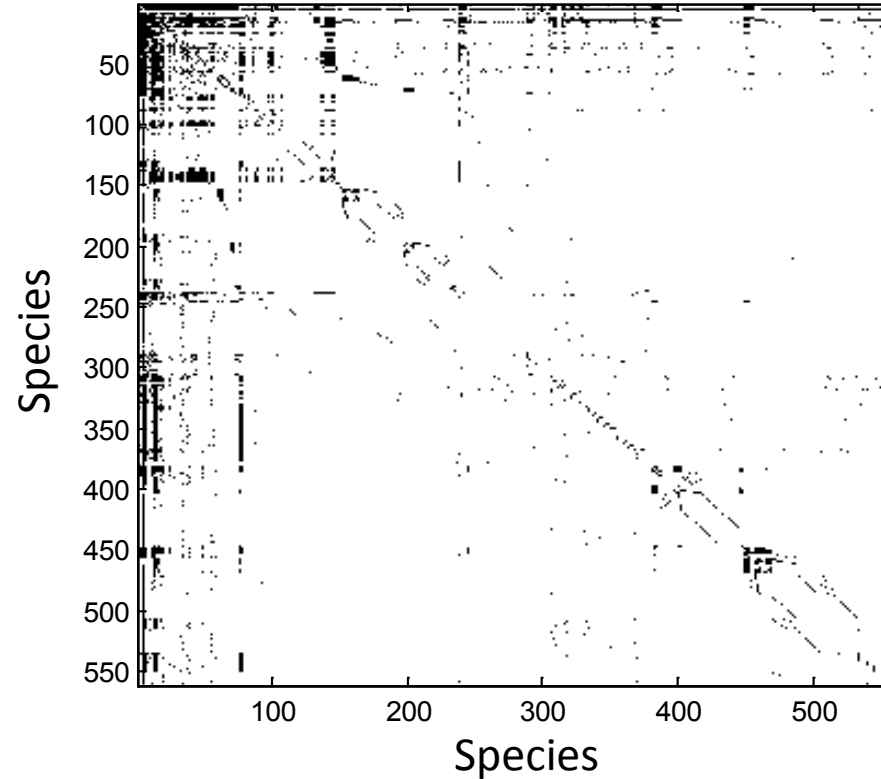
$$\mathbf{J} = \frac{d\mathbf{g}}{d\mathbf{y}}$$

$$\mathbf{J} = \begin{bmatrix} \frac{\partial g_1}{\partial y_1} & \frac{\partial g_1}{\partial y_2} & \dots & \frac{\partial g_1}{\partial y_n} \\ \frac{\partial g_2}{\partial y_1} & \frac{\partial g_2}{\partial y_2} & \dots & \frac{\partial g_2}{\partial y_n} \\ \dots & \dots & \dots & \dots \\ \frac{\partial g_n}{\partial y_1} & \frac{\partial g_n}{\partial y_2} & \dots & \frac{\partial g_n}{\partial y_n} \end{bmatrix}$$

Sparse Species Couplings in Detailed Chemistry



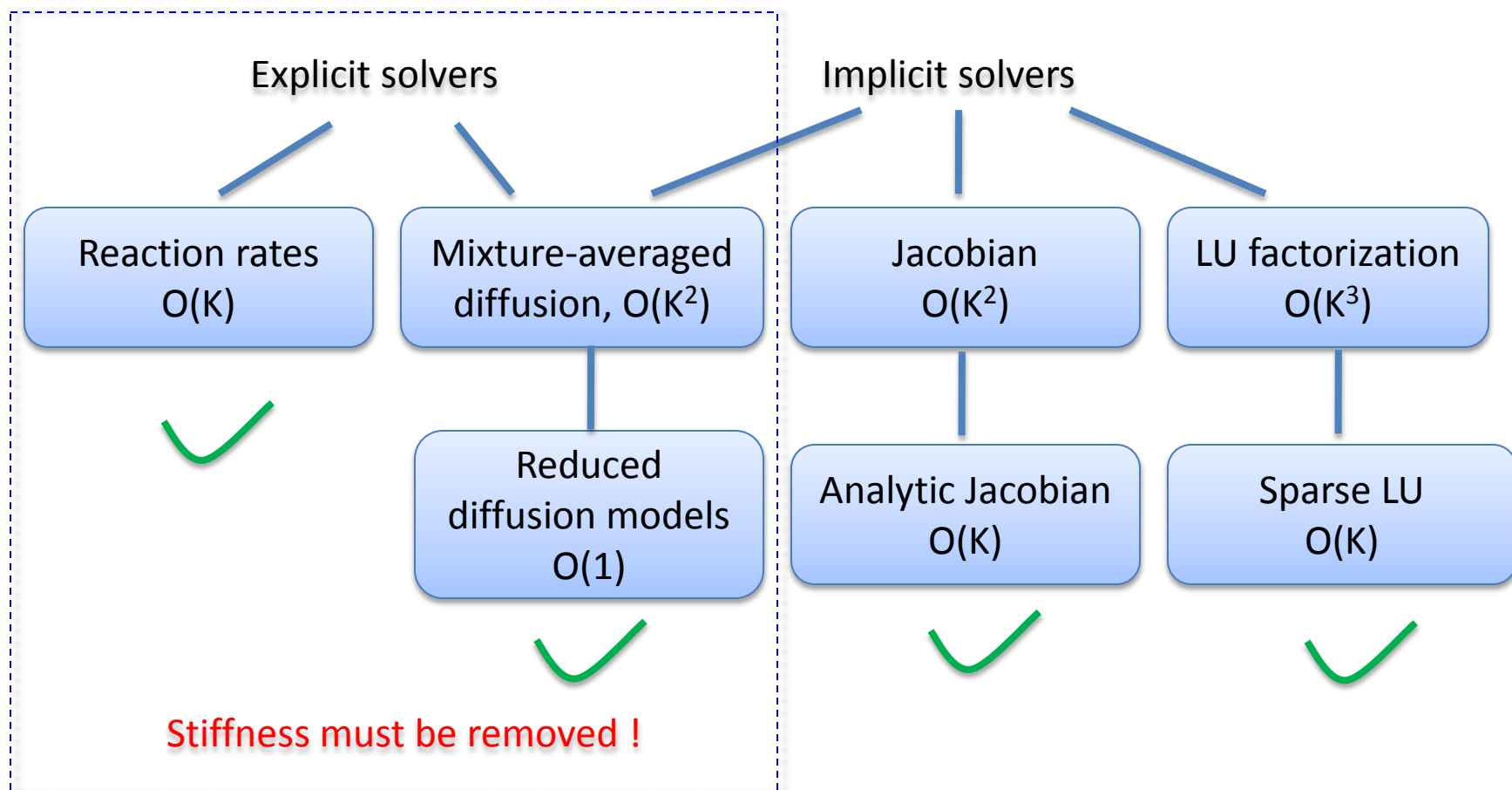
n-heptane
(LLNL, 561 species)



Black pixel: a pair of directly coupled species,
appearing together in any reaction



Advanced Chemistry Solvers



- Both implicit and explicit solvers can achieve linear scaling, i.e. $O(K)$, for computational cost



Approaches for Mechanism Reduction

- Skeletal reduction
 - Sensitivity analysis
 - Principal component analysis
 - Graph based methods, e.g. direct relation graph ([DRG](#))
 - ...
- Timescale based reduction
 - Quasi steady state approximations ([QSSA](#))
 - Partial equilibrium approximations
 - Rate controlled constrained equilibrium
 - Intrinsic low dimensional manifold (ILDLM)
 - Computational singular perturbation (CSP)
 - ...
- HyChem
- Other methods
 - Tabulation, e.g. in situ adaptive tabulation
 - Optimization
 - Solver techniques
 - ...

Reaction State Sampling



The Law of Mass Action

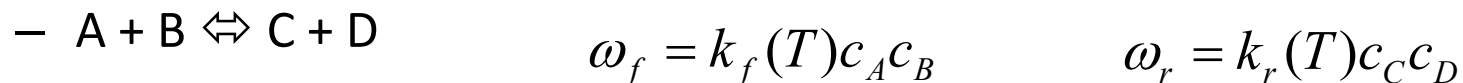
- For a reaction in general form



- The reaction rate of the reaction is given by

$$\omega_f = k_f(T) \prod_{i=1}^K c_i^{v_i'} \quad \omega_r = k_r(T) \prod_{i=1}^K c_i^{v_i''}$$

- For example:

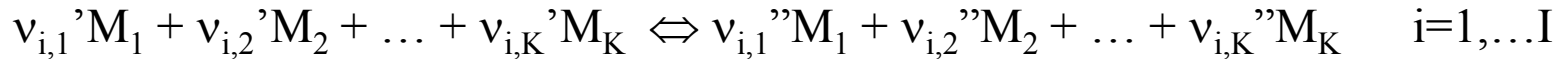


- Calculation of reverse rate $K_C(T) = \frac{k_f(T)}{k_r(T)}$



Reaction Rates of Multi-Reaction Systems

- For a system with the following reactions



- The rate for the i th reaction is:

$$\omega_i = \omega_{if} - \omega_{ir} = k_{if}(T) \prod_{k=1}^K c_i^{v_{i,k}'} - k_{ir}(T) \prod_{k=1}^K c_i^{v_{i,k}''}$$

- In matrix form: $\frac{d\mathbf{c}}{dt} = \mathbf{S} \cdot \boldsymbol{\omega} + \dots$

$$\mathbf{c}_{K \times 1} = \begin{pmatrix} c_1 \\ c_2 \\ \dots \\ c_K \end{pmatrix} \quad \mathbf{S}_{K \times I} = \begin{pmatrix} \Delta v_{1,1} & \Delta v_{2,1} & \dots & \Delta v_{I,1} \\ \Delta v_{1,2} & \Delta v_{2,2} & \dots & \Delta v_{I,2} \\ \dots & \dots & \dots & \dots \\ \Delta v_{1,K} & \Delta v_{2,K} & \dots & \Delta v_{I,K} \end{pmatrix} \quad \boldsymbol{\omega}_{I \times 1} = \begin{pmatrix} \omega_1 \\ \omega_2 \\ \dots \\ \omega_I \end{pmatrix}$$



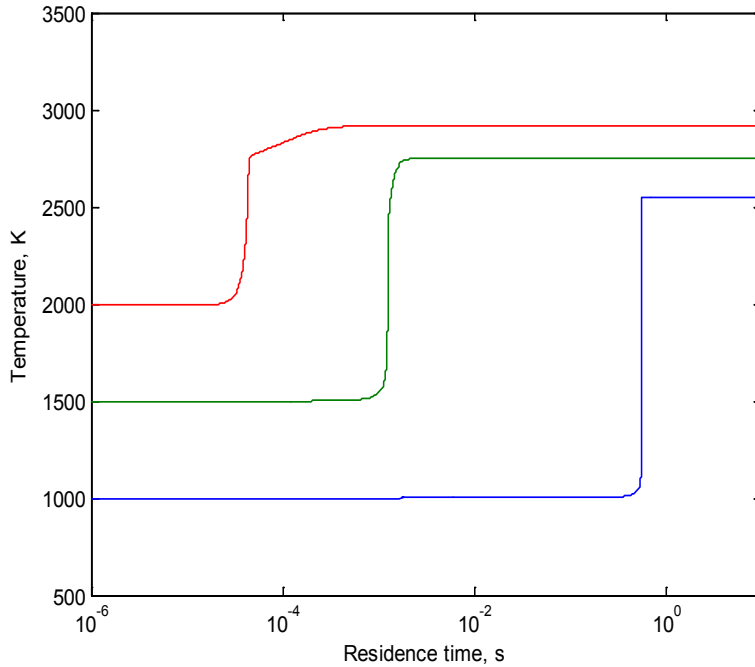
Identification of Important Pathways

- Reaction rates are determined by temperature and species concentrations (T, C), i.e. local reaction states
- Different reaction pathways are controlling at different reaction states
- Any mechanism reduction is specific to a target set of reaction states
 - Important reactions cannot be identified without concentration information, i.e. only using the rate parameters or potential surface information
 - **Reaction state sampling** from representative reactors is required for reduction
- Reactors for reaction state sampling
 - **Auto-ignition**
 - **Perfectly stirred reactors (PSR)**
 - 1-D laminar flames
 - Turbulent flames?

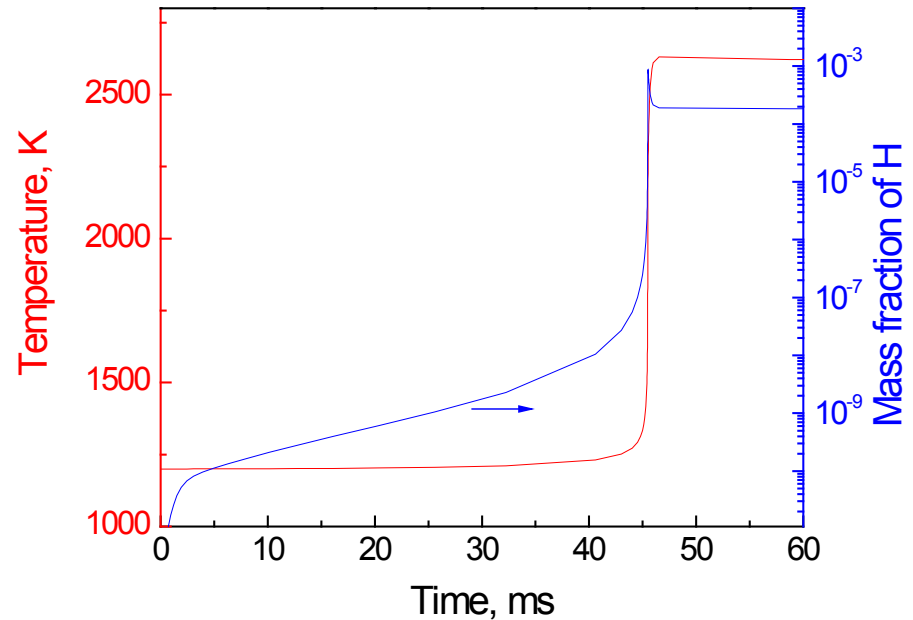


Sampling from Auto-ignition

Methane-air, $\phi = 1.0$, $p = 1$ atm



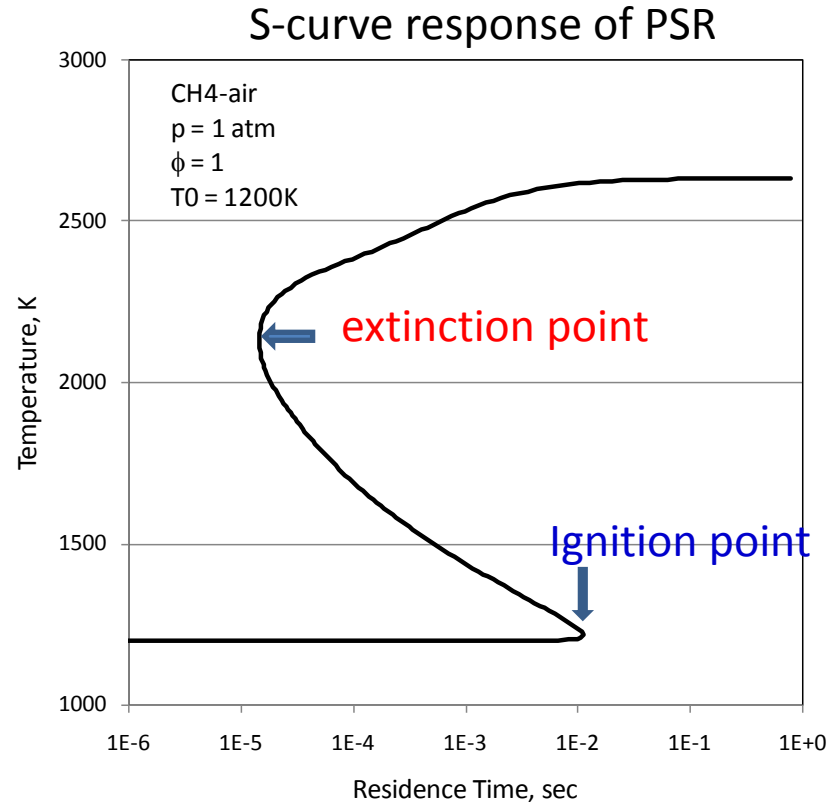
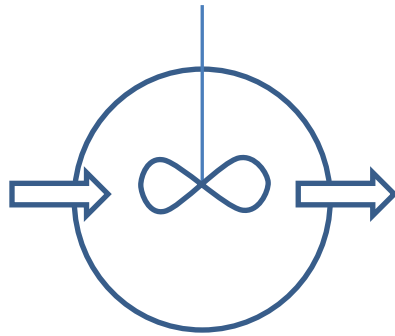
Methane-air,
 $\phi = 1.0$, $p = 1$ atm, $T_0 = 1200$ K



- Auto-ignition typically involves radical explosion and thermal runaway stages
- The radical explosion is slow (in milliseconds), and typically dominates ignition delay time
- Thermal runaway is typically much faster (in microseconds)
- Radical explosion stage can be bypassed in (laminar and turbulent) flames for fast burning
- Sample reaction states from auto-ignition are representative for ignition chemistry, important for compression ignition engines, detonation waves etc.



Sampling from PSR

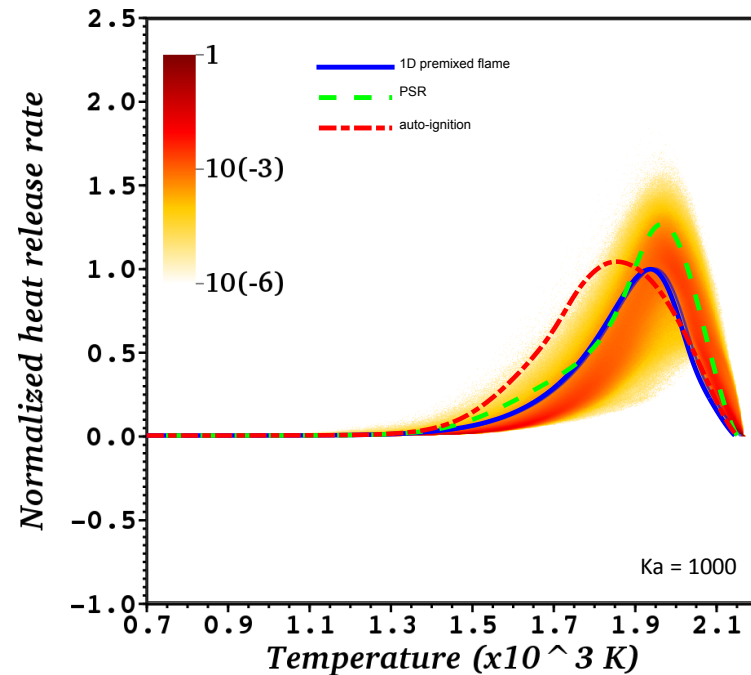
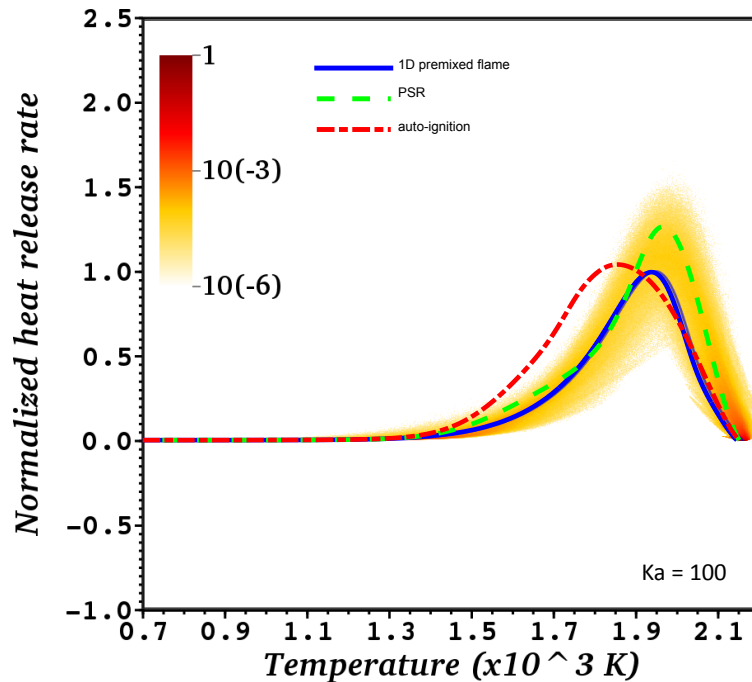


- PSR and other continuous flow reactors feature S-curve responses
- The turning points are corresponding to extinction and ignition states
- The extinction state is determined by how fast chemistry can be
- The states from the upper and middle branches are representative to flame chemistry, important for spark ignition engines, jet engines, flame holding etc.



Reaction States in Different Flames

n-dodecane/air
 $P = 30 \text{ atm}, \phi = 0.7, T_0 = 700 \text{ K}$



DNS of premixed C12/air flame by Alexei Poludnenko

Skeletal Reduction



Skeletal Reduction

- Throwing away **unimportant** species and/or reactions
- Example methods for skeletal reduction
 - Global sensitivity analysis (GSA):
arbitrary reduction methods combined with reduced model validation
 - Local sensitivity analysis
 - Detailed reduction (Wang & Frenklach)
 - Principal component analysis (Turanyi et. al.)
 - Computational singular perturbation (CSP): (Lam)
 - Connectivity based methods, e.g. directed relation graph (DRG) (Lu & Law),
DRG with error propagation (Pepiot & Pitsch)
 - ...
- Error control is critical for computational cost
 - Method with *a priori* error control do not require reduced model validation
 - **Any method** without *a priori* error control requires reduced model validation, is effectively a GSA
- No reduction method is “wrong”, as long as the reduced model is validated



Skeletal Reduction with Directed Relation Graph (DRG) (Lu & Law 2005)

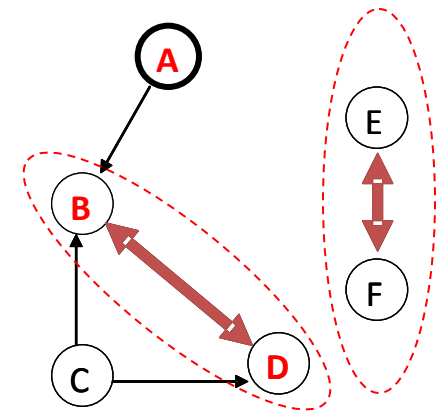
- ▶ Targeted at rigorously reducing extremely large mechanisms
- ▶ Starts with pair-wise reduction errors (Luo et al, 2010)

$$r_{AB} \equiv \frac{\max_i (|\nu_{A,i} \omega_i \delta_{Bi}|)}{\max_i (|\nu_{A,i} \omega_i|)} \quad \delta_{Bi} = \begin{cases} 1, & \text{If reaction } i \text{ involves species } B \\ 0, & \text{otherwise} \end{cases}$$

$\nu_{A,i}$: stoichiometric coefficient of A in the i^{th} reaction

ω_i : net reaction rate of the i^{th} reaction

- ▶ Construction of DRG
 - ▶ Vertex: species (A, B, C, \dots)
 - ▶ Edges: species dependence, $r_{AB} > \epsilon$
 - ▶ Starting vertices: target species
e.g. H, fuel, oxidizer, product, a pollutant, ...

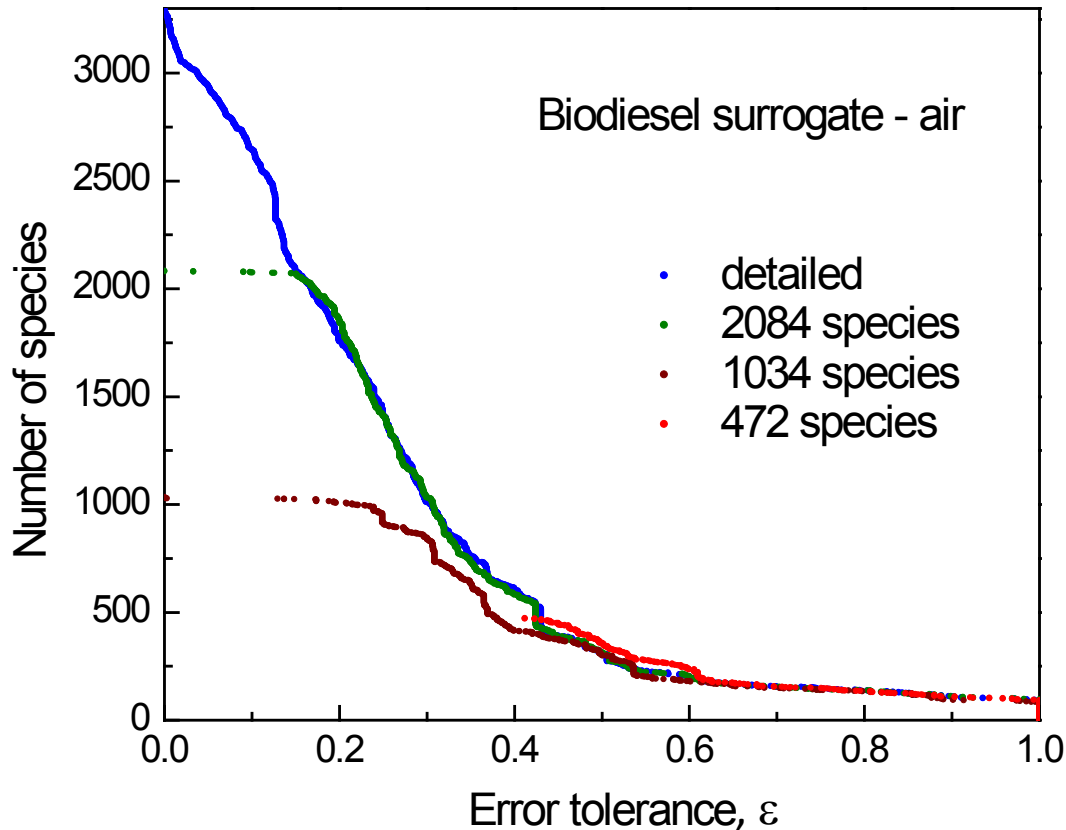


- ▶ Graph search: **revised depth-first search (RDFS)** (Lu & Law, CNF 2006)



Reduction Curves of DRG

Biodiesel (MD+MD9D+C7) – Air



▶ Detailed mechanism (LLNL 2010):

- ▶ 3329 species
- ▶ 10,806 reactions

▶ Skeletal Mechanism

- ▶ 472 species
- ▶ 2337 reactions

▶ Error $\epsilon/(1 + \epsilon)$: ~30% (worst case)

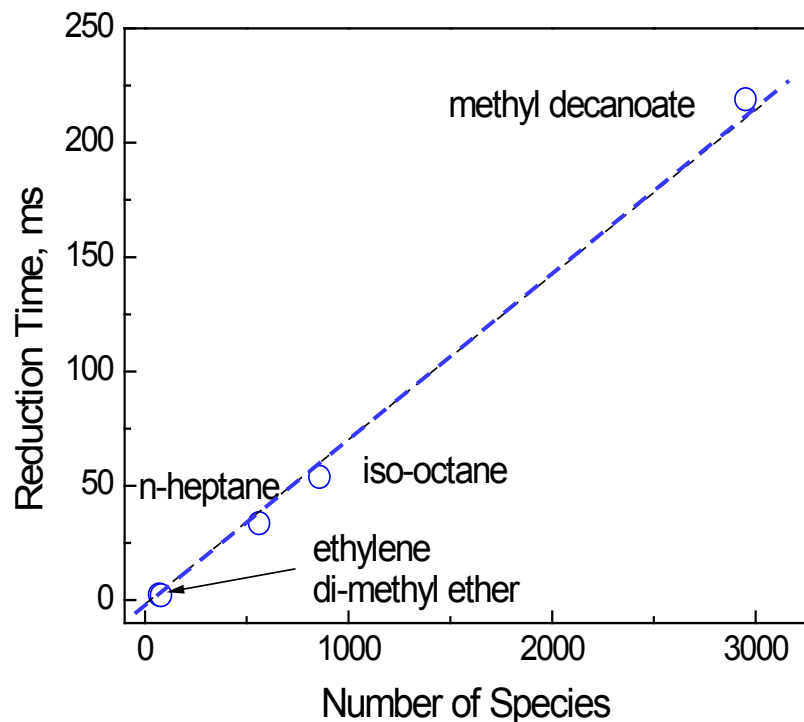
▶ Parameter range:

- ▶ p : 1-100 atm
- ▶ ϕ : 0.5 - 2.0
- ▶ Ignition & extinction
- ▶ $T_0 > 1000\text{K}$ for ignition

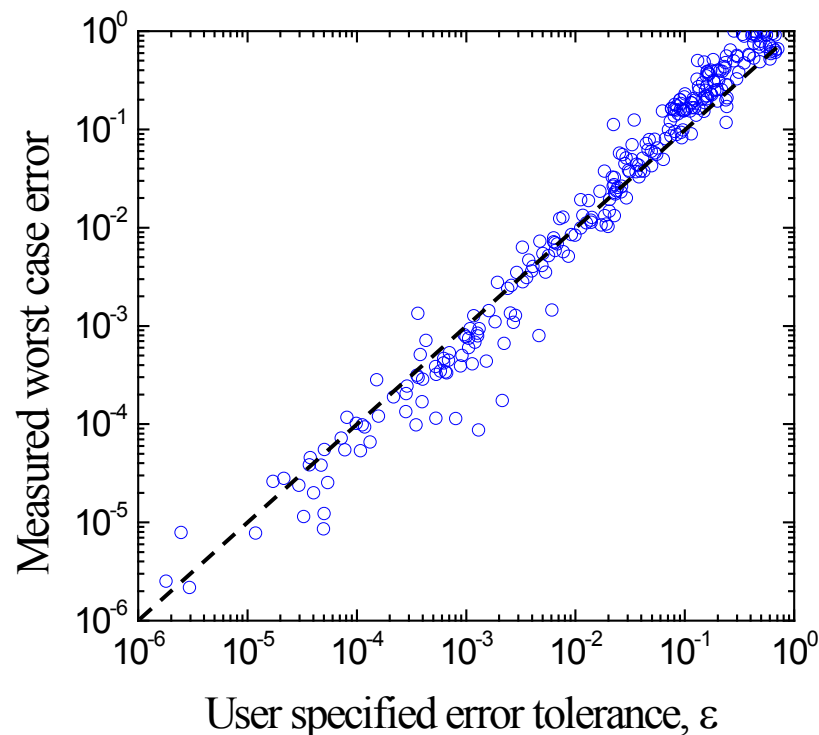


Efficiency and Error Control of DRG

- Linear reduction time
i.e. reduction time \sim # of species



- ▶ A priori error control
Worse-case measured error $\sim \epsilon$



- ▶ Most suitable for
 - ▶ The first reduction step for extremely large mechanisms
 - ▶ Dynamic adaptive chemistry (DAC)



Other DRG-Based Methods

- DRG with error propagation (DRGEP), (Pepiot-Desjardins & Pitsch 2008; Liang et al, 2009; Shi et al 2010)
- Path flux analysis (PFA): (Sun et al, 2009)
- Transport flux based DRG (on-the-fly reduction): (Tosatto et al, 2011)
- DRG with expert knowledge (DRGX): (Lu et al, 2011)

- DRG aided sensitivity analysis (DRGASA), (Zheng et al, 2007; Sankaran et al 2007)
- DRGEP with sensitivity analysis (DRGEPSA): (Niemeyer et al 2010)

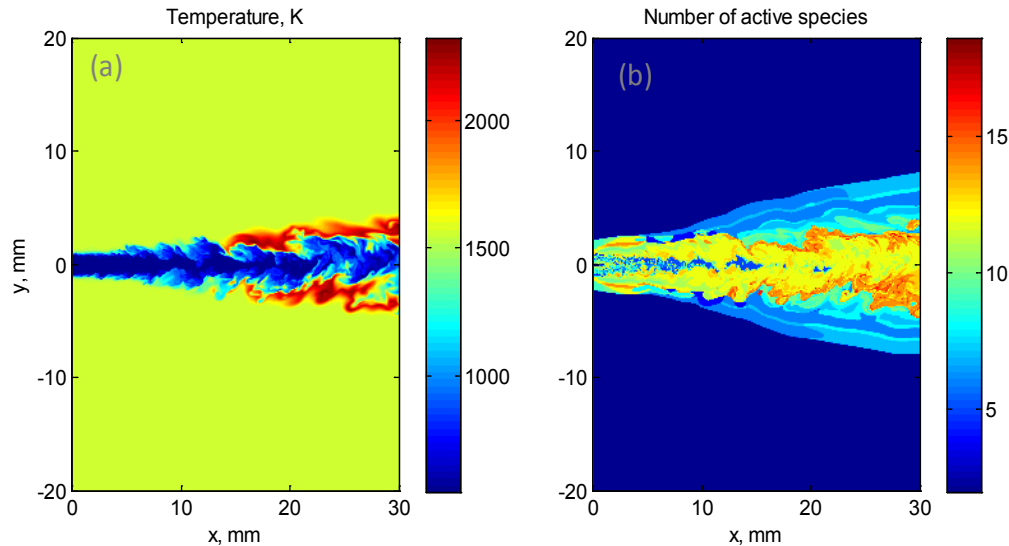
- Dynamic adaptive chemistry (DAC) with DRG or DRGEP (Liang et al 2009; Yang et al 2013)



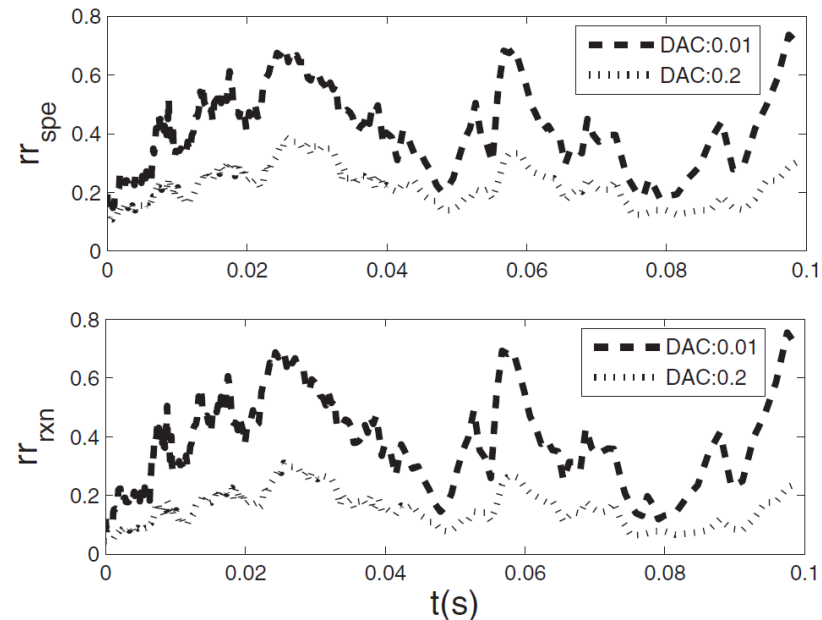
On-the-fly Reduction with Dynamic Adaptive Chemistry (DAC)

- Number of active species varies dramatically spatially and temporally
- DRG-based methods feature low overhead for DAC (Long et al, 2009)
- Compatible with in situ adaptive tabulation (ISAT) (Pope, CST 1997)

A lifted ethylene jet flame
(Yoo et al, PCI 2011)



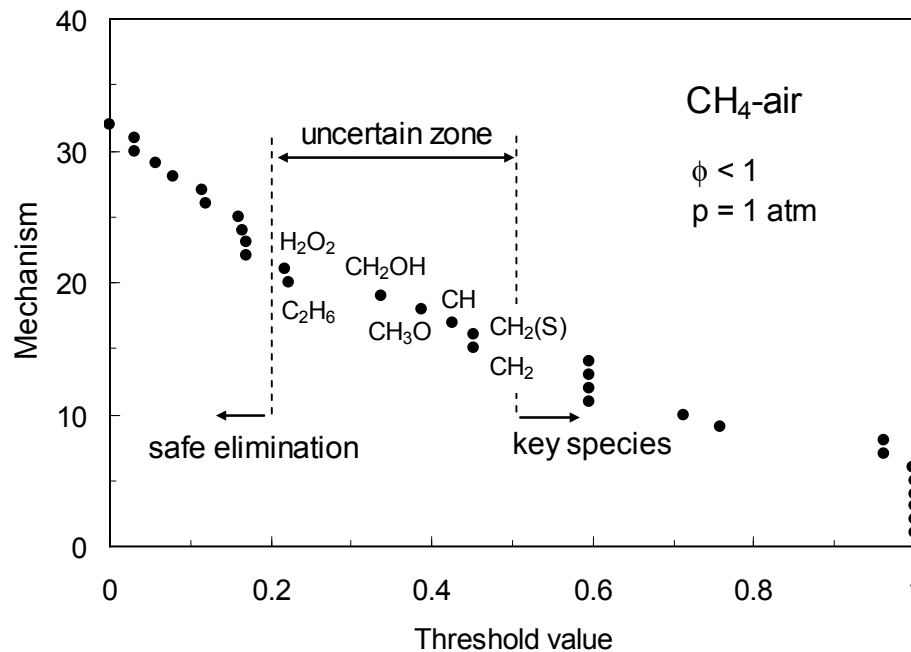
PaSR of non-premixed CH₄/Air
(Yang et al, CTM 2013)





DRG Aided Sensitivity Analysis (DRGASA)

- Species cannot be eliminated by DRG may be eliminated through GSA
- Species elimination sequence exploits DRG information for reduced computational cost
- Resulting skeletal mechanism is minimal
- Substantially more computationally demanding than DRG



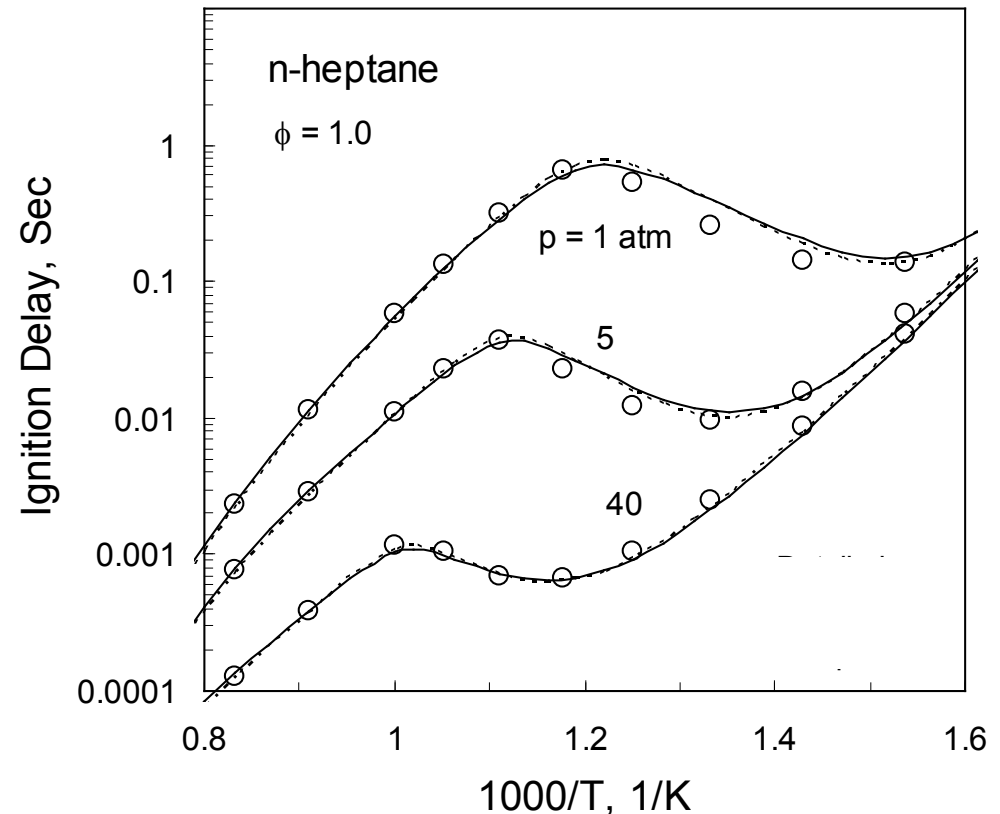
(Zheng et al, 2007;
Sankaran et al 2007)



Example Skeletal Mechanism by DRG+DRGASA

- Detailed
 - 561 species
 - 2539 reactions
- DRG
 - 188 species
 - 939 reactions
- DRGASA
 - 78 species
 - 317 reactions

n-heptane (LLNL)



Timescale Based Reduction



Timescale based Reduction

- Detailed chemistry involves vastly different timescales
- Fast chemical processes (species or reactions) quickly become exhausted and result in algebraic equations
- Example methods based on timescale analysis
 - Quasi steady state (QSS) & Partial equilibrium (PE) assumption
 - Rate-controlled constrained equilibrium (RCCE)
 - Intrinsic low dimensional manifold (ILDM) (Maas & Pope)
 - Computational singular perturbation (CSP) (Lam & Goussis)
 - ...



General Approaches: ILDM & CSP

- The ODEs: $\frac{dy}{dt} = \mathbf{g}(\mathbf{y})$ \mathbf{y} : vector of variables,
e.g. species concentration

$$\frac{d\mathbf{g}}{dt} = \mathbf{J} \cdot \mathbf{g}(\mathbf{y}), \quad \mathbf{J} = \frac{d\mathbf{g}}{d\mathbf{y}}$$

\mathbf{J} is time dependent in general

- Basis change: $\mathbf{f} = \mathbf{B} \cdot \mathbf{g}$ \mathbf{f} : modes,
 \mathbf{B} : basis vectors,
is time dependent in general

$$\frac{d\mathbf{f}}{dt} = \mathbf{\Lambda} \cdot \mathbf{f}, \quad \mathbf{\Lambda} = \left(\frac{d\mathbf{B}}{dt} + \mathbf{B} \cdot \mathbf{J} \right) \cdot \mathbf{A}, \quad \mathbf{A} = \mathbf{B}^{-1}$$



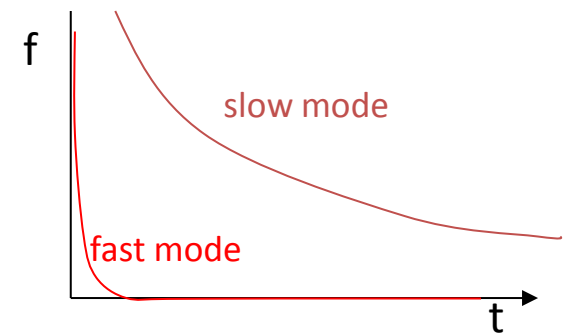
Intrinsic Low Dimensional Manifold (ILDMM)

- Assuming constant \mathbf{J} (local linear model)
- Diagonal (or triangular) $\mathbf{\Lambda}$ can be obtained by eigenvalue decomposition (or Shur decomposition)
- Rates in the directions of the eigenvalues associated with the fast odes vanish in transient time

$$\frac{d\mathbf{f}}{dt} = \mathbf{\Lambda} \cdot \mathbf{f}, \quad \mathbf{\Lambda} = \mathbf{V}^{-1} \cdot \mathbf{J} \cdot \mathbf{V}$$

$$\frac{df_i}{dt} = \lambda_i f_i \quad \text{Time scale of mode: } \tau_i = 1/|\lambda_i|$$

$$f_i \rightarrow 0 \quad \text{If } \lambda_i \text{ is large negative number}$$



Computational Singular Perturbation (CSP)



- \mathbf{J} is time dependent
- In general, Λ can not be diagonalized
- CSP refinement
 - Find a set of basis vectors \mathbf{A} and \mathbf{B} , such that Λ is approximately block-diagonal
 - Eigenvalues of Λ_f are all large negative numbers

$$\Lambda = \left(\frac{d\mathbf{B}}{dt} + \mathbf{B} \cdot \mathbf{J} \right) \cdot \mathbf{A}$$

$$\Lambda = \begin{bmatrix} \Lambda_f & \\ & \Lambda_s \end{bmatrix}$$

$$\mathbf{f} = \begin{pmatrix} \mathbf{f}_{fast} \\ \mathbf{f}_{slow} \end{pmatrix} = \begin{pmatrix} \mathbf{B}_{fast} \\ \mathbf{B}_{slow} \end{pmatrix} \cdot \mathbf{g}$$

$\mathbf{f}_{fast} \rightarrow 0$ in transient time



Comments on CSP

- Advantage: fast processes handled universally
- Time consuming
 - Jacobian evaluation
 - CSP refinement
- Coupling of fast species is typically sparse
 - Classical approaches of QSS and PE could be more efficient



Quasi Steady State Assumptions

- Example



- Destruction much faster than creation
- B is a QSS species:

$$\frac{dB}{dt} = A - \frac{B}{\varepsilon} \approx 0 \quad \longrightarrow \quad B \approx A\varepsilon$$

- Question:
 - How to identify QSS species?



Partial Equilibrium Assumptions

- An example:



- Forward and backward rates are much faster than the net rate
- Reaction $B \leftrightarrow C$ is in PE:

$$\frac{B}{\varepsilon} - \frac{C}{\varepsilon} \approx 0 \quad \longrightarrow \quad B \approx C$$

- Question: **How to apply PE assumptions?**



Properties of QSS & PE

QSS Species	PE involved species
Concentration $\sim O(\varepsilon)$	$O(1)$
Can hide from governing equations	Has to be retained in governing equations
Can be directly applied back for rate computation	Should not be directly applied back for rate computation
Both are fast to apply	

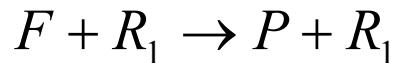
QSS and PE species need to be treated differently



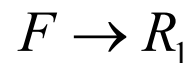
Identification of QSS Species

- Conventional criteria
 - Low concentrations
 - Small normalized net production rates
 - Short lifetime (or diagonal elements of Jacobian)
- These are only **necessary conditions** for QSSA
- Example:

$$\tau_i = 1/J_{i,i} = 1/\frac{dg_i}{dy_i}$$



$$k_{1f} = 1/\varepsilon$$



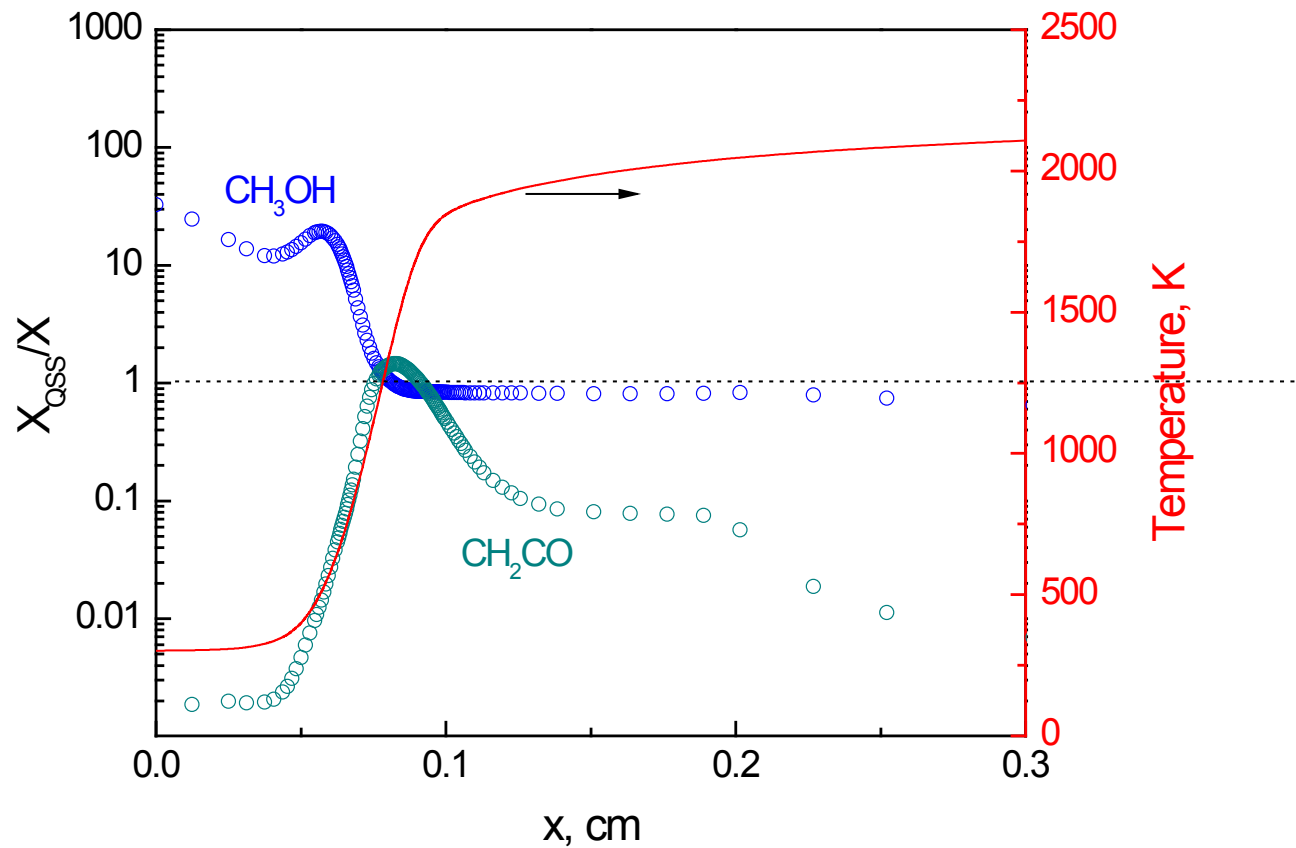
$$k_{2f} = \varepsilon$$



$$k_{3f} = k_{3r} = 1/\varepsilon$$



Error Induced by Bad QSSA





Selection of QSS Species

- A criterion based on fast-slow separation (CSP, ILDM, or eigenvalue decomposition)

$$\frac{dy}{dt} = \mathbf{g}(\mathbf{y}) \quad \frac{d\mathbf{g}}{dt} = \mathbf{J} \cdot \mathbf{g}(\mathbf{y}), \quad \mathbf{J} = \frac{d\mathbf{g}}{d\mathbf{y}}$$

$$\mathbf{f} = \mathbf{B} \cdot \mathbf{g}, \quad \frac{d\mathbf{f}}{dt} = \mathbf{\Lambda} \cdot \mathbf{f}, \quad \mathbf{\Lambda} = \left(\frac{d\mathbf{B}}{dt} + \mathbf{B} \cdot \mathbf{J} \right) \cdot \mathbf{A}, \quad \mathbf{A} = \mathbf{B}^{-1}$$

$$\mathbf{\Lambda} = \begin{pmatrix} \mathbf{\Lambda}_{fast} & \\ & \mathbf{\Lambda}_{slow} \end{pmatrix}, \quad \mathbf{A} = \begin{pmatrix} \mathbf{A}_{fast} & \mathbf{A}_{slow} \end{pmatrix}, \quad \mathbf{B} = \begin{pmatrix} \mathbf{B}_{fast} \\ \mathbf{B}_{slow} \end{pmatrix}$$

$$\mathbf{Q} = \mathbf{A}_{slow} \mathbf{B}_{slow}$$

Necessary & sufficient condition:

$$Q_{i,i} < \varepsilon \iff \text{Species } i \text{ is in QSS}$$

ε : relative induced error



Selection of QSS Species (CH₄)

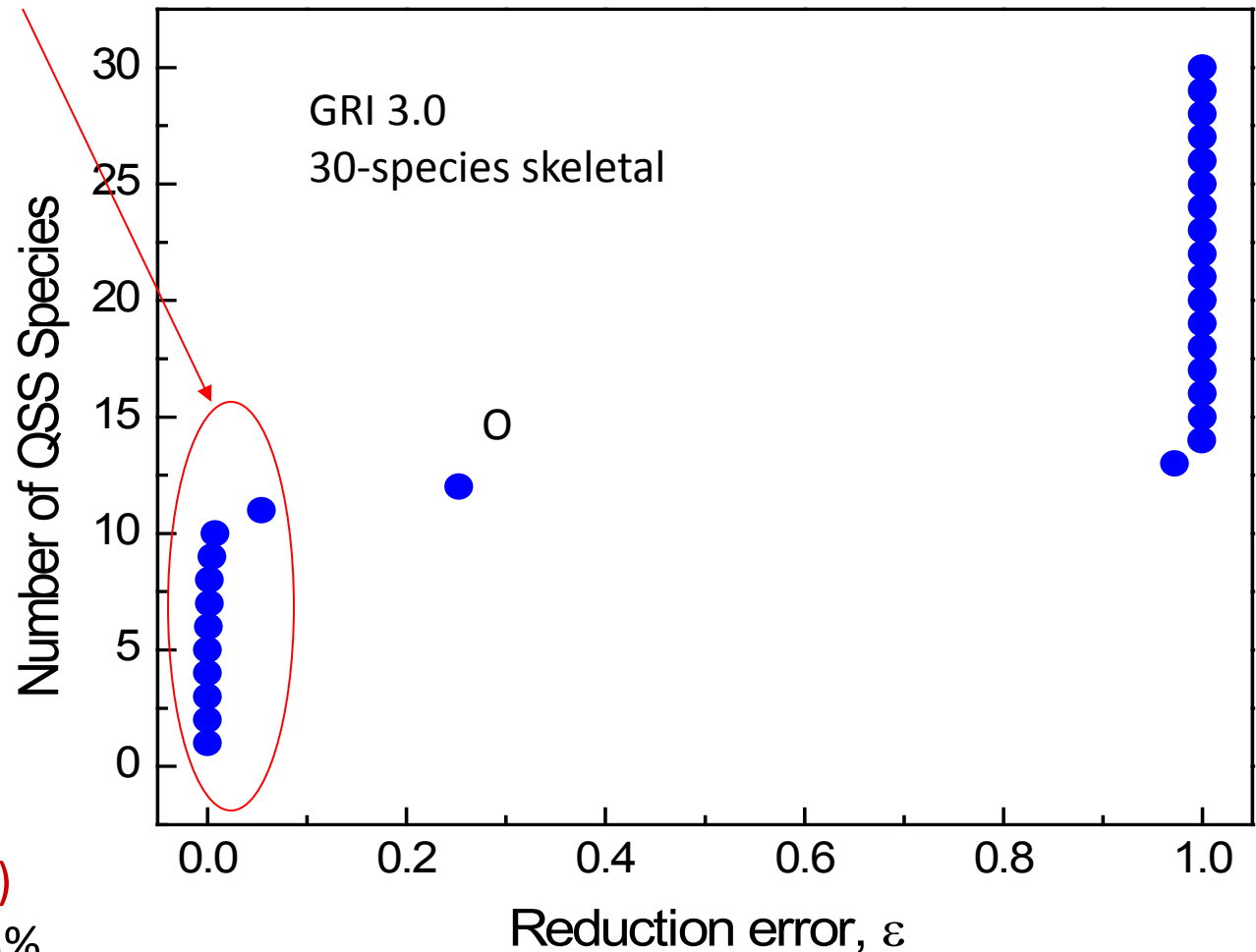
11 QSS species:

HCCO
CH₂
C₂H₅
C₂H₃
CH₃O
HCO
CH
CH₂(S)
CH₂OH
C
CH₂CHO

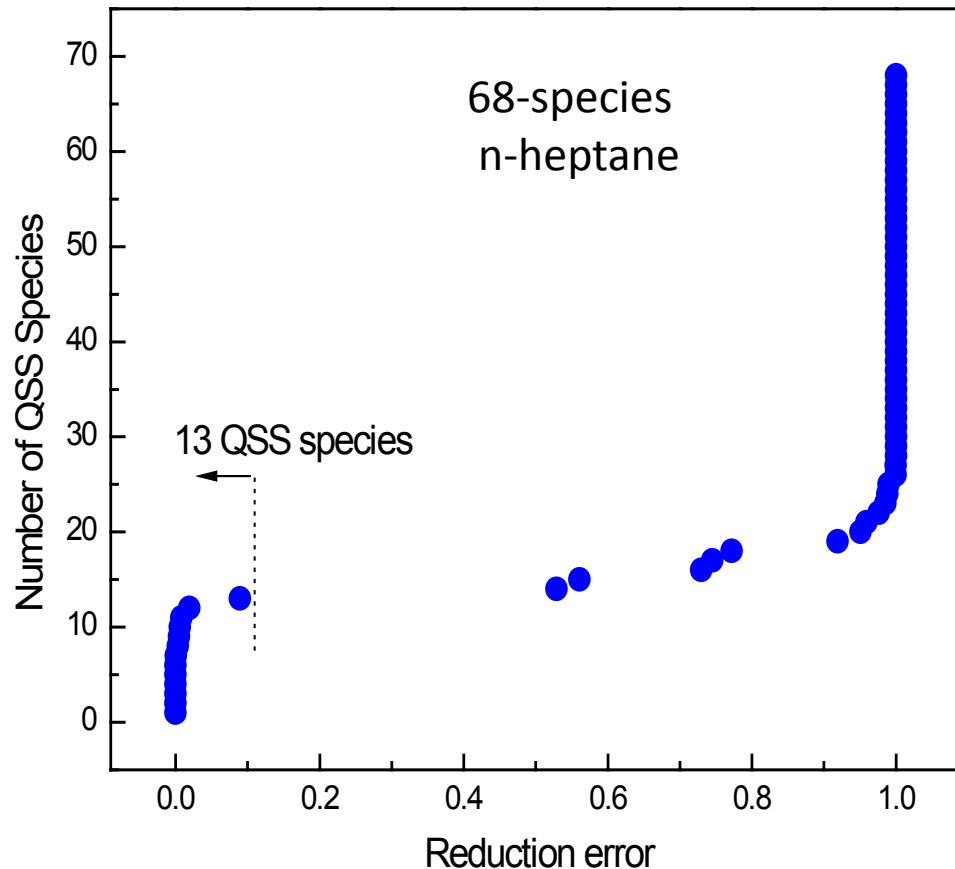
Reduced:

15-step (19 species)

Reduction error: 13%



Selection of QSS Species (heptane)



Reduced: 55 species (51-step)



Next Step: Solving QSS Equations

$$\frac{d\mathbf{y}_{QSS}}{dt} = \mathbf{g}_{QSS}(\mathbf{y}_{QSS}; \mathbf{y}_{major}, p, T) = \mathbf{0}$$

- Traditional approach: **algebraic iterations**
 - Slow convergence (inefficiency)
 - Divergence (crashes, ...)
- New approach: **analytic solution**
 1. Linearization
 2. Solving linearized QSSA with graph theory

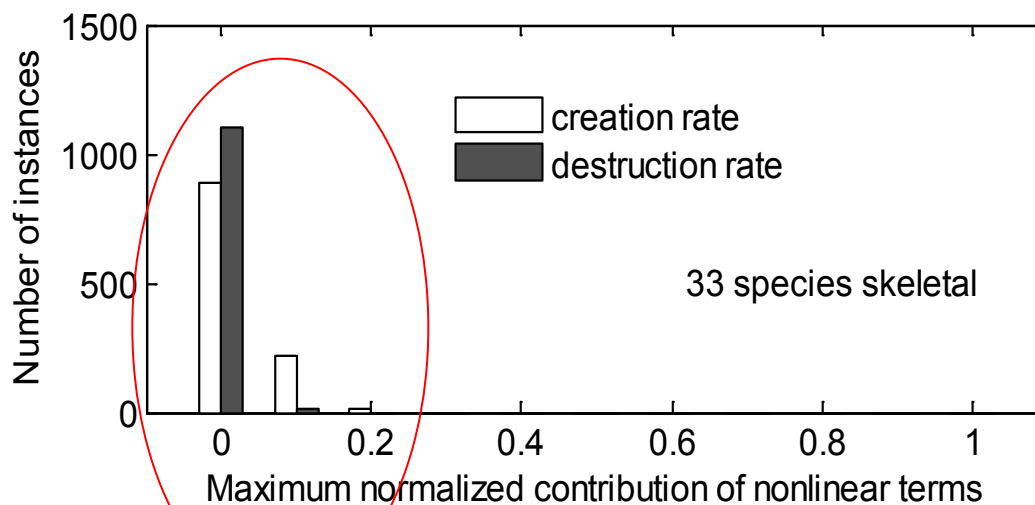


Linearized QSSA (LQSSA)

- QSS species are in low concentrations, say $O(\varepsilon)$
- Reactions with more than one QSS reactant are mostly unimportant; reaction rate: $O(\varepsilon^2)$

Example: [ethylene](#)

>1000 sampled instances, 12 QSS Species





Analytic Solution of LQSSA

Equation LQSSA:

$$D_i x_i = \sum_{k \neq i} C_{ik} x_k + C_{i0} \quad D_i > 0, C_{ik} \geq 0, C_{i0} \geq 0$$

Destruction rate Creation Rate involving other QSS species Creation Rate involving major species

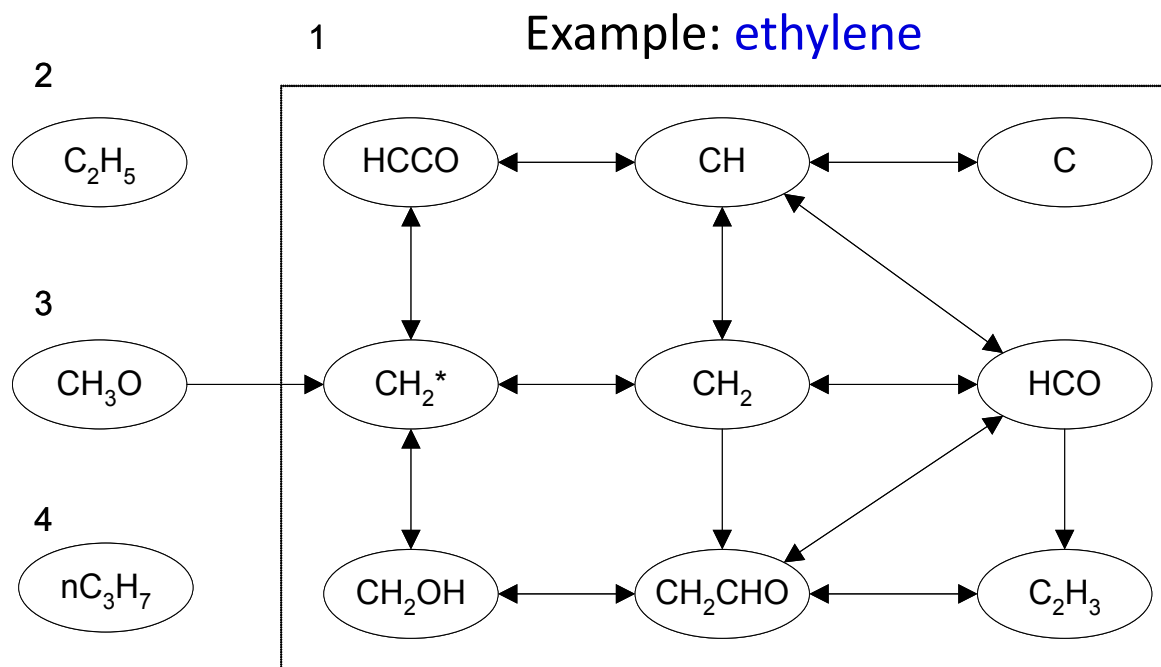
Standard form: $x_i = \sum_{j \neq i} A_{ij} x_j + A_{i0}$ $A_{ij} \geq 0, A_{i0} \geq 0$

- Gaussian elimination $\sim N^3$
- The coefficient matrix **A** is **sparse**



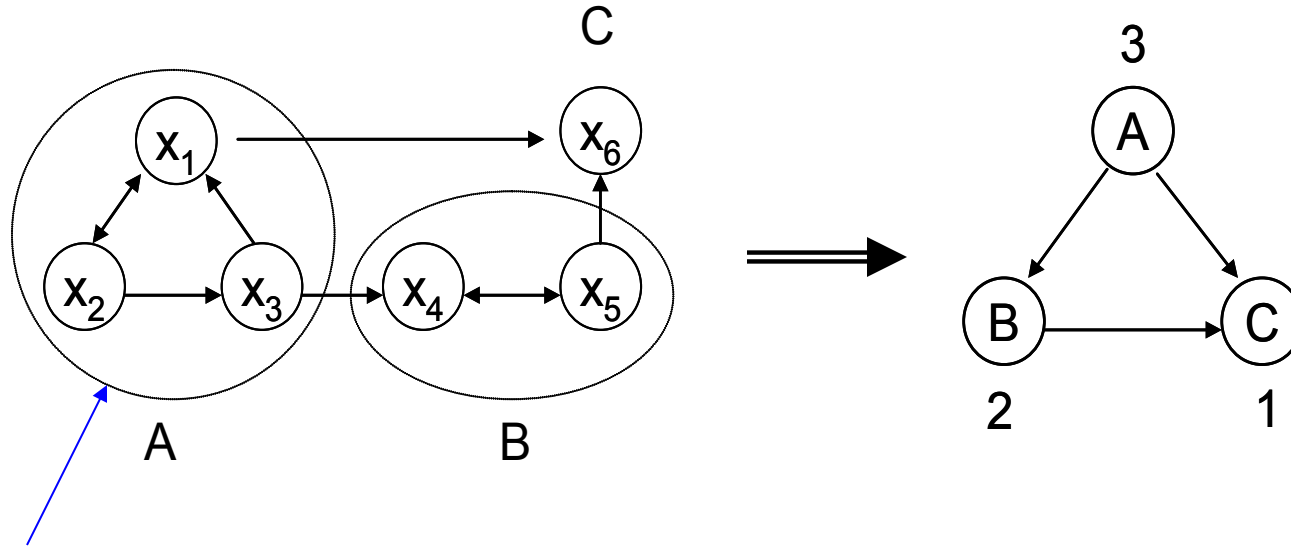
QSS Graph (QSSG)

- Each vertex is a QSS species
- $x_i \rightarrow x_j$ iff $A_{ij} > 0$, $x_i = \sum_{j \neq i} A_{ij} x_j + A_{i0}$





Decouple Species Groups by Topological Sort



Strongly connected component (SCC): coupled with cyclic path

Identification of SCC:

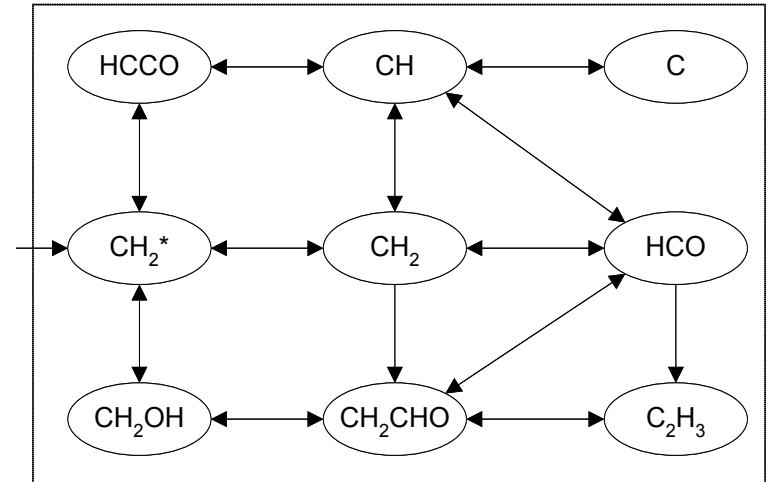
Depth-First Search for G and G^T

- Treat SCC as composite vertex
- Acyclic graph obtained by topological sort
- Species groups can be solved **explicitly** in topological order



Solving Implicit Kernels

- Paper & pencil:
eliminate the most isolated variables first
- Systematic: **a spectral method**



$$\mathbf{c} = \mathbf{L} \cdot \mathbf{c}$$

$$\mathbf{c} = (c_1, c_2, \dots, c_M)^T$$

$$L_{ij} = E_{ij} / \sum_{k=1}^M E_{kj}$$

c: Expansion cost vector,

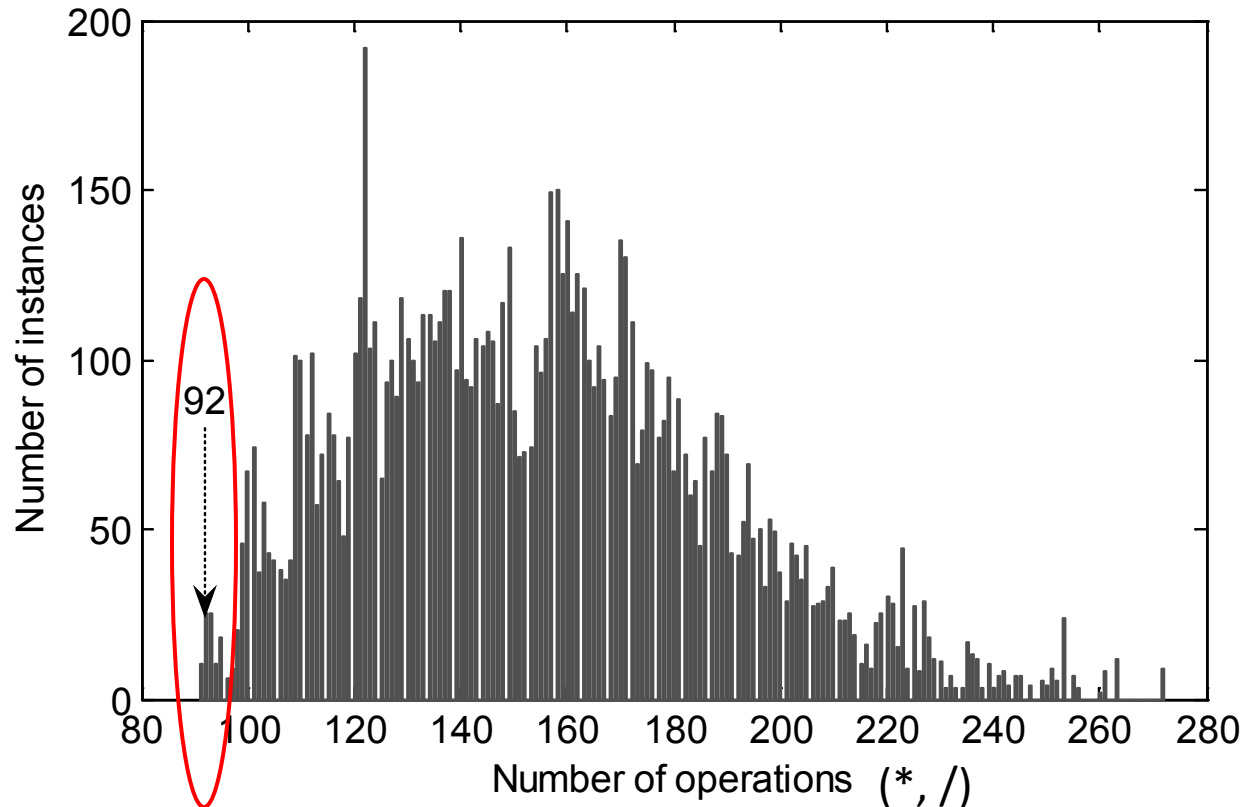
L: Averaging operator

E: the adjacency matrix



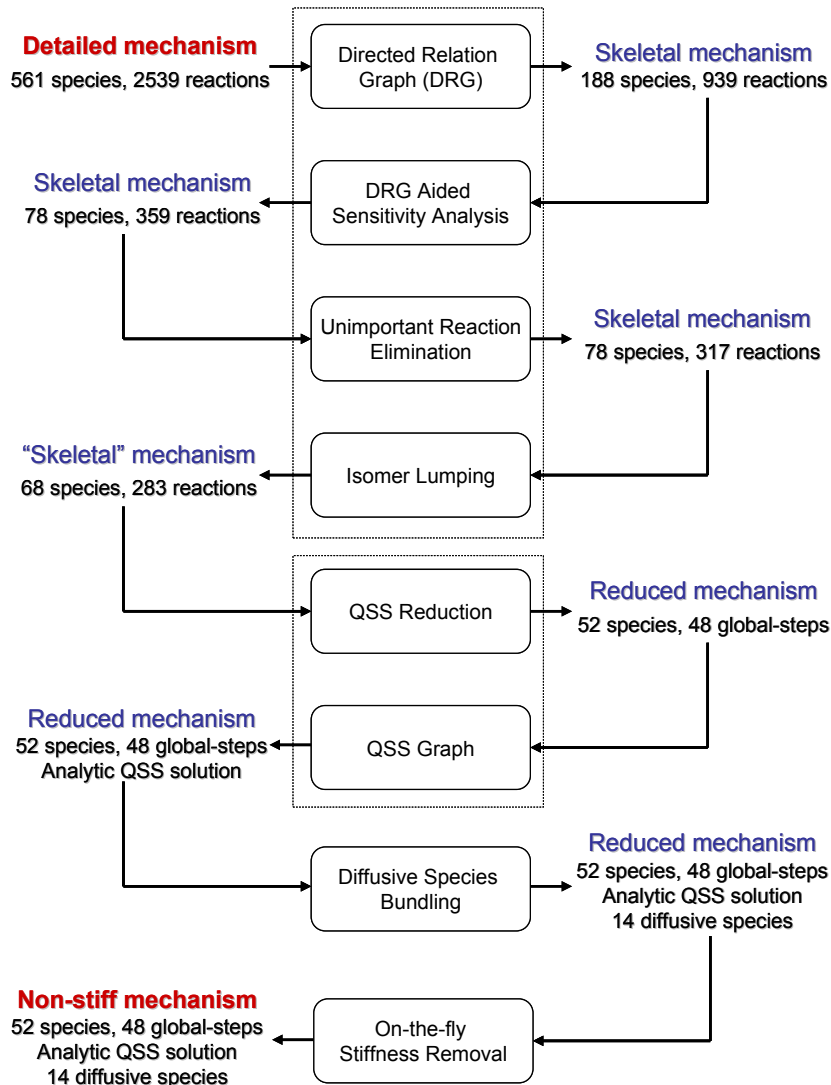
Efficiency of the Analytic Solution

Ethylene/air, 9-species SCC,
10000 random sequences





A Systematic Reduction Approach



Sample reduced mechanisms:

- ▶ CH₄ (GRI3.0): 53 → 19 species
- ▶ C₂H₄ (USC Mech II): 75 → 22 species
- ▶ DME (Zhao et al): 55 → 30 species
- ▶ Ethanol (Mittal et al): 145 → 28 species

- ▶ n-Heptane (LLNL): 561 → 52 species
- ▶ iso-Octane (LLNL): 874 → 99 species
- ▶ PRF (LLNL): 1271 → 116 species
- ▶ n-Dodecane (LLNL): 2115 → 106 species
- ▶ Biodiesel (LLNL): 3299 → 115 species

- ▶ Download at <http://www.engr.uconn.edu/~tlu/mechs>

(Lu & Law PECS 2009)

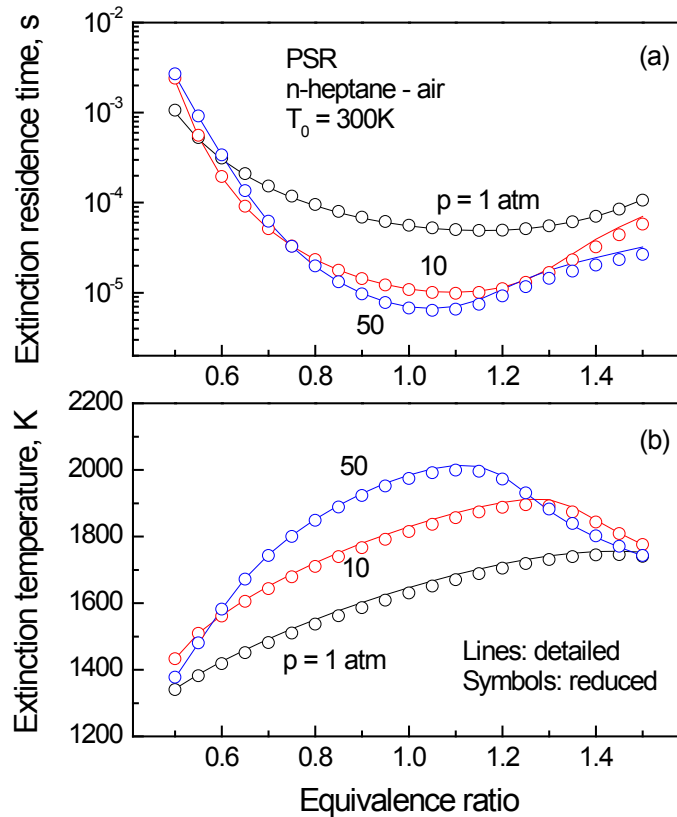


Accuracy of Reduced Mechanisms:

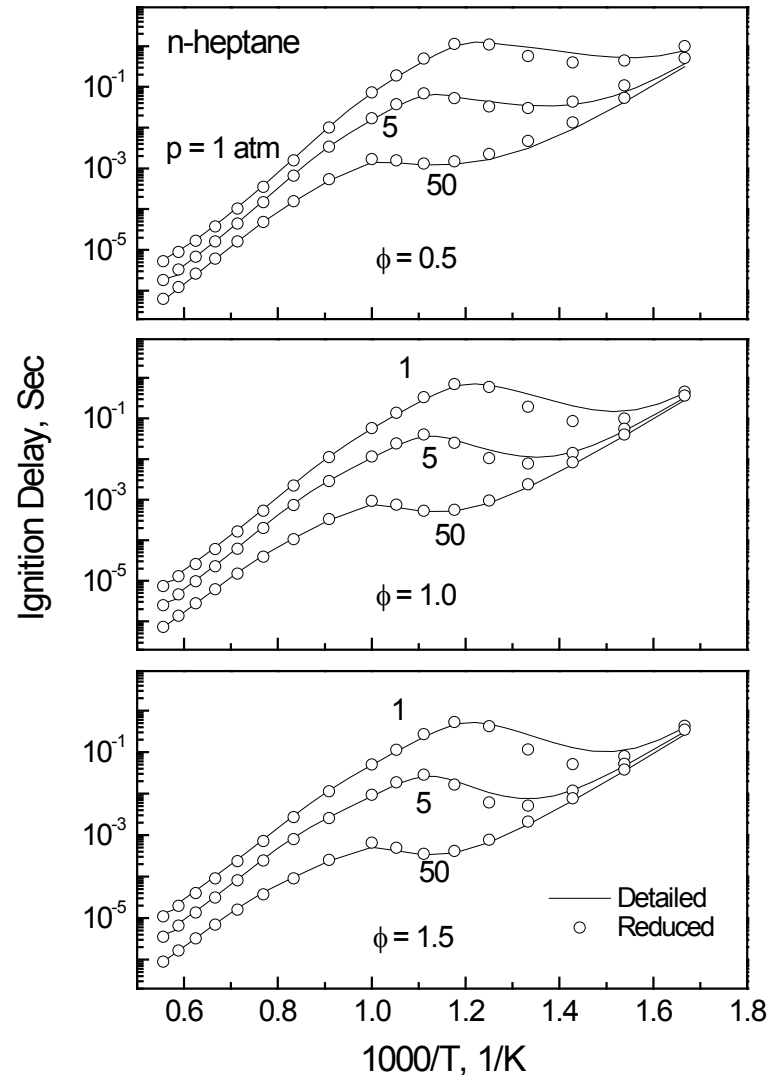
n-C₇H₁₆ (1/2)

- ▶ Detailed (LLNL): 561 species
- ▶ Reduced: 58 species

Perfectly Stirred Reactor



Auto-ignition

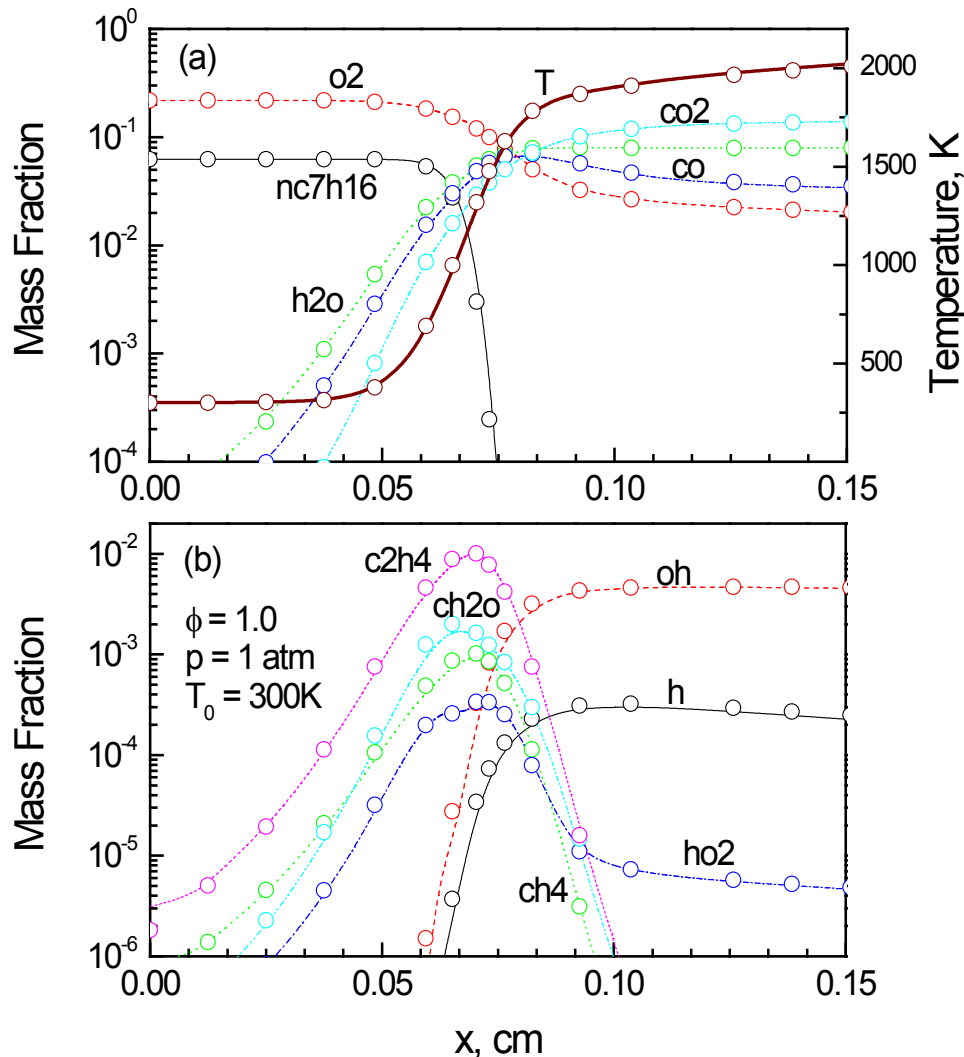




Accuracy of Reduced Mechanisms:

n-C₇H₁₆ (2/2)

Premixed Flame Structure



Other reduced mechanisms (All suitable for DNS)

- ▶ CH₄ (GRI3.0): 19 species
- ▶ C₂H₄ (USC Mech II): 22 species
- ▶ DME (Zhao et al): 30 species
- ▶ nC₇H₁₆ (LLNL): 58 species
- ▶ Biodiesel (LLNL): 73 species
- ▶ ...

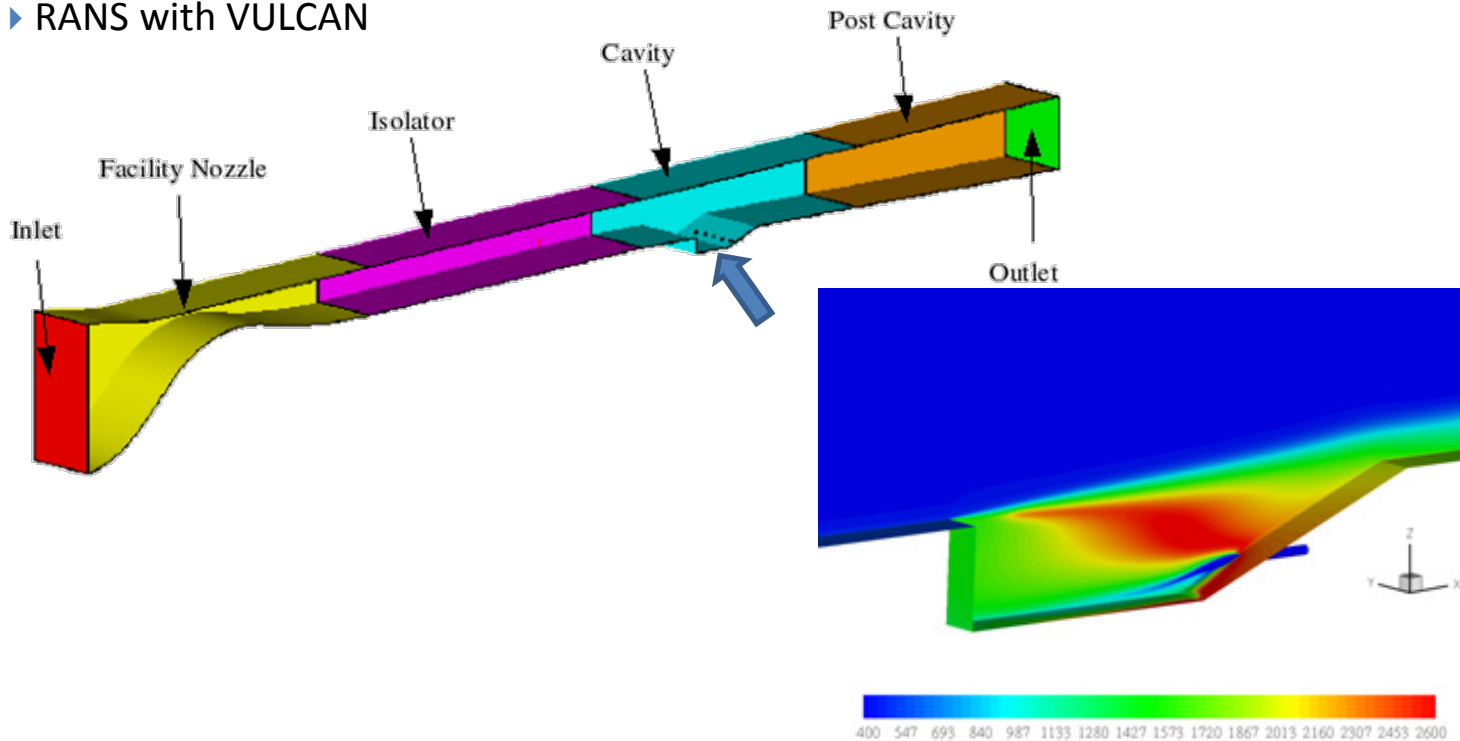
More reduced mechanisms:

<http://www.engr.uconn.edu/~tlu>

Sample Simulations: Scramjet Flame Holding (RANS)



- ▶ 3-D cavity stabilized ethylene flame at scramjet conditions
- ▶ C_2H_4 , 19 species
(from Qin et al 2000, 70 species)
- ▶ RANS with VULCAN

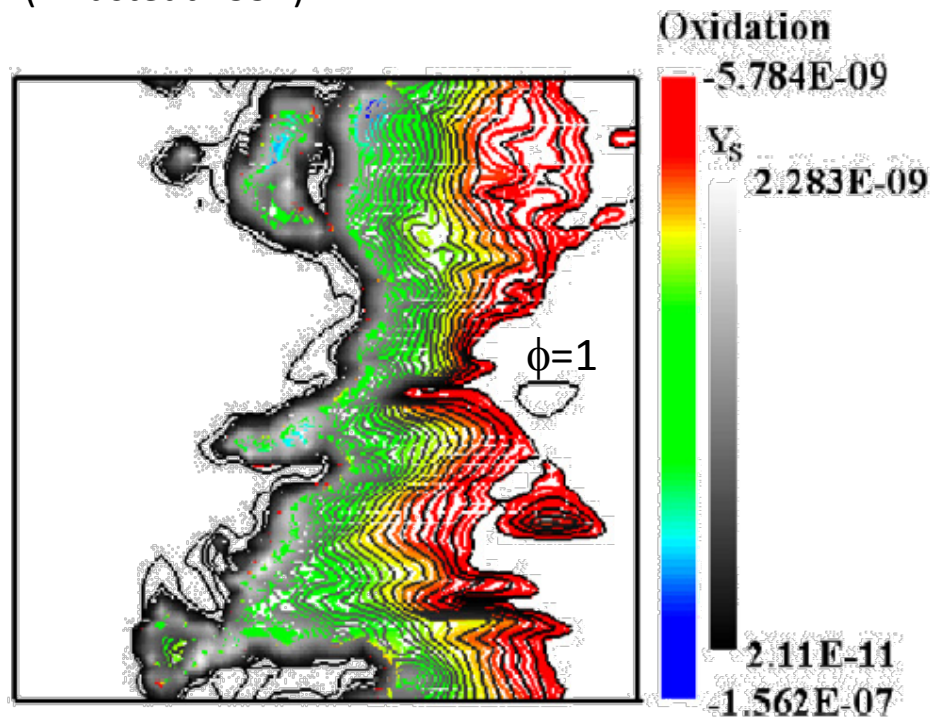


Liu et al, AIAA/ASM 2006

Sample Simulations: Premixed Sooting Flame (LES)



- ▶ 3-D premixed sooting flame
- ▶ C_2H_4 , 19-species (from Qin et al 2000)
- ▶ LEM + Simplified soot model (Lindstedt 1994)
- ▶ C_2H_2 as soot precursor



Sample Simulations:

Premixed Bunsen Flame (DNS)

- ▶ 3-D premixed Bunsen flame
- ▶ CH_4 -air (lean): 13 species, (from GRI1.2)
- ▶ Re: 800
- ▶ Grids: 50 million
- ▶ Time steps: 1.3 million
- ▶ CPU hours: 2.5 million (50Tflops Cray)

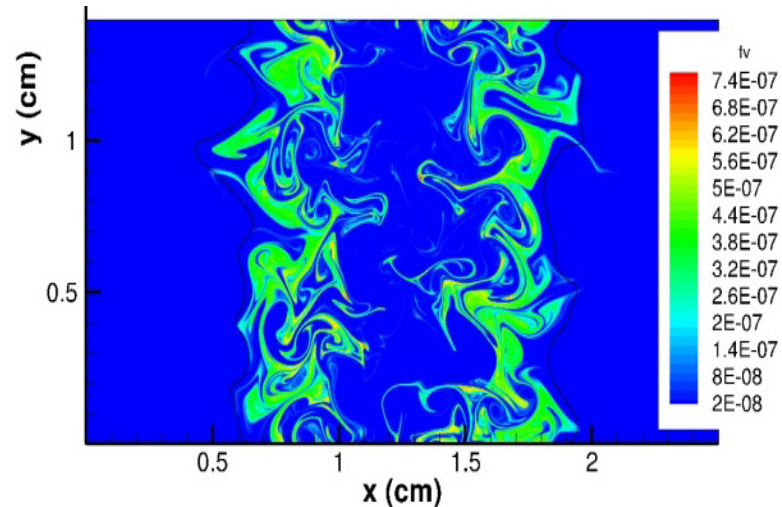
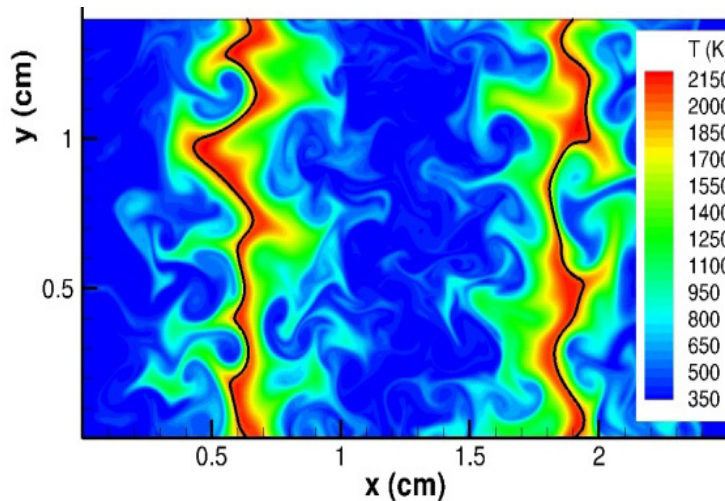


Sankaran et al, PCI 2007



Sample Simulations: Non-Premixed Sooting Jet Flame (DNS)

- 2-D temporally evolving sooting jet flame
- C_2H_4 -air+PAH, 60 species, non-stiff
(Luo et al, from the ABF-mech, 100 species)
- Detailed soot model (Roy & Haworth)
- Pyrene as soot precursor



Arias et al, Paper# C-05



UC DAVIS
UNIVERSITY OF CALIFORNIA



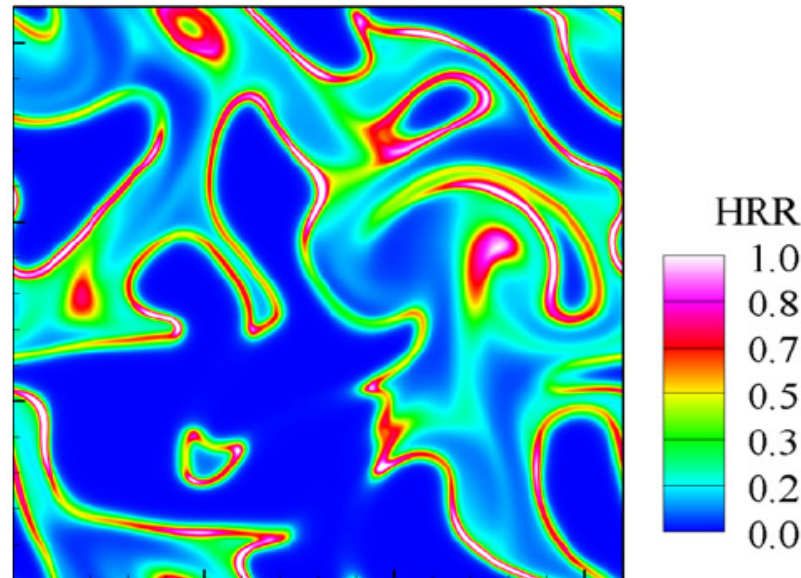
PENN STATE



Sample Simulations: HCCI Combustion (DNS)



- ▶ 2-D HCCI
- ▶ $n\text{C}_7\text{H}_{16}$ -air, 58 species, non-stiff (from LLNL C7, 561 species)
- ▶ $\phi = 0.3$, $p = 40\text{atm}$
- ▶ $T_{\text{mean}} = 900\text{K}$, $T' = 100\text{K}$ (RMS)
- ▶ $u' = 5\text{m/s}$ (isotropic turbulence)



Yoo et al, CNF 2011



Sample Simulations: A Petascale Lifted Jet Flame (DNS)

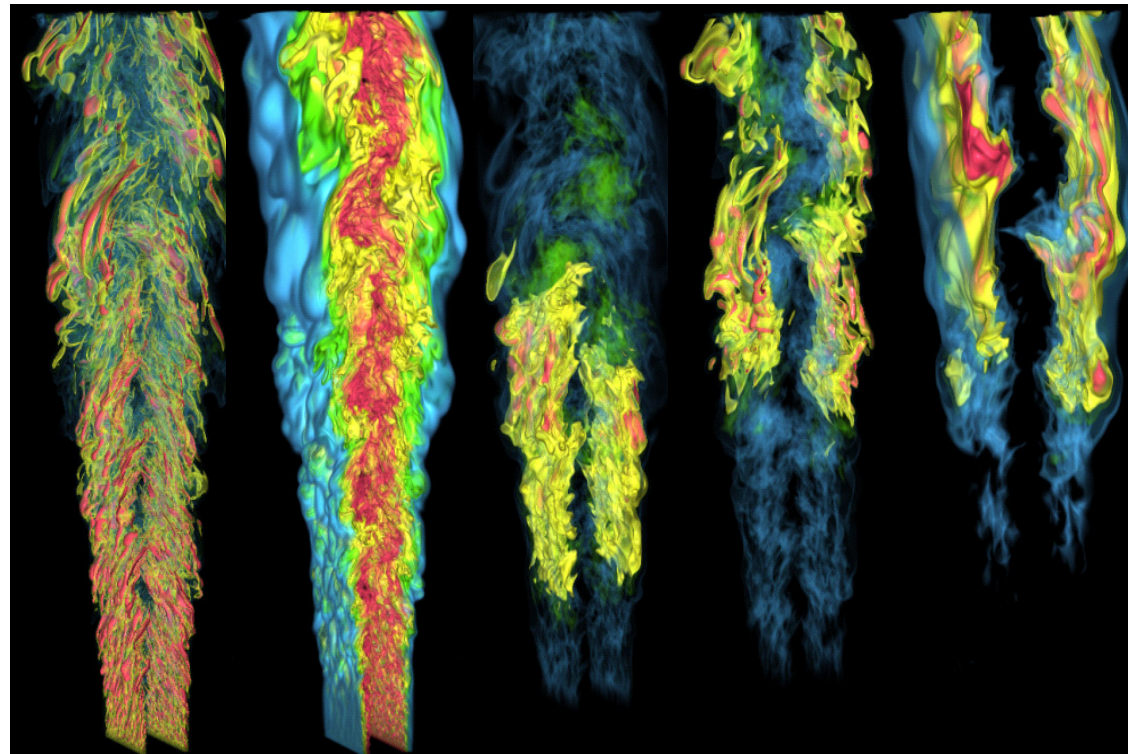
- 3-D lifted ethylene jet flame (Yoo et al, PCI, 2011)
- 22-species, non-stiff (from USC Mech II)
- $Re = 10,000$

- 1.3 billion grid points
- 14 million CPU hours

- **240 TB output data**
- Difficult to save
- Difficult to transfer
- Difficult to use

- **Systematic methods needed to extract salient information**

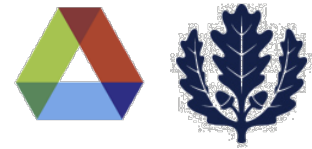
Scalar
Dissipation Rate **Mixture Fraction** **HO₂** **CH₃** **CH₂O**



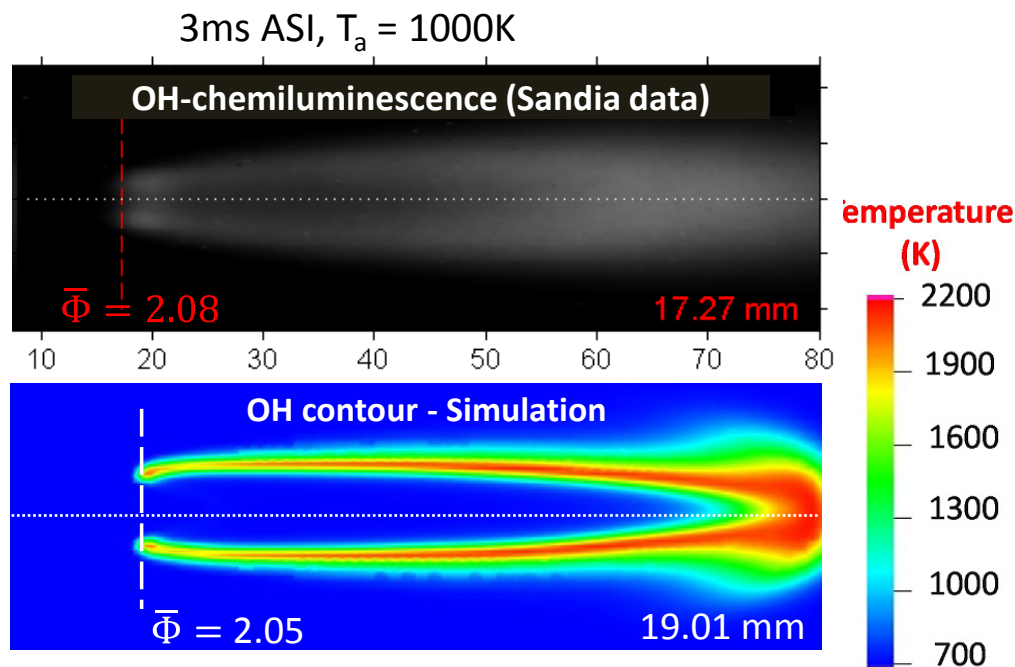
DNS by C. S. Yoo

Volume rendering by
H. Yu at Sandia

Sample Simulations: A Lifted Biodiesel Jet Flame (RANS, LES)

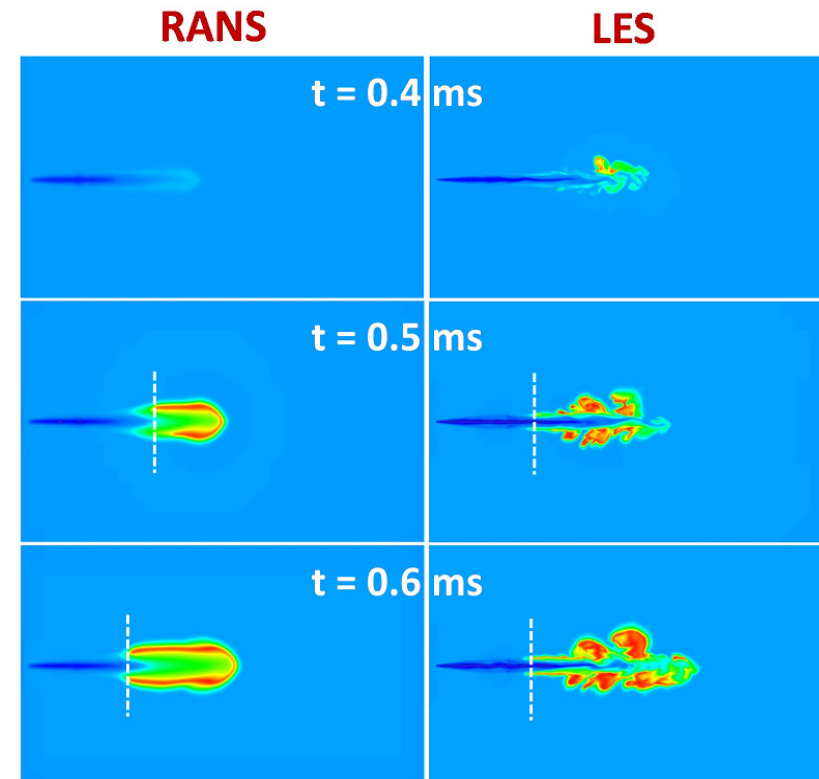


- ▶ Lifted biodiesel jet flame at diesel engine conditions (CONVERGE)
- ▶ Detailed (LLNL): 3329 species, 10806 reactions
- ▶ 115-species skeletal mechanism with low-T chemistry
- ▶ Surrogate: MD+MD9D+C7



Luo et al, Fuel 2012

Experiment: Pickett et al



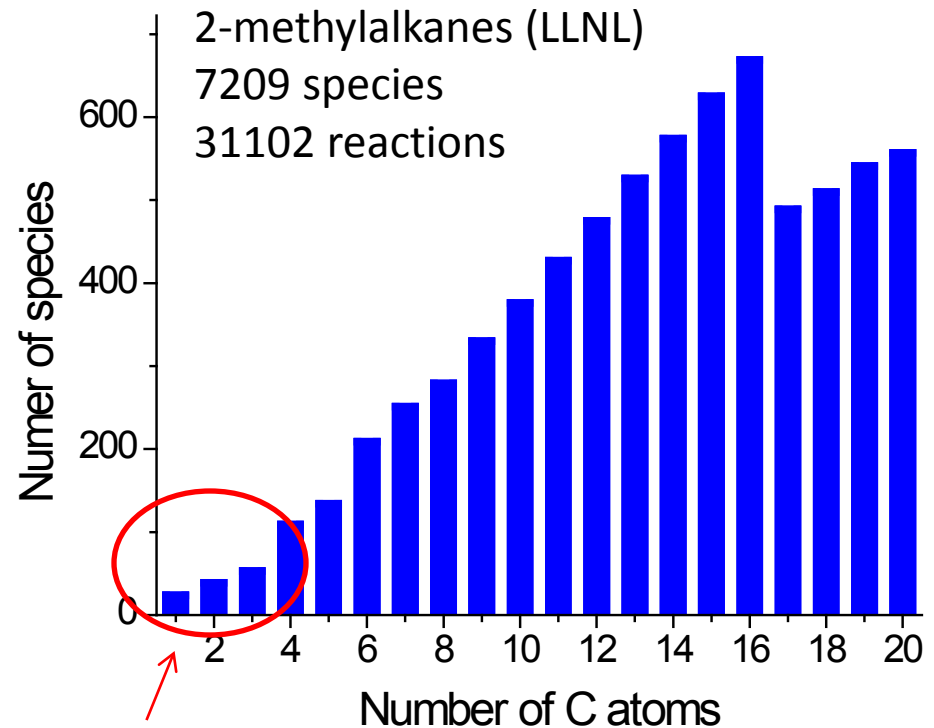
Som et al, JERT 2012

Reduced HyChem Models for Real Fuels



The HyChem Approach for High-T Combustion (Hai Wang & Colleagues)

- Fuel cracking through beta-scission is fast at high-T conditions
- Pyrolysis products (C0-C4) rate-controls high-T oxidation
- Fuel cracking can be approximated as semi-global steps
- Fuel cracking product ratios (CH₄, C₂H₄, C₃H₆ ...) are not sensitive to flame conditions and can be determined with experimental data

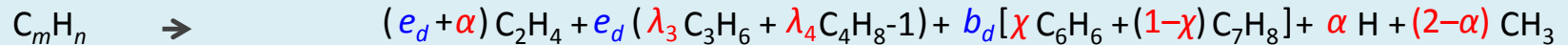


controlling species
at high-T

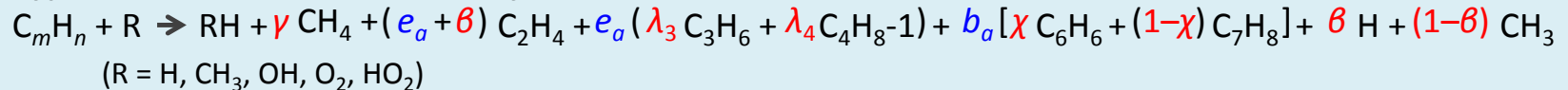


Lumped Pyrolysis Model in HyChem

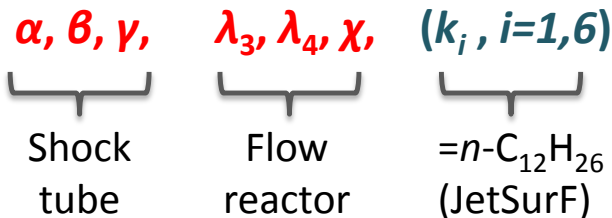
Type I: C-C fission like reaction (Reaction 1)



Type II: H-abstraction followed by fuel radical breakdown (Reaction 2-6)



The problem is cast into a system of equations with 12 independent variables



Hybrid high-T model for real fuels:

lumped pyrolysis model (fuel, CH₄, C₂H₄, C₃H₆, C₄H₈ etc.) +
Detailed CO-C₄ kernel (20~30 species)

(Xu et al., US Meeting 2017)

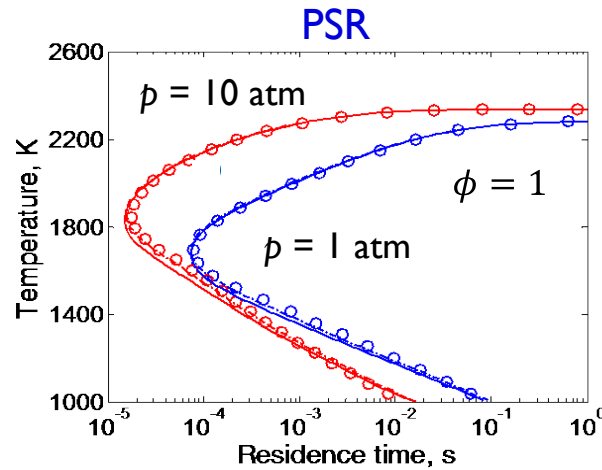
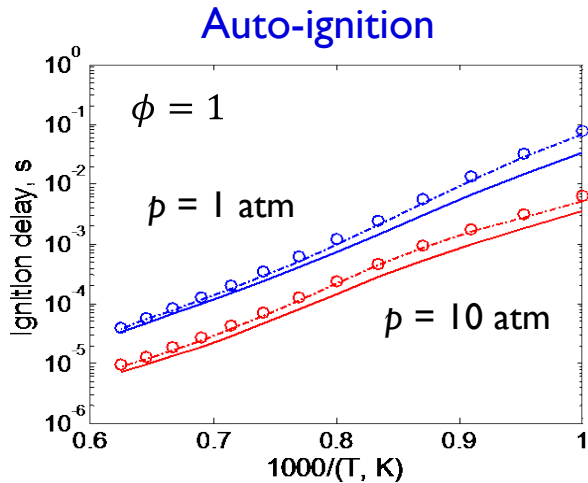


A High-T Reduced Model for n-Dodecane

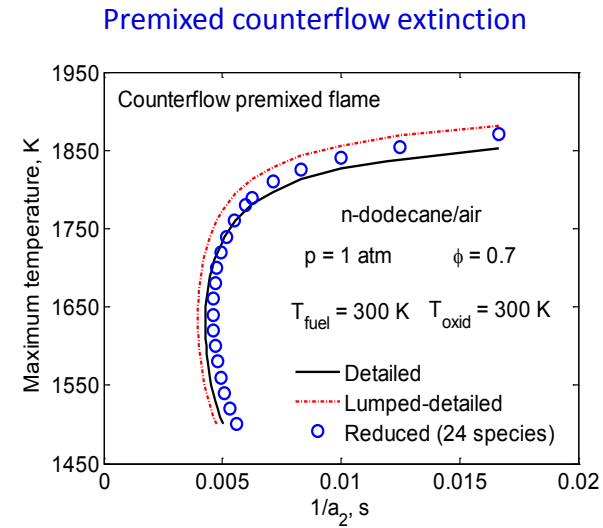
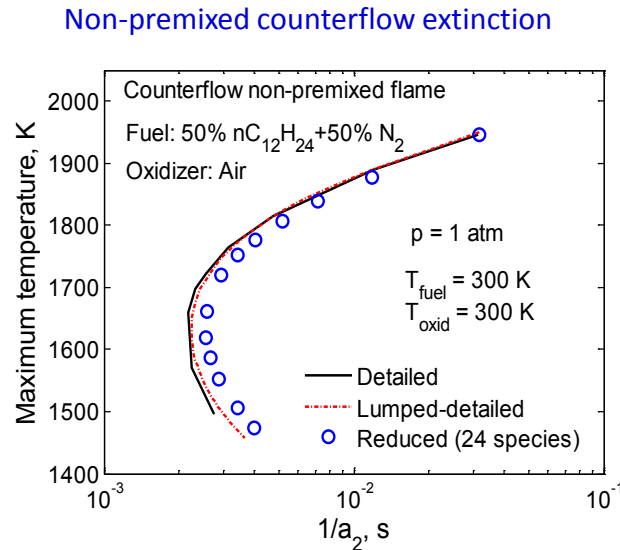
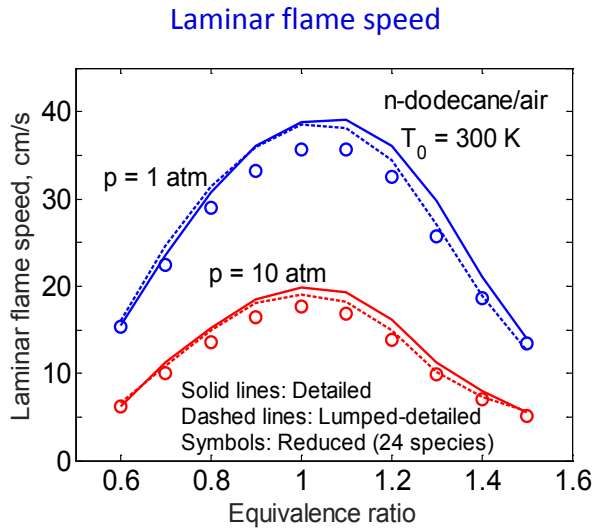
- Detailed (JetSurF 1.0): 194 species
- Lumped-detailed model (Sirjean et al, 2009): 123 species
- Reduction methods:
DRG, sensitivity analysis, QSSA (Lu & Law, PECS 2009)
- Reaction state sampling for model reduction
 - Auto-ignition ($p = 1-10$ atm, $\phi = 0.5-1.5$, $T_0 = 1000-1600$ K)
 - Extinction in PSR ($p = 1-10$ atm, $\phi = 0.5-1.5$, $T_0 = 300$ K)
- Reduced models (Vie et al., PCI 2015, Gao et al. CNF 2015)
 - Skeletal: 31 species
 - Reduced: 24 species, (22 for C_0-C_4 + n-dodecane, 1-hexene)



Performance of the Reduced C12 Model



Solid: Detailed
Dashed: Lumped-detailed
Symbols: Reduced





Reduced Models for Real Jet Fuels

- Target version 2 HyChem models: Cat A2, C1 and C5
- Parameter range
 - $\phi = 0.5-1.5$
 - $p = 0.5-30$ atm
 - $T_{in} = 300$ K for PSR
 - $T_0 = 1000-1600$ K for auto-ignition
- Size of reduced models

Models	Cat A2	Cat C1	Cat C5
Detailed <i>HyChem</i>	119	119	119
Skeletal	41	34	41
Reduced	31	26	31

- Extended validation: laminar flame speed, counter flow flame extinction, PSR LBO (in addition to ignition delay & PSR extinction)

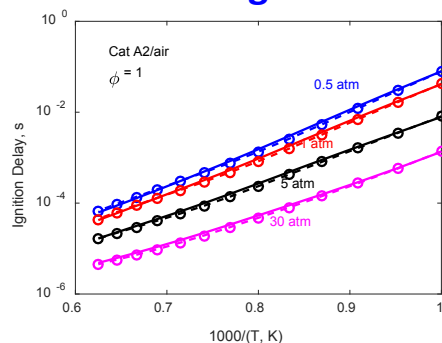
(Gao et al., US Meeting 2017)

Validation of Ignition Delay, PSR and Flame Speed

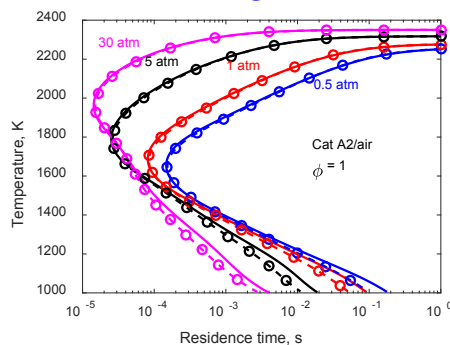


A2

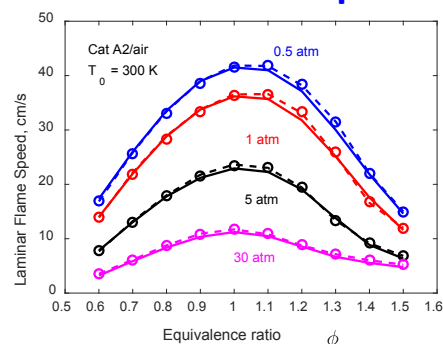
Auto-ignition



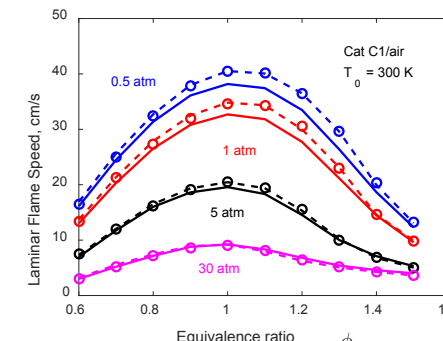
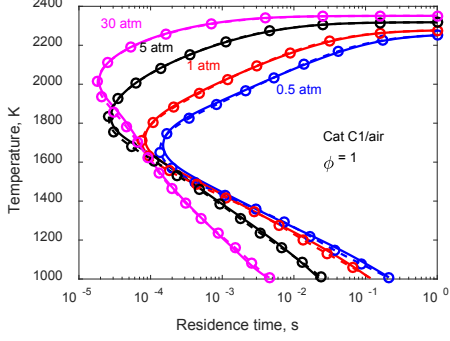
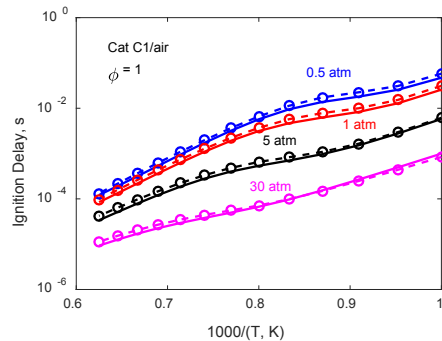
PSR



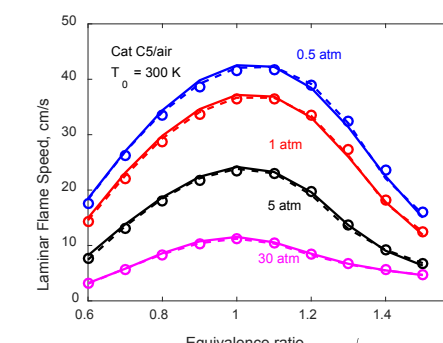
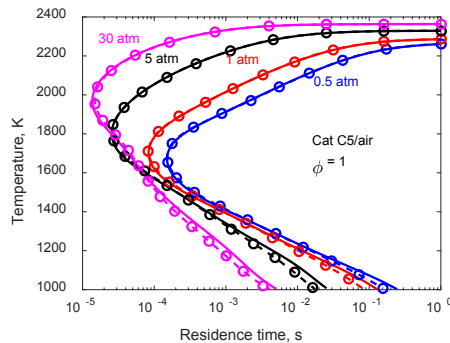
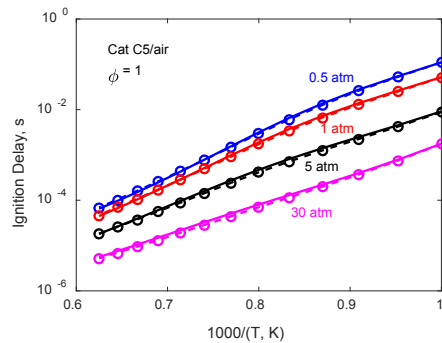
Laminar flame speed



C1



C5

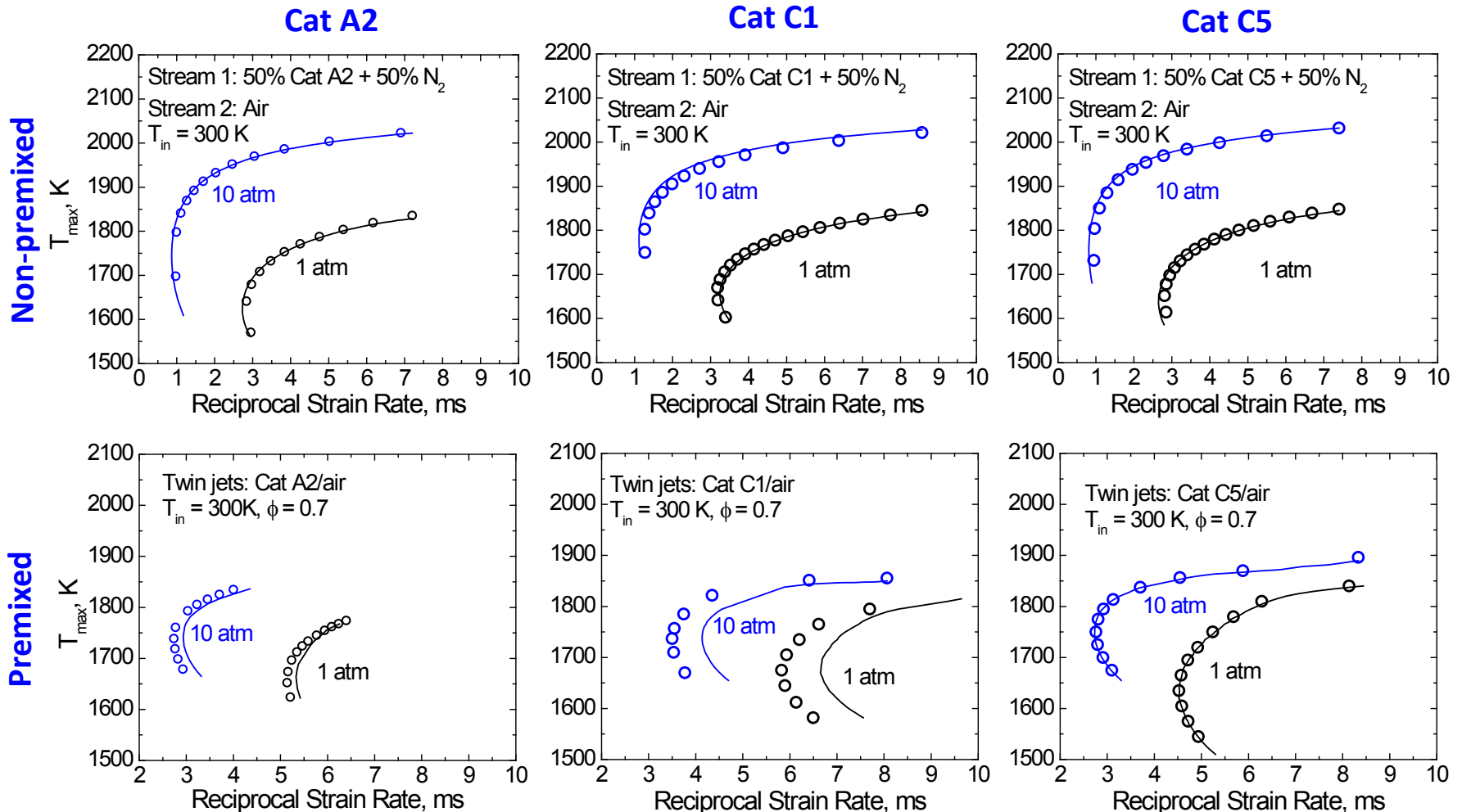


Solid: Detailed
Dashed: Skeletal
Symbols: Reduced

Similar agreements for $\phi=0.5$ and 1.5



Validation of Counterflow Extinction

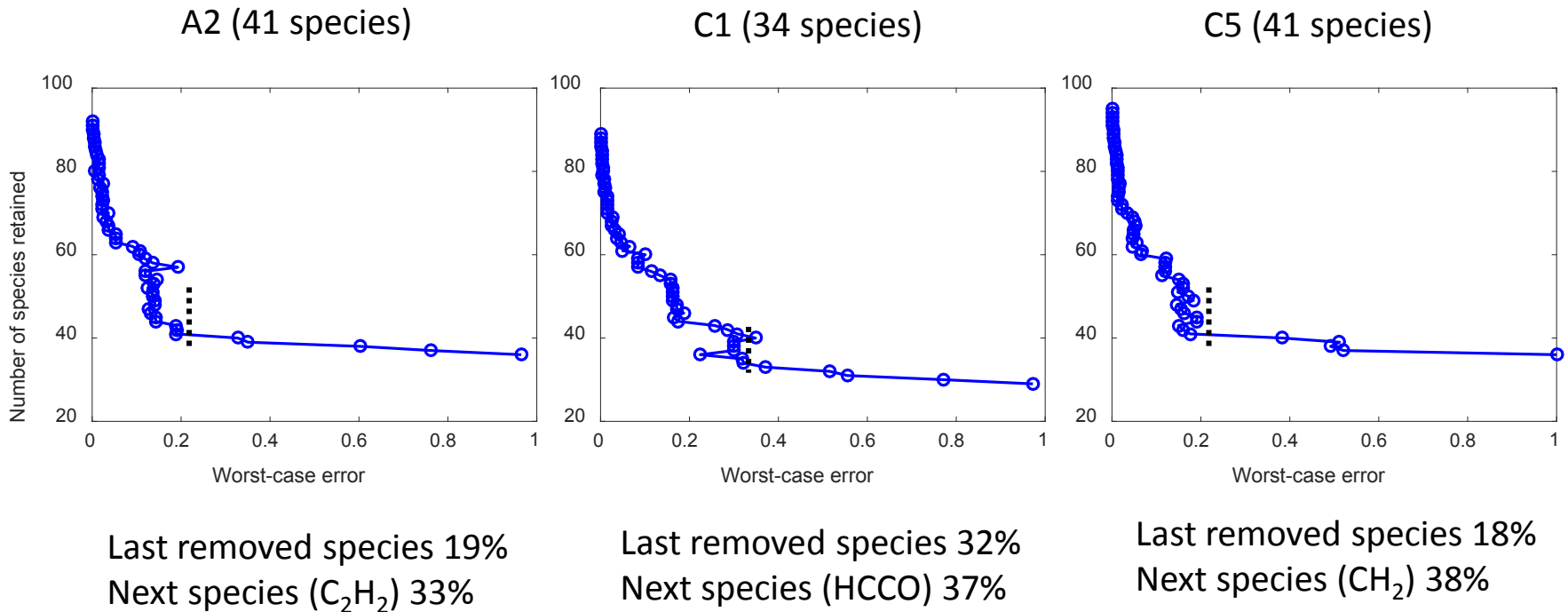


Solid: detailed;

Symbols: reduced



Errors in Sensitivity Analysis



- Worst-case errors grow rapidly with further skeletal reduction
- Further increased reduction error may incur incorrect trend of fuel sensitivity



A Reduced Model for n-Dodecane with Lumped NTC Chemistry (Yao et al., Fuel 2017)

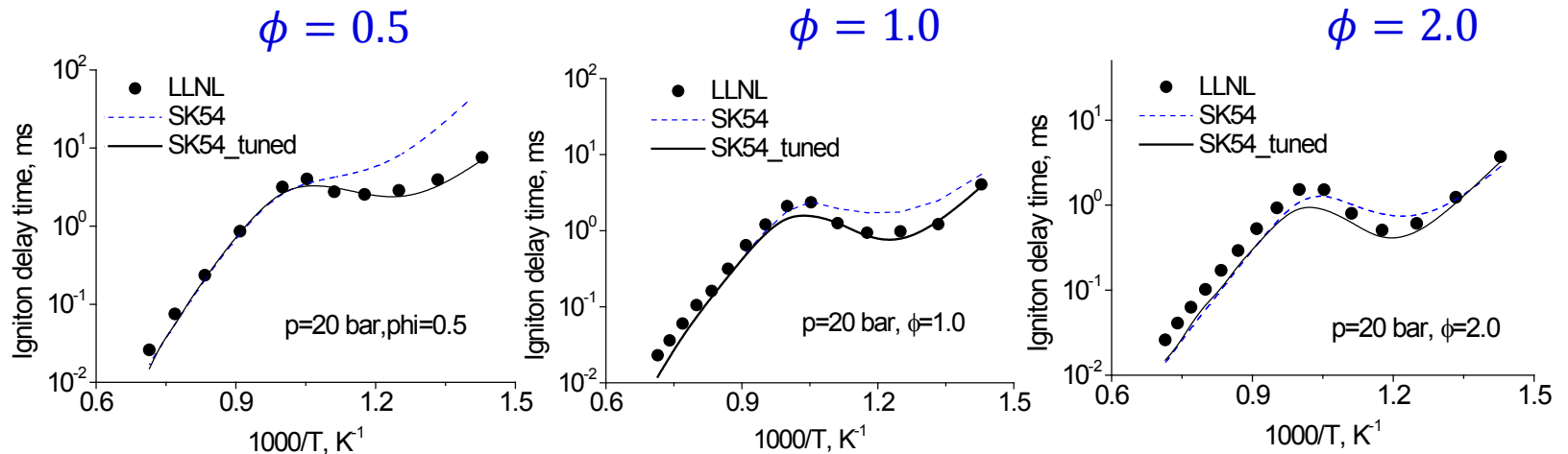
- C_0 - C_4 core chemistry
 - A high-T skeletal model based on JetSurf
 - 32 species, 191 reactions
- C_5 - C_{12} sub-mechanism
 - Starting model: (You et al, PCI 2009)
 - Skeletal sub-model: 18 species, 60 reactions
- Low-T sub-mechanism
 - Semi-global scheme (4 species, 18 lumped reactions) (Bikas & Peters, CNF 2001)
 $C_{12}H_{25}O_2$, $C_{12}OOH$, $O_2C_{12}H_{24}OOH$, $OC_{12}H_{23}OOH$
 - Rate parameters need tuning
- Final models (Yao et al., US Meeting 2015):
 - Skeletal: 54-species, 269 reactions
 - Reduced: 37 species



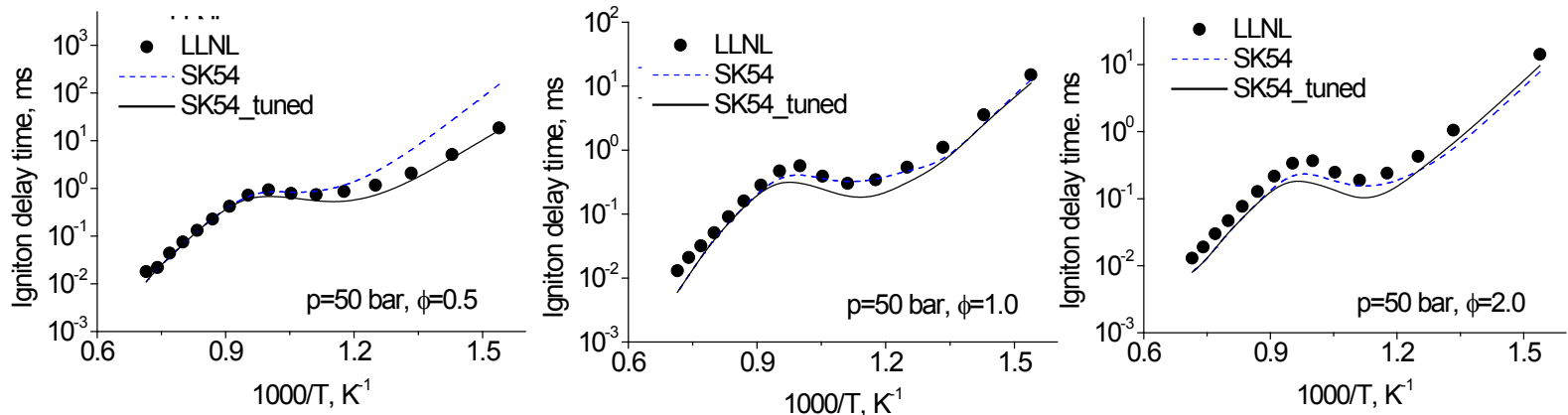
Tuning Against the LLNL Mechanism

- Rate parameter tuning (where experimental data not available)
 - Low-T steps tuned against LLNL mechanism (Westbrook et al, CNF 2009)
 - High-T reactions unchanged

20 bar



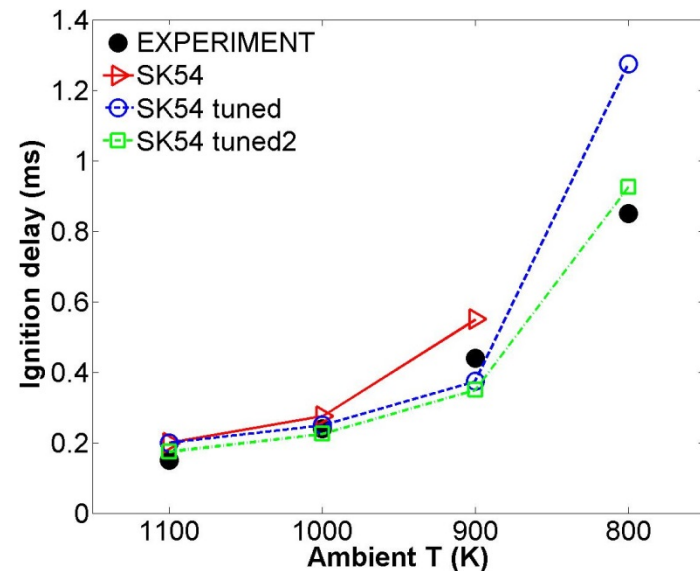
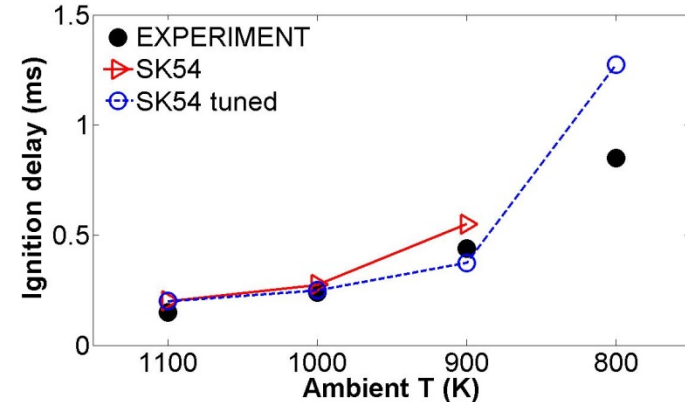
50 bar



Tuning Based on ECN Data

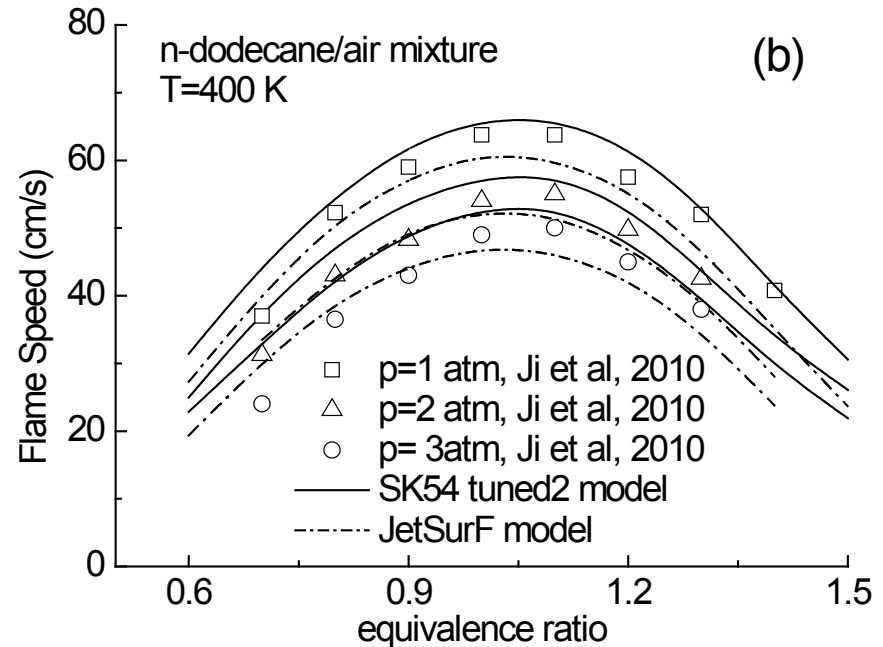
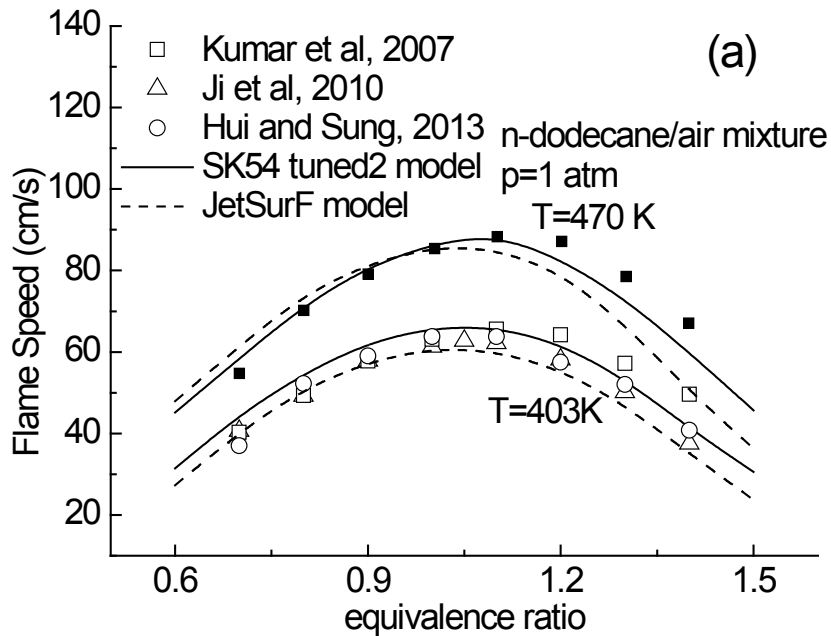


- Experimental data from ECN (Spray A, lifted n-dodecane jet flame)
- CFD at ANL: RANS (CONVERGE)
 - First-stage ignition occurs in lean mixture
 - Second-stage ignition occurs first in rich mixture
 - **~25% longer Ignition delay at 800K**
- Tuning against experiments
 - Based on ignition sensitivity analysis
 - Reactions only with high sensitivities for 800 K tuned down by ~25%
 - Final mechanism: “SK54_tuned2”





Laminar Flame Speed



- Overall good agreement with experimental data
- High-T flame behaviors inherited from USC-Mech II (flame speed, extinction, high-T ignition delay ...), unaffected by the tuning



On the Tuning of Over-Reduced Models (1/2)

- It is a widely adopted approach to obtain over-reduced models and then tune the rate parameters to fit a target dataset (ignition delay, flame speed etc.): the extreme case is the one- or a few-step semi-global models
- The tuning of rate parameters against experimental data is a common practice in detailed mechanism compilation
- There are severe over-fitting issues in tuning complex models with many parameters
- Consider a comprehensive model with a set of M model parameters, $\mathbf{x} = \begin{pmatrix} \mathbf{y} \\ \mathbf{z} \end{pmatrix}$, that can accurately describe a set of N (N can be larger than M) targets (ignition delay, flame speed, extinction properties etc.,

$$\mathbf{f}(\mathbf{x}) = \begin{pmatrix} \mathbf{g}(\mathbf{y}, \mathbf{z}) \\ \mathbf{h}(\mathbf{y}, \mathbf{z}) \end{pmatrix} = 0$$

- Let an over-reduced model be denoted by a modified subset of parameters, \mathbf{z} , and the tuning be performed on the remaining subset of parameters, \mathbf{y} , to fit a selected subset of targets, \mathbf{g}

$$\mathbf{g}(\mathbf{y} + \mathbf{y}', \mathbf{z} + \mathbf{z}') = 0$$



On the Tuning of Over-Reduced Models (2/2)

- For simplicity, assume that the changes in model parameters are small perturbations

$$g(\mathbf{y} + \mathbf{y}', \mathbf{z} + \mathbf{z}') \approx g(\mathbf{y}, \mathbf{z}) + \frac{\partial g}{\partial \mathbf{y}} \mathbf{y}' + \frac{\partial g}{\partial \mathbf{z}} \mathbf{z}' = J_{11} \mathbf{y}' + J_{12} \mathbf{z}' = 0$$

- The solution of the optimization is

$$\mathbf{y}' = -(J_{11}^T J_{11})^{-1} J_{11}^T J_{12} \mathbf{z}', \quad J = \frac{\partial f}{\partial \mathbf{x}} = \begin{bmatrix} J_{11} & J_{12} \\ J_{21} & J_{22} \end{bmatrix}$$

- Let \mathbf{h} denote the targets (flame blow out behaviors, flame responses in turbulent environments etc.) not included in the optimization processes

$$\mathbf{h}(\mathbf{y} + \mathbf{y}', \mathbf{z} + \mathbf{z}') \approx \mathbf{h}(\mathbf{y}, \mathbf{z}) + J_{21} \mathbf{y}' + J_{22} \mathbf{z}' = \left(J_{22} - J_{21} (J_{11}^T J_{11})^{-1} J_{11}^T J_{12} \right) \mathbf{z}' = \mathbf{A} \mathbf{z}'$$

- There is absolutely no guarantee that the nontrivial $\mathbf{A} \mathbf{z}'$ is inconsequential, i.e. the tuning can mess up flame behaviors not included in the optimization.
- Possible approaches to avoid severe overfitting
 - Avoid over-reduction if possible at all
 - Tune only compact models with a small number of parameters
 - Include as many different types of targets as possible
 - If experiment data is scarce, tune against the hybrid of experimental data and detailed model prediction
 - Use training/test/validation sets

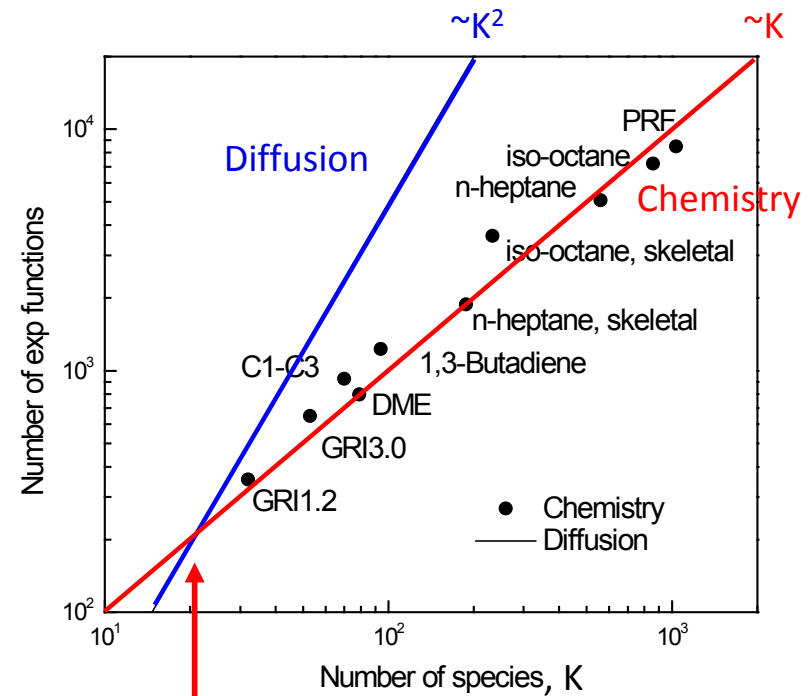
Reduced Molecular Diffusion Models

(Gao et al., US Meeting 2017)



Background on Molecular Diffusion Models

- Accurate modeling of molecular diffusion is important to predict combustion problems
 - Near-limit flame behaviors, e.g. ignition and extinction/blowout
 - Premixed flame propagation
 - Both laminar and turbulent flames
- Multi-component diffusion (MCD) model is computationally expensive
 - Matrix inversion operations, $O(K^3)$, K is the number of species
 - Prohibitive in large-scale CFD simulations
- Mixture-averaged diffusion (MAD) model is widely used in flame simulations
 - Good accuracy in many cases
 - Computational cost $\sim O(K^2)$
 - Relatively lower computational cost than MCD, but may still be significant for CFD, particularly DNS



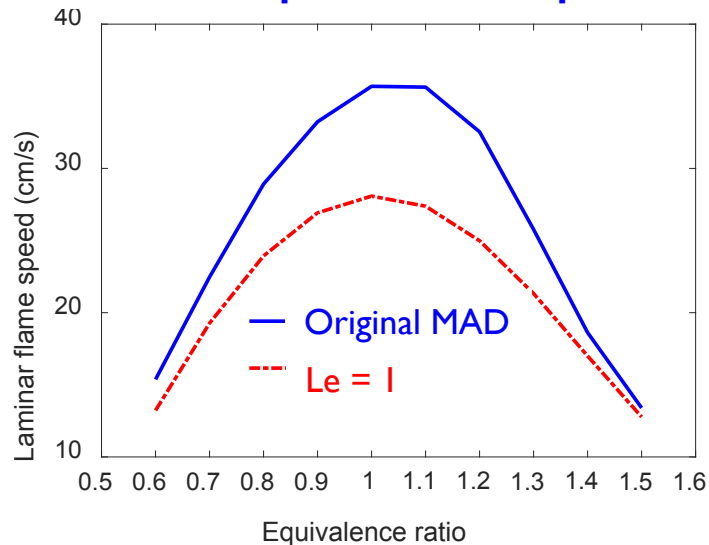
the crossing point:
 $K \sim 20$



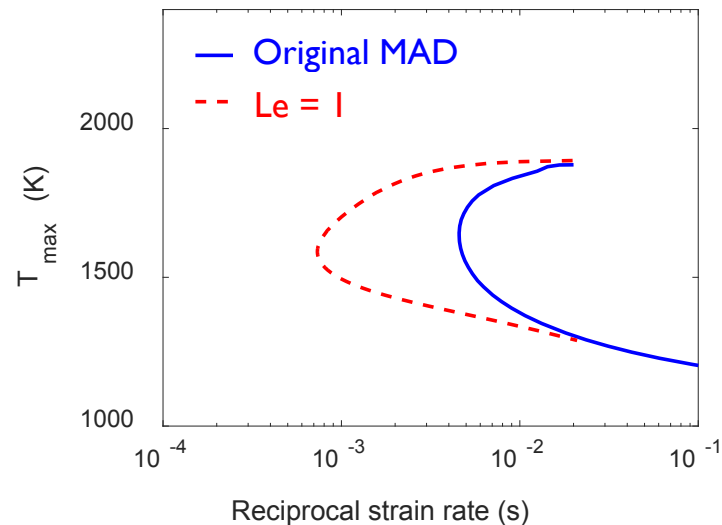
MAD vs. Unity Lewis Number

$$nC_{12}H_{26}/air$$
$$p = 1 \text{ atm}, T_{in} = 300 \text{ K}$$

Laminar premix flame speed



Twin premixed counterflow flame



24-species reduced model
Gao et al., CNF 2016

- Over-reducing molecular diffusion model may induce significant errors to flame responses
- Systematic reduction with controlled errors is important

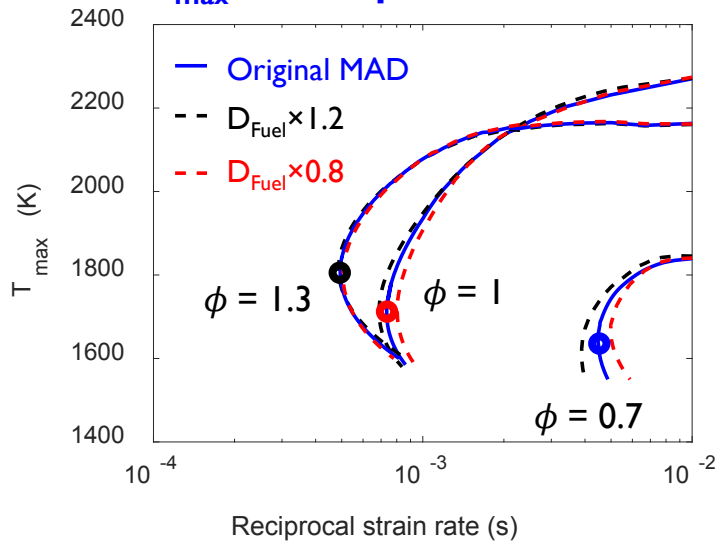


Effects of Fuel Diffusivity on Counterflow Flames

$nC_{12}H_{26}/air$
 $p = 1 \text{ atm}, T_{in} = 300 \text{ K}$

Twin premixed counterflow flame

T_{max} vs. Reciprocal strain rate



For lean case $\phi = 0.7$

$$\text{Sensitivity} = \frac{d \ln(\text{Reciprocal strain rate})}{d \ln(D_{Fuel})}$$

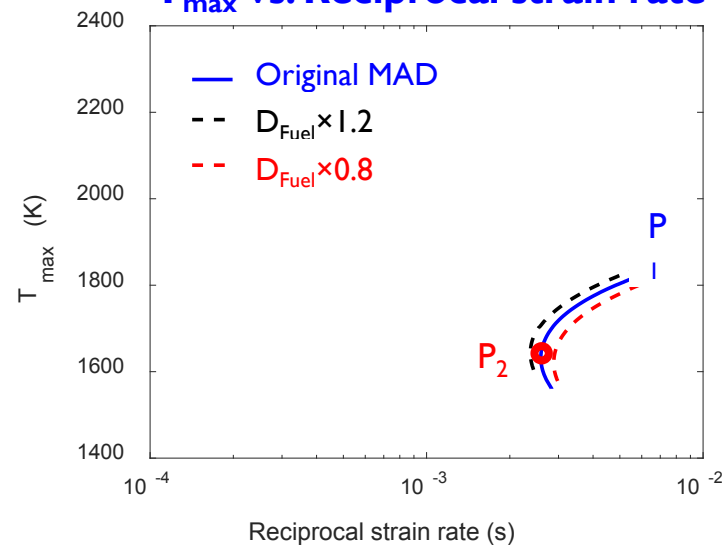
$D_{Fuel} \times 1.2$: -0.774

$D_{Fuel} \times 0.8$: -0.486

$nC_{12}H_{26}/air$
 $p = 1 \text{ atm}, T_{in} = 300 \text{ K}$
50% (mole) Fuel+N₂ vs. Air

Diffusion counterflow flame

T_{max} vs. Reciprocal strain rate



$$\text{Sensitivity} = \frac{d \ln(\text{Reciprocal strain rate})}{d \ln(D_{Fuel})}$$

$D_{Fuel} \times 1.2$: -0.473

$D_{Fuel} \times 0.8$: -0.485



Mixture-Averaged Diffusion

- Species diffusion velocity for the i th species:

$$V_i = -\bar{D}_i \frac{\nabla X_i}{X_i}$$

- Mixture-averaged diffusivity for the i th species:

$$\bar{D}_i = \frac{1 - Y_i}{\sum_{j \neq i}^K X_j / D_{i,j}}$$

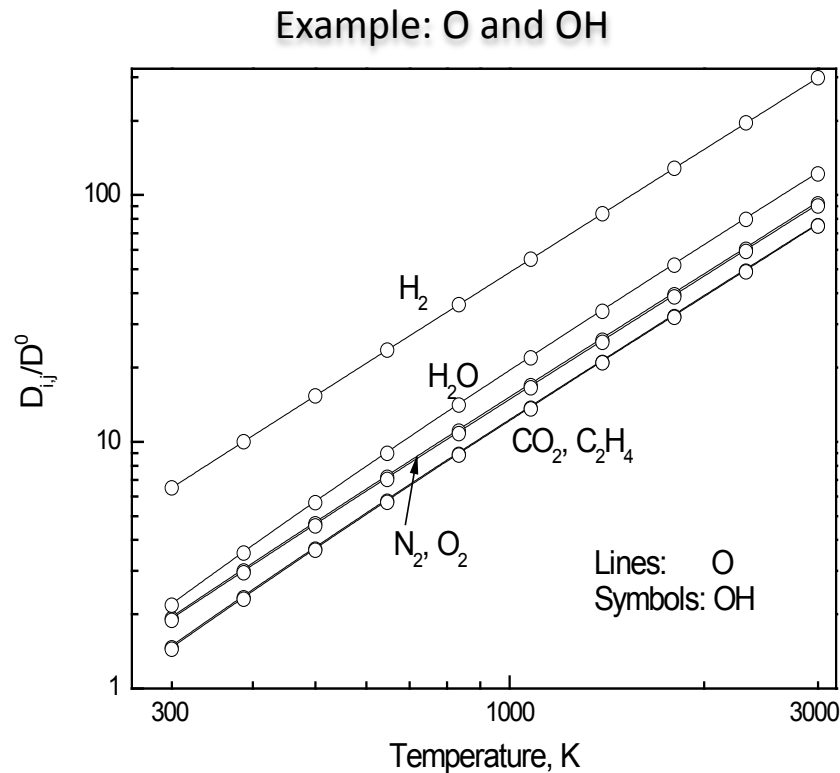
- Y_i, X_j : mass fraction, mole fraction for species i and j
- $D_{i,j}$: binary diffusion coefficient between species i and j
- Evaluation of the matrix $\mathbf{D} = \{D_{i,j}\}$ is time-consuming, typically tabulated with polynomials

$$pD_{i,j} \approx \exp\left(\sum_{n=0}^N a_{n,i,j} (\ln T)^n\right)$$



Diffusive Species Bundling (Lu & Law, CNF 2007)

- Many species have similar diffusivities



- Species with similar diffusivities can be lumped, their diffusivities evaluated as a group



Diffusive Species Bundling (cont.)

- Species with similar binary diffusion coefficients $D_{i,j}$ due to similar
 - Molecular Weight
 - Cross section parameters
 - Molecular structure
- Can be lumped into groups, with worst-case difference as

$$\varepsilon_{i,j} = \max_{\substack{k=1,\dots,K \\ T_{min} < T < T_{max}}} \left| \ln \left(\frac{D_{i,k}}{D_{j,k}} \right) \right|$$

$D_{i,k}$: binary diffusion coefficient between i and k

- If and only if $\varepsilon_{i,j} < \varepsilon$, i and j are bundled into the same group
- Less than 20 needed for almost every fuel and reaction mechanism for about 10% worst-case error



Formulation of Diffusive Species Bundling

- ▶ Strategy: divide species to least numbers of group for given threshold error
- ▶ A **Binary Integer Programming** problem
- ▶ $x_i =$ 1: representative species
0: group member

$$\text{Minimize: } \sum_{i=1}^K x_i$$

$$\text{Subject to: } \sum_{j=1}^K A_{i,j} x_j \geq 1, i = 1, 2, \dots, K$$

$$x_i \in \{0, 1\}, i = 1, 2, \dots, K$$

User specified
error tolerance



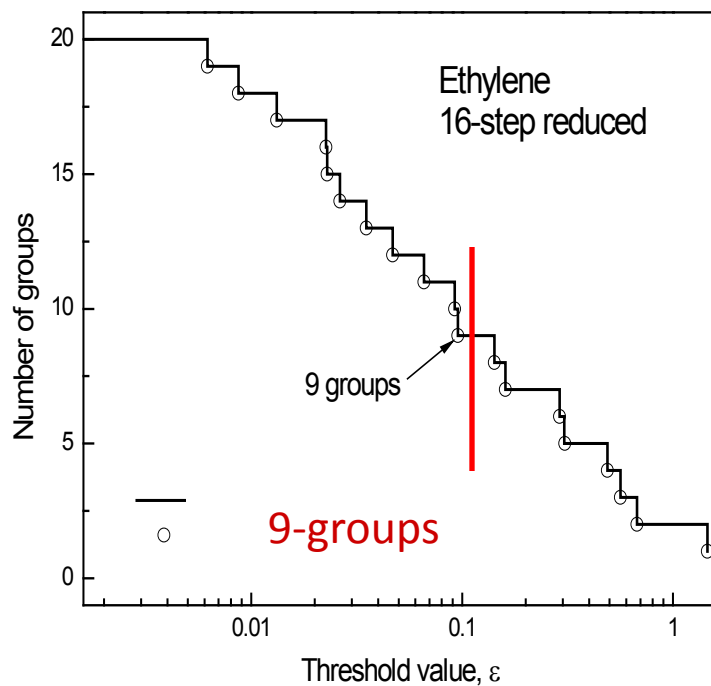
$$A_{i,j} = \begin{cases} 1, & \text{if } \varepsilon_{i,j} < \varepsilon \\ 0, & \text{otherwise} \end{cases}$$

$$\varepsilon_{i,j} = \max_{\substack{k=1, \dots, K \\ T_{\min} < T < T_{\max}}} \left| \ln \left(\frac{D_{i,k}}{D_{j,k}} \right) \right|$$

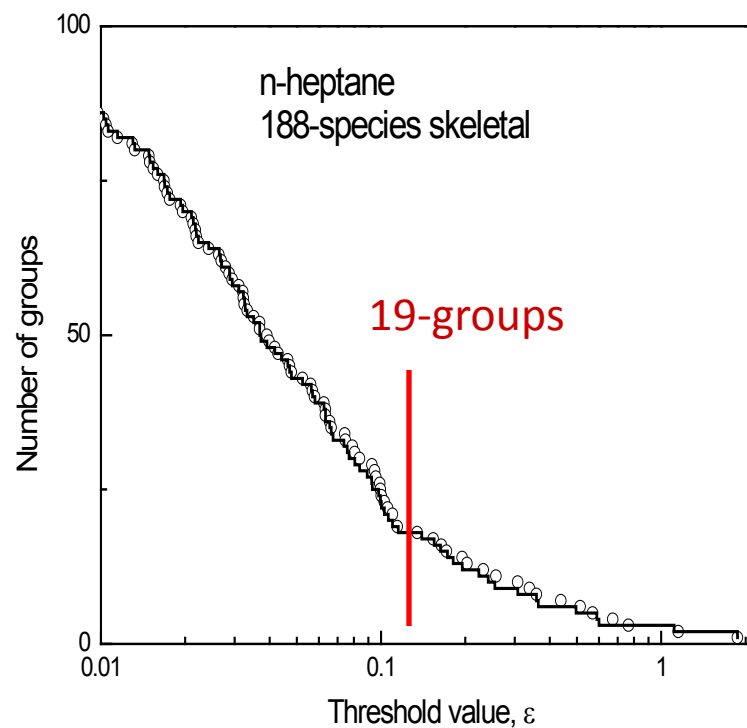


Reduction Curve

Ethylene, 20 species



Heptane, 188 species

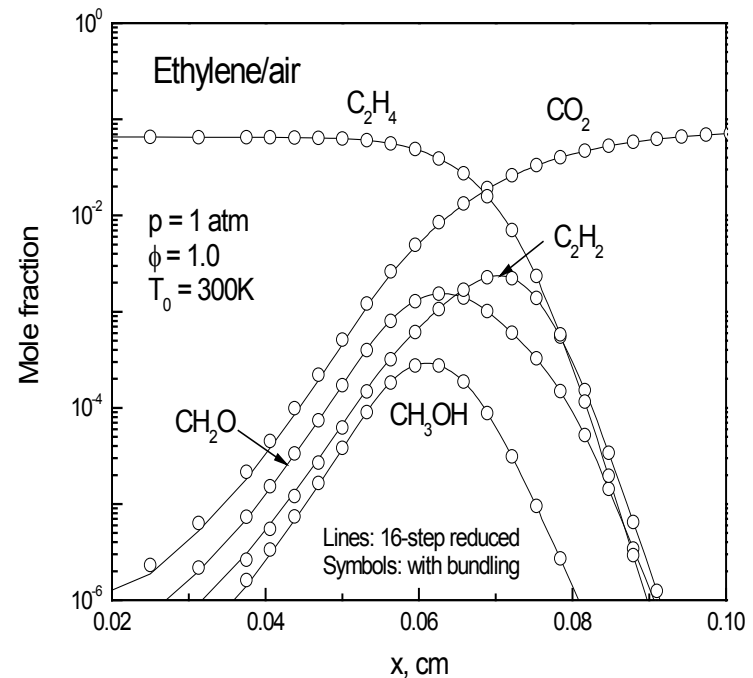
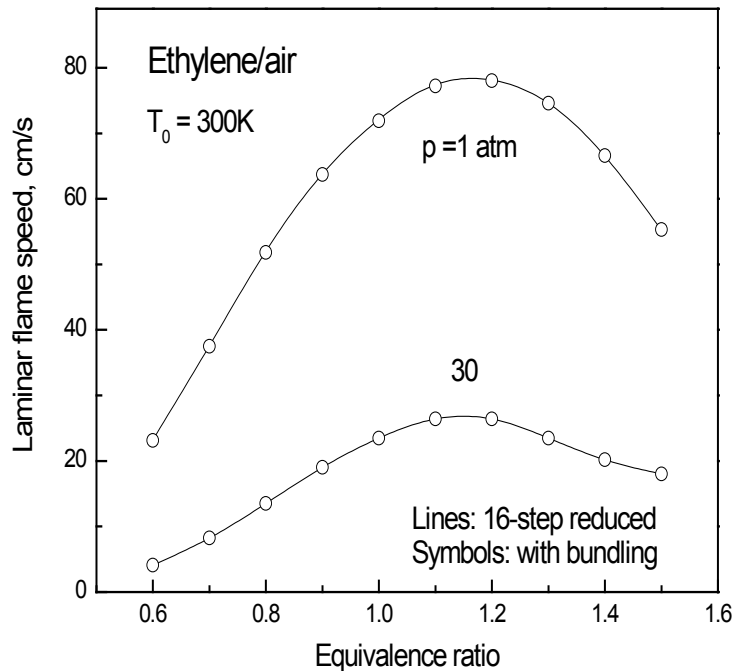




Validation - Ethylene

16-step: 20 species

With bundling: 9-groups





Further Reduction based on Reaction States Sampling

- *i*th species diffusivity w/ bundling

$$\bar{D}_i = \frac{1 - Y_i}{Q_{g(i)} - \frac{X_i}{DG_{g(i),g(i)}}}$$
$$Q_n = \sum_{m=1}^{KG} Q_{n,m}, Q_{n,m} = \frac{XG_m}{DG_{n,m}}$$

Not every $Q_{n,m}$ has the same effect on Q_n

$$I_{n,m} \equiv \frac{|Q_{n,m}|}{\max_{j=1,KG} |Q_{n,j}|}$$

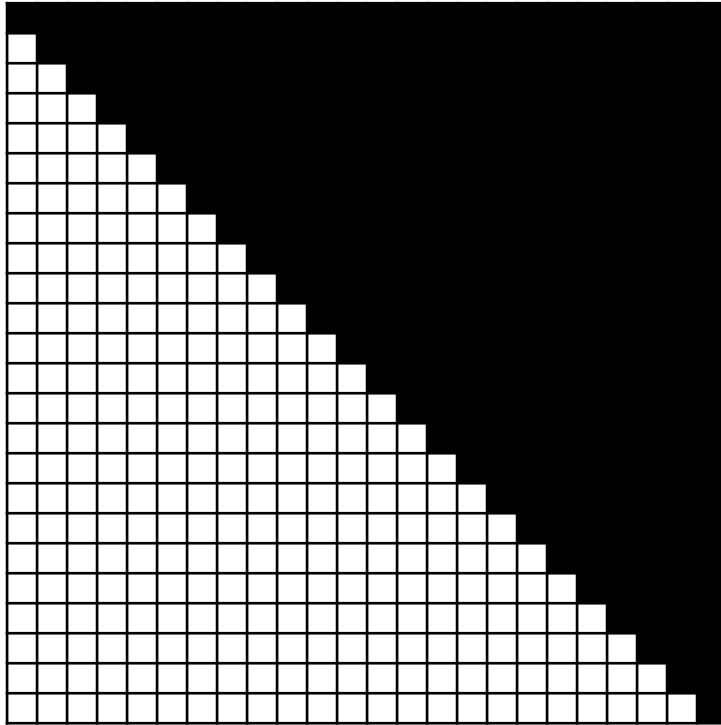
- If $I_{n,m} > \varepsilon$, $Q_{n,m}$ is large/important
→ $DG_{n,m}$ needs to be evaluated
- Primarily dominated by mole fraction XG_m

- $I_{n,m}$ depends on local condition
→ Sample from wide range of reaction states



Pattern of the Reduced Binary Diffusion Coefficient Matrix

Original, half 24×24



24-species *n*-dodecane reaction model (Gao et al., CNF 2016)

Reaction states sampling:

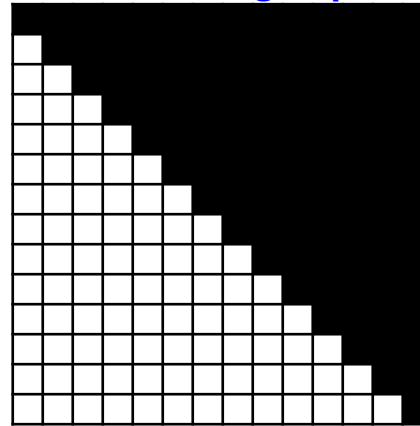
$p = 0.5\text{-}30$ atm

$\phi = 0.5\text{-}1.5$

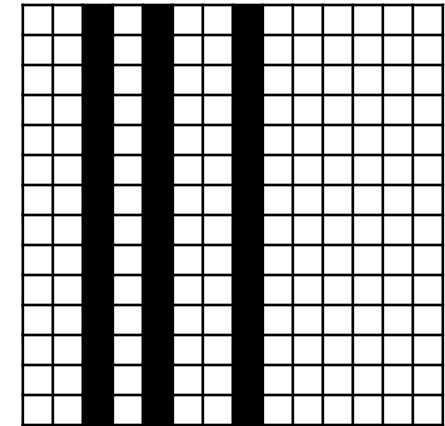
$T_0 = 1000\text{-}1600$ K for auto-ignition

$T_{in} = 300$ K for PSR

**Bundled, half 14×14
 $\varepsilon = 0.1$, 14 groups**



**Important binary coefficients
Method 1, $\varepsilon = 0.1$, 3 columns**



1) H₂O, 2) N₂, O₂, CO, HO₂, H₂O₂, 3) CO₂

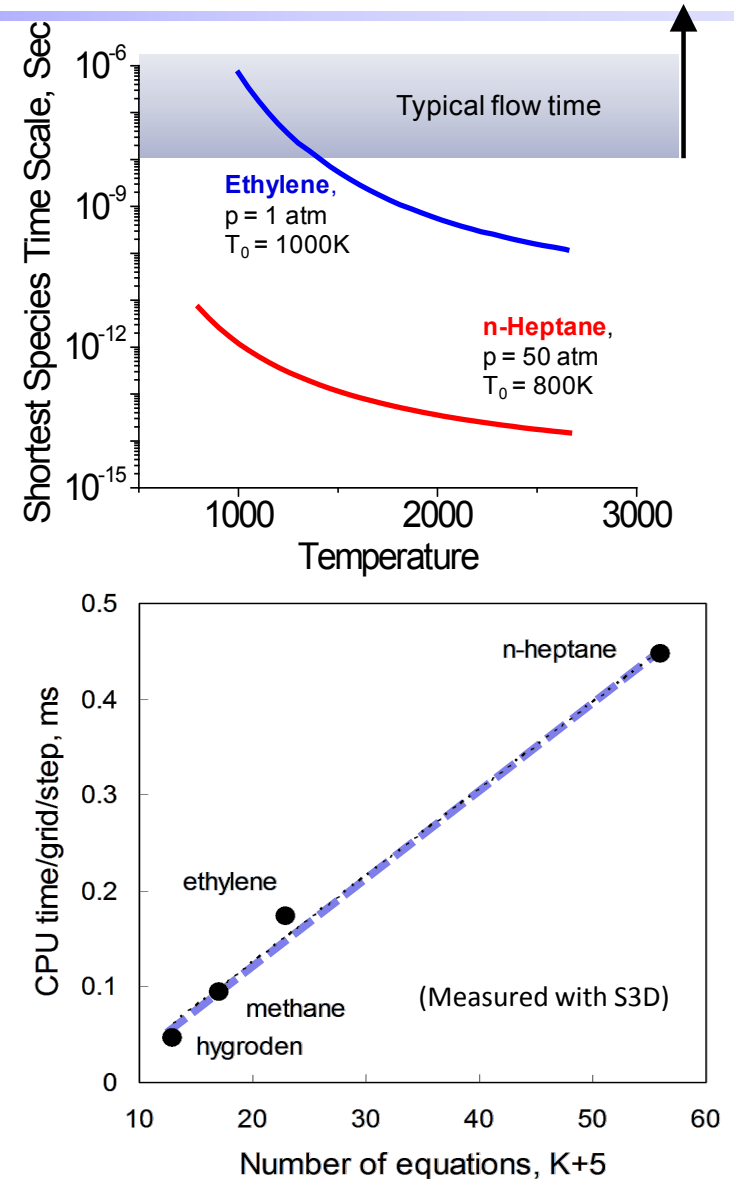
- The MAD model for *n*-dodecane is reduced to 3×14 groups with 10% worst-case error

Advanced Chemistry Solvers



Dynamic Chemical Stiffness Removal (DCSR) (Lu et al, CNF 2009)

- Mechanisms are still stiff after skeletal reduction & global QSSA
- Implicit solvers needed for stiff chemistry
 - Cost in evaluation of Jacobian $\sim O(K^2)$
 - Cost in factorization of Jacobian $\sim O(K^3)$
- Idea of DCSR
 - Chemical stiffness induced by fast reactions
 - Fast reactions results in either QSSA or PEA, Classified *a priori* Analytically solved on-the-fly
- Explicit solver can be used after DCSR
 - Time step limited by CFL condition
 - Cost of DNS: $\sim O(K)$
- Typically applicable to compressible flows with time steps $< \sim 20$ ns





The Strang Splitting Scheme

- Spatially discretized governing equations

$$\frac{d\Phi}{dt} = \mathcal{S}(\Phi) + \mathcal{T}(\Phi), \quad \mathcal{S}: \text{chemical}, \mathcal{T}: \text{transport}$$

- Chemistry and transport substeps:

$$\frac{d\Phi}{dt} = \mathcal{S}(\Phi^{(1)}), \quad \Phi^{(1)}(x, 0) = \Phi(x, t_n) \text{ on } [t_n, t_n + \Delta t/2]$$

$$\frac{d\Phi}{dt} = \mathcal{T}(\Phi^{(2)}), \quad \Phi^{(2)}(x, 0) = \Phi^{(1)}(x, \Delta t/2) \text{ on } [t_n, t_n + \Delta t]$$

$$\frac{d\Phi}{dt} = \mathcal{S}(\Phi^{(3)}), \quad \Phi^{(3)}(x, 0) = \Phi^{(2)}(x, \Delta t) \text{ on } [t_n + \Delta t/2, t_n + \Delta t]$$

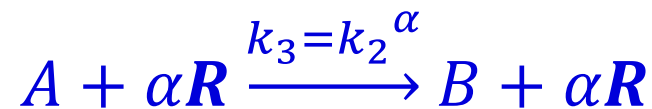
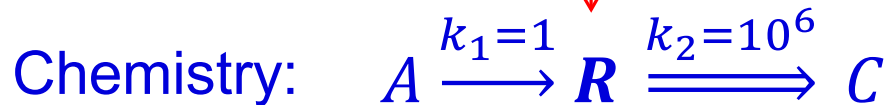
- Could the splitting incur major problems?



A Toy Problem

Transport:

$$T_R = 1$$

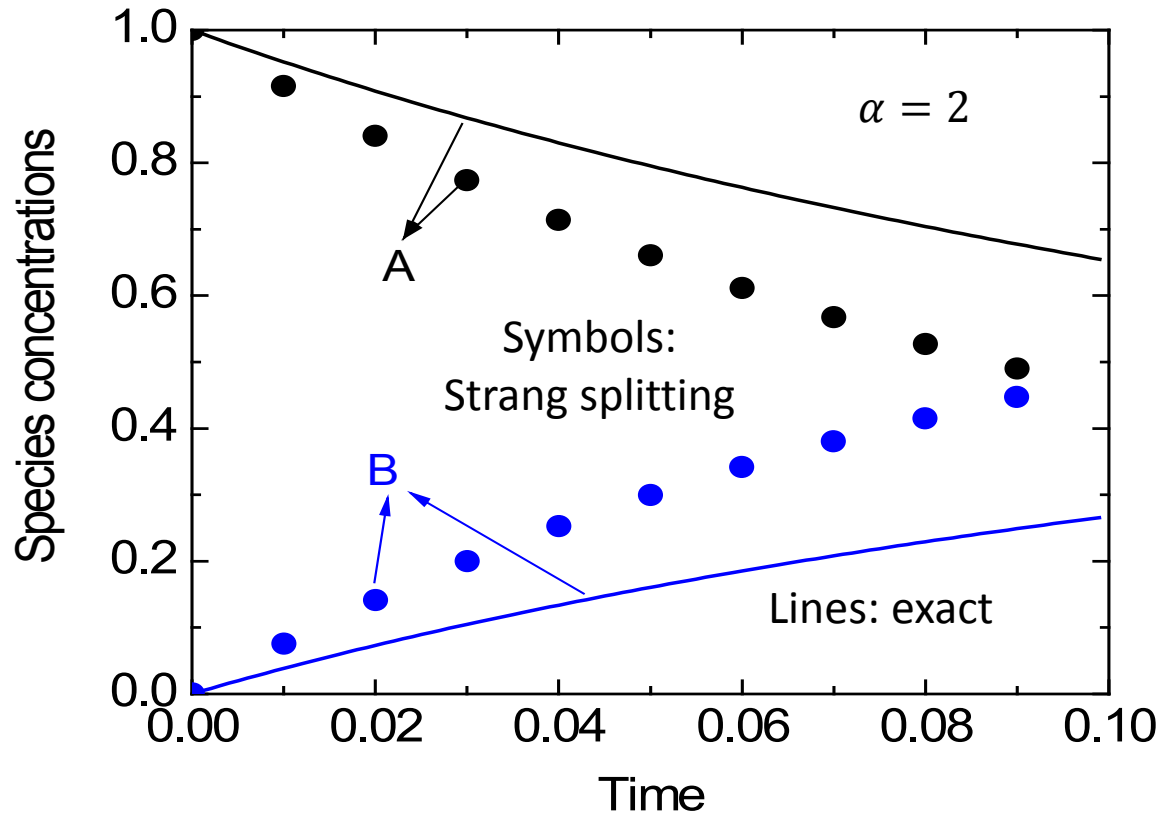


Radical \mathbf{R} :

- ▶ Timescale: $\tau = k_2^{-1} = 10^{-6} \rightarrow$ stiffness
- ▶ In quasi steady state (QSS): $\omega_2 \approx (\omega_1 + T_R)$
- ▶ Transport source (T_R) \sim chemical formation rate (ω_1)
- ▶ R is catalytic for the main path (R_3)
- ▶ $\alpha \neq 1$ induces nonlinearity



O(1) Errors in Strang-Splitting



- ▶ Sufficiently small splitting time step: $\Delta t = 10^{-5}$
- ▶ Fully-explicit integration applicable at $\Delta t = 10^{-6}$



Mechanism of the Error: Erroneous Radical Concentrations

- R is in QSS:

$$\underbrace{\omega_2 = k_2 R}_{\text{consumption rate}} \approx \underbrace{\omega_1 + T_R}_{\text{production rate}} = k_1 A + T_R$$

- Correct concentration:

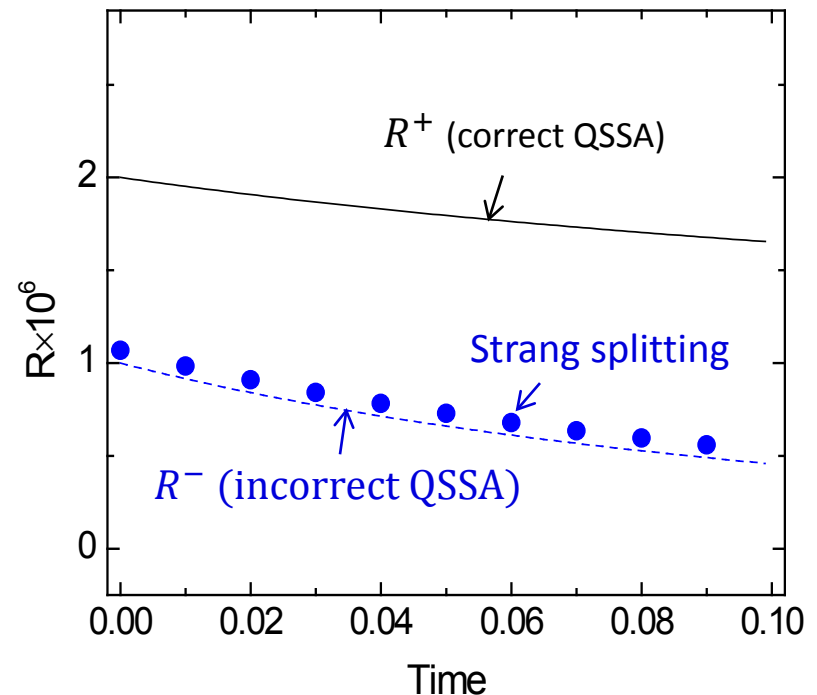
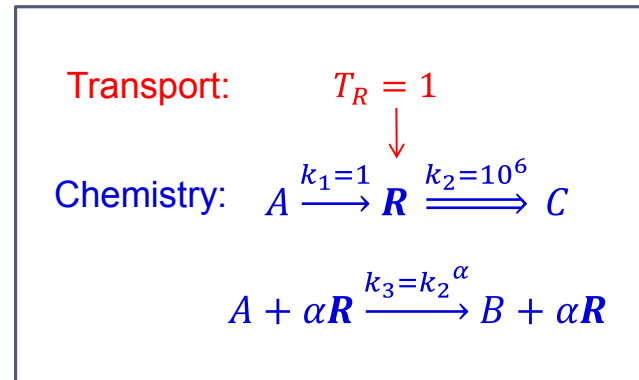
$$R^+ \approx \frac{k_1 A + T_R}{k_2}$$

- Excluding transport:

$$R^- \approx \frac{k_1 A}{k_2} < R^+$$

- Error source:

Splitting chemical & transport
→ incorrect radical pool level
→ incorrect reactivity





Development of Advanced Chemistry Solvers: Dynamic Adaptive Hybrid Integration (AHI)

- Governing equations

$$\frac{d\Phi}{dt} = \mathcal{S}(\Phi) + \mathcal{T}(\Phi), \quad \mathcal{S}: \text{chemical source}, \mathcal{T}: \text{transport}$$

- Integrate chemistry and transport together
 - Fast chemistry treated implicitly
 - Slow chemistry & transport treated explicitly
(cost comparable to splitting schemes)
 - Fast species & reactions identified by a CSP criterion (Lam CNF 2013)
 - A 1st order scheme constructed (Gao et al, CNF 2015)

$$\frac{d}{dt} \begin{bmatrix} \Phi_f \\ \Phi_s \end{bmatrix} = \mathcal{S}_f + \mathbf{g}_s$$

$$\mathcal{S}_f = \sum_{i=1}^m \nu_i \Omega_i,$$

Fast chemistry

$$\mathbf{g}_s = \sum_{i=m+1}^{n_r} \nu_i \Omega_i + \mathcal{T}$$

Slow chemistry & transport

Separation of Fast & Slow Chemistry



- Timescale of a reaction (Lam, CNF 2013)

$$\tau_i \equiv |\mathbf{J}_i \cdot \mathbf{v}_i|^{-1}, \mathbf{J}_i = \frac{\partial \Omega_i}{\partial \mathbf{c}} = \begin{bmatrix} \frac{\partial \Omega_i}{\partial c_1} & \frac{\partial \Omega_i}{\partial c_2} & \dots & \frac{\partial \Omega_i}{\partial c_k} & \dots & \frac{\partial \Omega_i}{\partial c_{n_s}} \end{bmatrix}$$

\mathbf{J}_i : Jacobian of reaction rate Ω_i , \mathbf{v}_i : stoichiometric coefficients

- Criterion for a fast reaction (i)

$$\tau_i < \tau_c, \quad \tau_c : \text{typically the integration time step}$$

- Criterion for a fast species (k)

$$\left| \frac{\partial \Omega_i}{\partial c_k} \right|^{-1} < \tau_c, \quad \text{any } i$$

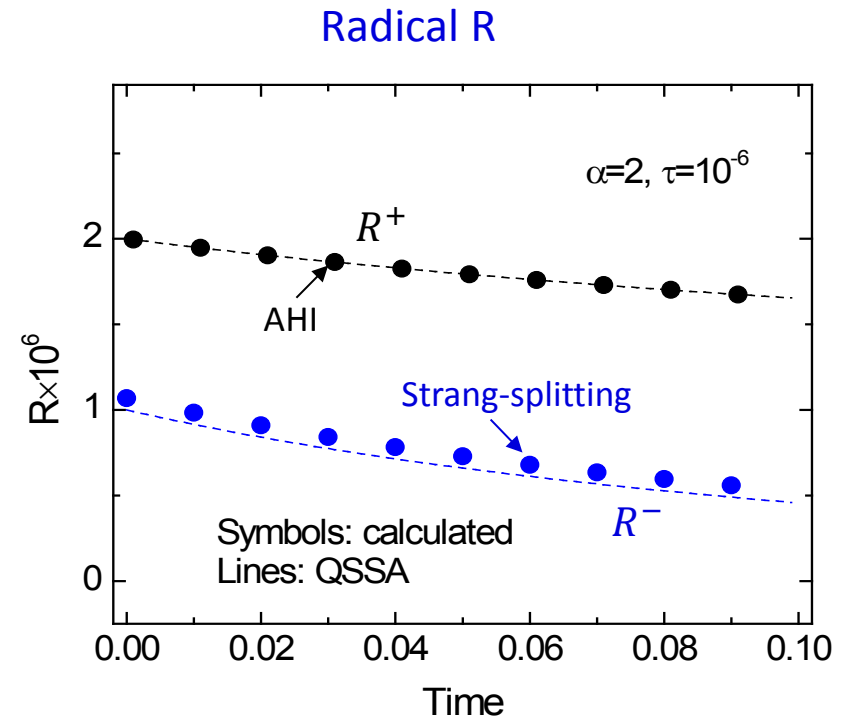
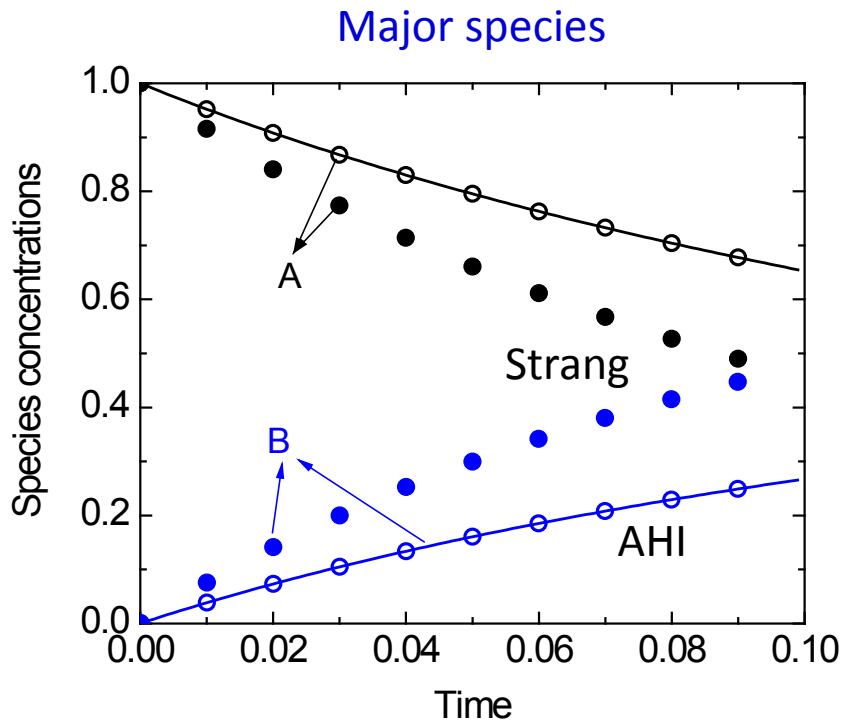
- A first-order AHI scheme

$$\frac{1}{h} \begin{bmatrix} \Phi_f^{n+1} - \Phi_f^n \\ \Phi_s^{n+1} - \Phi_s^n \end{bmatrix} = \mathbf{S}_f(\Phi_f^{n+1}, \Phi_s^n) + \mathbf{g}_s(\Phi_f^n, \Phi_s^n)$$

n : the n th integration step, h : time step size



Comparison with Strang-Splitting

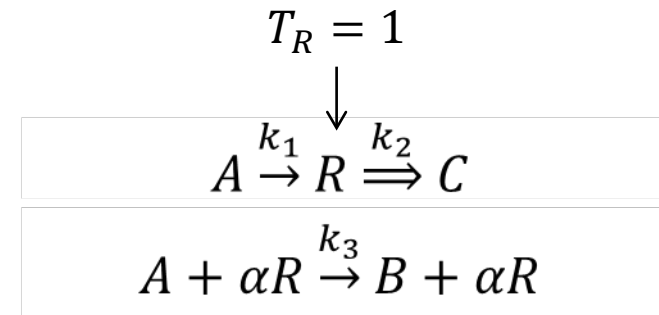
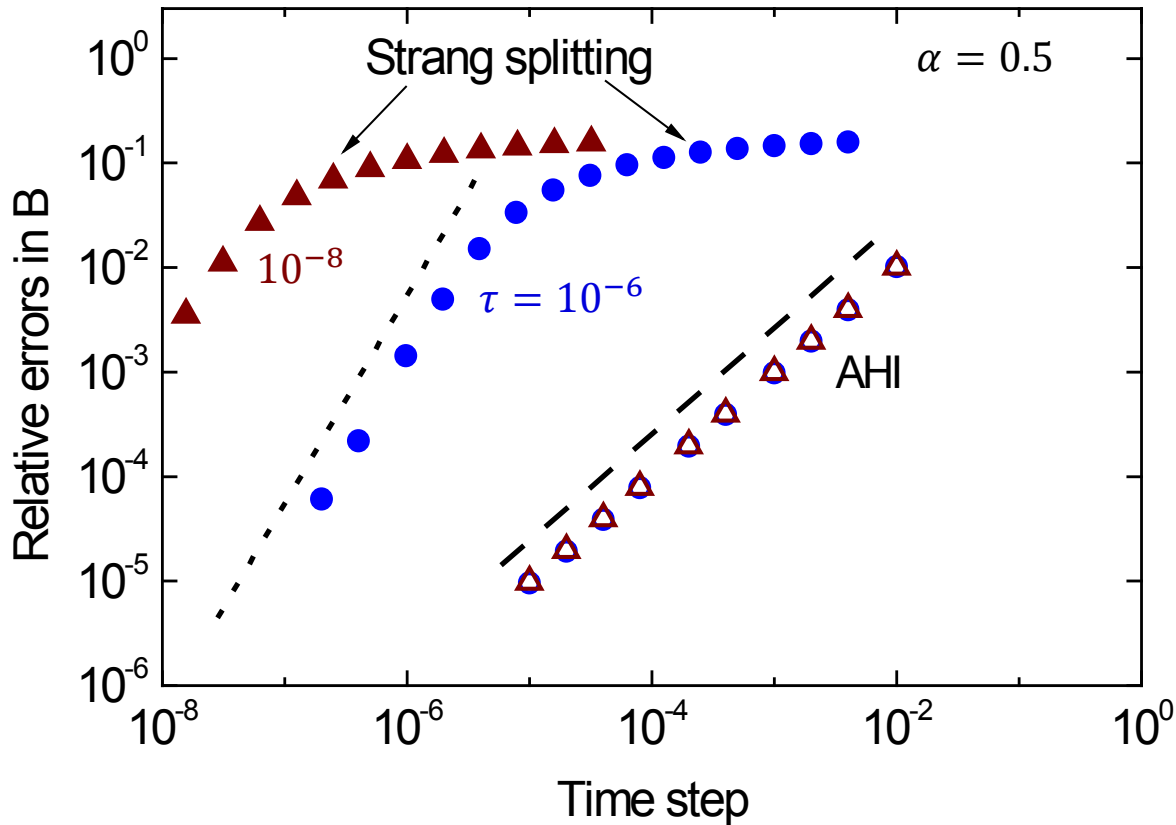


$$\Delta t = 10^{-5}$$

- Strang-Splitting: $O(1)$ errors in every species
- AHI: errors suppressed



Comparison with Strang Splitting: Accuracy for a Toy Problem

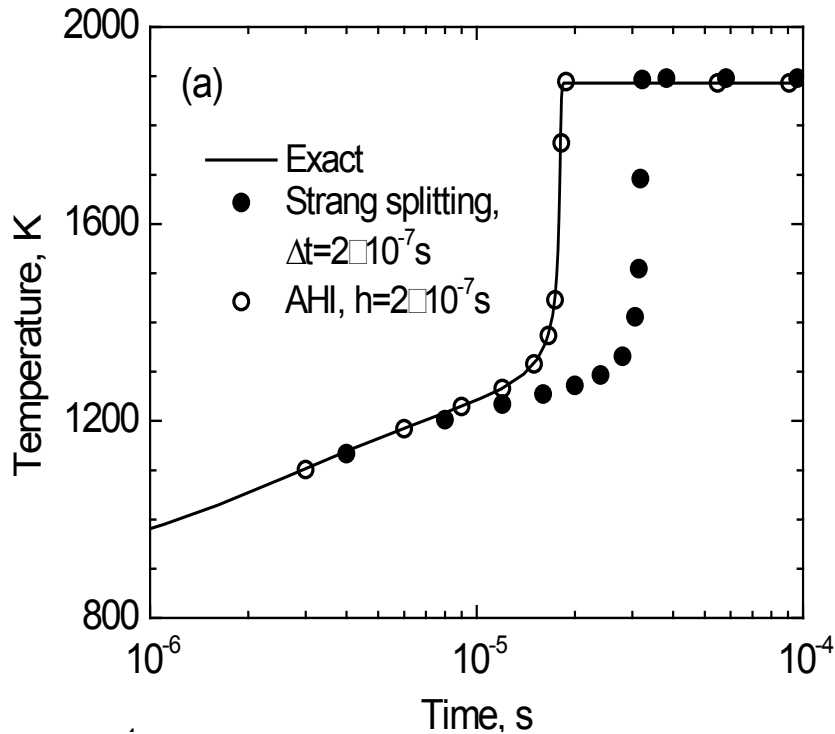


Timescale of R:
 $\tau = k_2^{-1} = 10^{-6}$

- Strang splitting: time step $\sim O(\tau)$ to show 2^{nd} order behavior
- AHI (1^{st} order): error significantly smaller and independent of τ

AHI vs. Splitting for H₂/Air

Force Ignition of H₂/air in PSR



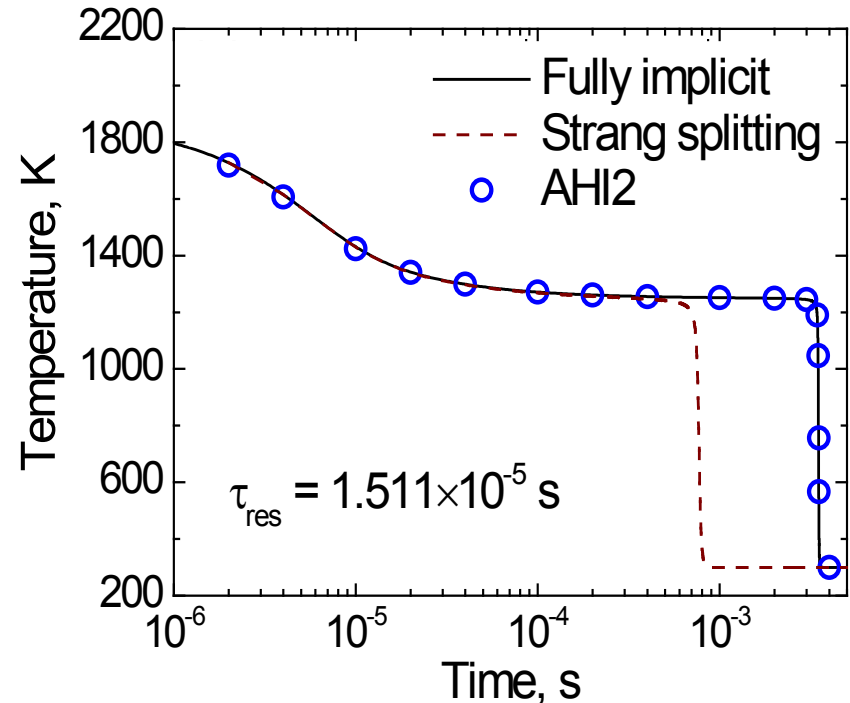
2% H at inlet stream (mole)

$p = 80 \text{ atm}, T_0 = T_{in} = 875 \text{ K}, \phi = 0.3$

$\Delta t = 2 \times 10^{-7} \text{ s}$

(Gao et al., CNF 2015)

Extinction of H₂/air in PSR



Initial condition perturbed from the extinction turning point

$p = 1 \text{ atm}, T_{in} = 300 \text{ K}, \phi = 1$

$\Delta t = 2 \times 10^{-6} \text{ s}$

(Gao et al., US Meeting 2015)



Analytic & Sparse Jacobian Techniques

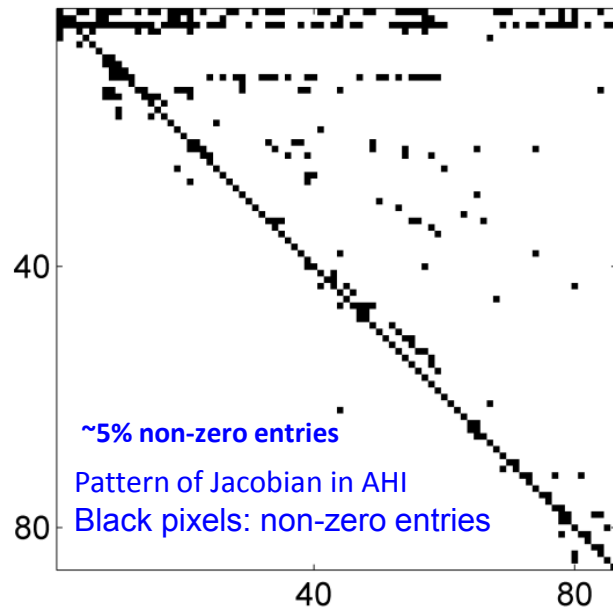
- Chemical Jacobian is sparse, even sparser with AHI
- High computational efficiency can be achieved by combining analytic Jacobian, AHI, Sparse techniques (AHI-S) (Xu et al., CNF submitted)

111-species USC-Mech II, CH₄/air

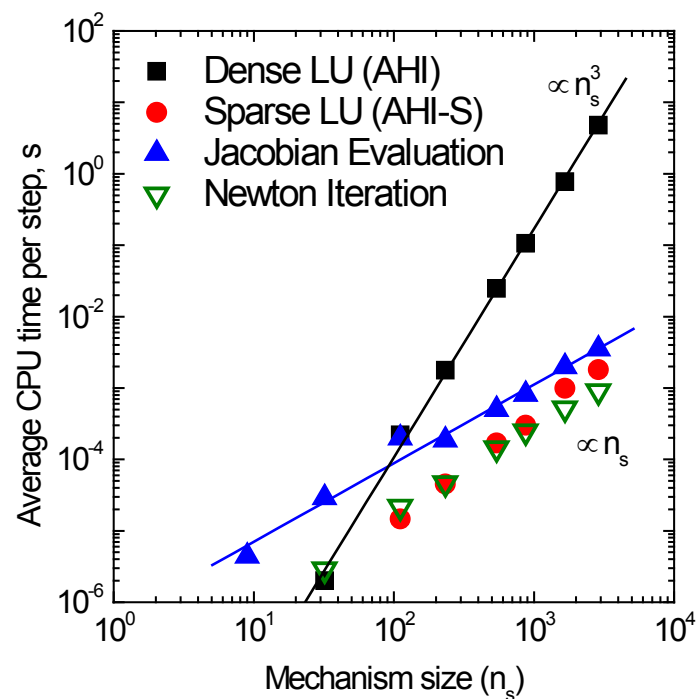
$\phi = 0.5$, $p = 50$ atm

$T_0 = 1200$ K, $\Delta t = 10^{-7}$ s

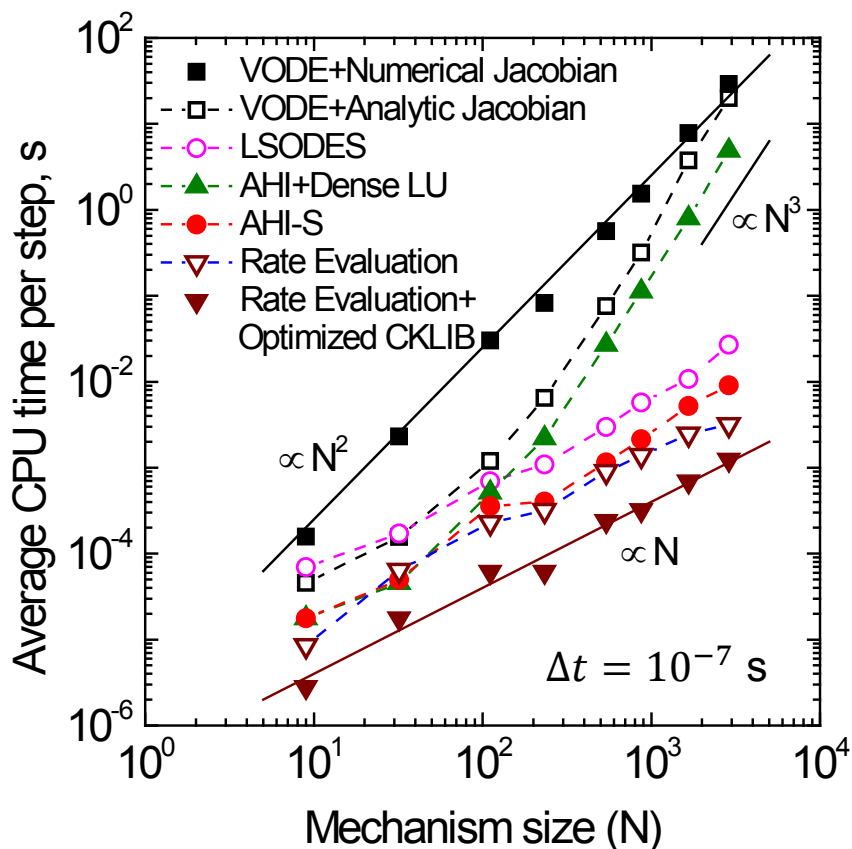
Time instance : $2\tau_{ign}$



Cost of major operations in typical stiff chemistry solvers



Comparison of Chemistry Solvers



VODE+Numerical Jacobian: $O(n_s^3)$

VODE+Analytic Jacobian: $O(n_s) \sim O(n_s^3)$

AHI+Dense LU: $O(n_s) \sim O(n_s^3)$

AHI-S: $O(n_s)$

Rate evaluation (CKLIB): $O(n_s)$

Rate evaluation (Optimized CKLIB): $O(n_s)$

CPU cost of **AHI-S**

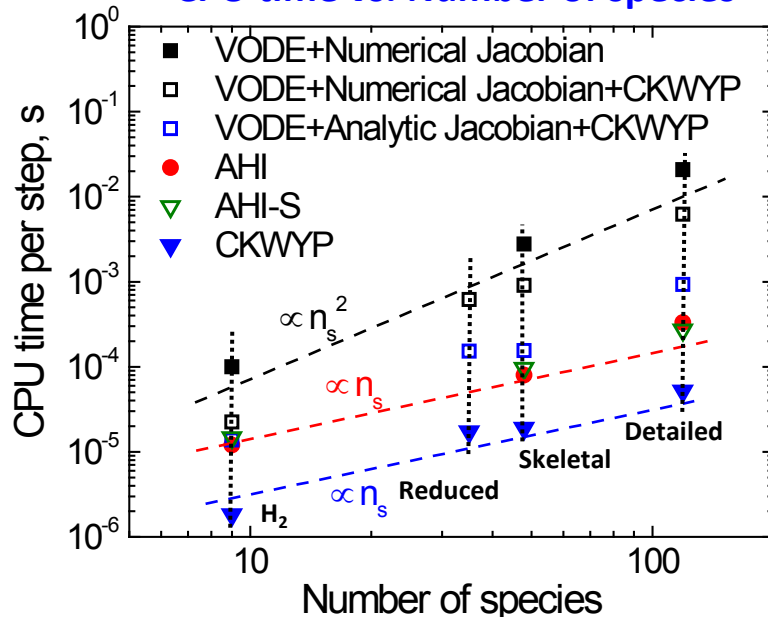
- ▶ Linearly correlated to mechanism size
- ▶ Much faster than dense solvers
- ▶ Up to 3 times as that of one rate evaluation using **CKLIB**



Advanced Chemistry Solvers for the Universal Reduced HyChem Model

- Implemented in HyChem models (fuel specific & universal)
 - Analytic Jacobian & Optimized rate subroutines (CKWYP)
 - Dynamic chemical stiffness removal + Explicit solver (Non-stiff reduced models)
 - AHI & AHI-S (sparse LU)
- Speedup by $O(10-100)$ without loss of accuracy
- Linear time scaling with mechanism size (explicit & explicit)

CPU time vs. Number of species



CPU time (s) per step

Solver	Reduced	Skeletal	Detailed
VODE + Num. Jac	N/A	2.8E-3	2.1E-2
VODE + Num. Jac + CKWYP	6.2E-4	9.1E-4	6.2E-3
VODE + Analytic Jac + CKWYP	1.5E-4	1.6E-4	9.3E-4
AHI	N/A	8.0E-5	3.3E-4
AHI-S	N/A	9.6E-5	2.7E-4
CKWYP (non-stiff)	1.7E-5	1.9E-5	5.2E-5

H₂ : 9 species
Universal reduced: 35 species
Universal skeletal: 48 species
Detailed HyChem: 119 species



Concluding Remarks

- Important aspects for model reduction
 - Sampling of representative reaction states
 - Effective error control/comprehensive validation
 - Be careful with rate parameter tuning
 - HyChem with systematic reduction can yield highly compact reduced models for high temperature real fuel applications
- Important aspects for advanced chemistry solvers
 - Be careful in using splitting schemes for forced-ignition and extinction problems
 - Substantial efficiency improvement can be achieved by using advanced chemistry solvers without loss of accuracy
 - Explicit time integration is possible for compressible flow simulations
 - Linear scaling is possible for both implicit solvers and explicit solvers with chemical stiffness removal