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Skeletal Mechanism Generation for Surrogate Fuels

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Outline of Presentation

- Motivation
- Objectives
- Description of Methodology
  - MARS
  - DRGEPSA
- Results
  - *n*-heptane
  - *iso*-octane
  - *n*-decane
- Conclusions and Future Work

Importance of Combustion

- Combustion of hydrocarbons: 85% of the US power production
- Demand to improve efficiency and reduce emissions:
  - Dwindling fuel sources and rising costs
  - Climate concerns due to emissions
- New combustor and engine designs driven by computational modeling
  - Advancements in computing power and numerical methods (e.g. RANS/LES) allow practical simulations
  - Integration of chemistry modeling requires special treatment

Importance of Detailed Chemistry

- Real fuels (e.g. gasoline, diesel, jet fuels) contain complex blends of hydrocarbons: **surrogate** models have been developed that contain mixtures of a small number of component species
- One- or multi-step semi-global reactions used historically to enable inclusion of chemistry
  - e.g. methane oxidation: $CH_4 + 2O_2 \rightarrow 2H_2O + CO_2$
  - Suitable for equilibrium, but inadequate over wide ranges of conditions as well as phenomena such as ignition and extinction
- Accurate prediction of fuel combustion and pollutant emissions requires comprehensive detailed chemical reaction mechanisms

Need for Mechanism Reduction

- However, detailed mechanisms for hydrocarbons of interest contain too many species/reactions and time scales to be used in practical simulations.
  - Detailed mechanism for *n*-alkanes C_8-C_{16}: **2115 species** and **8157 reactions** (Westbrook et al. *CNF* 2009)
  - Detailed mechanism for biodiesel surrogate methyl-decanoate: **2878 species** and **8555 reactions** (Herbinet et al. *CNF* 2009)
- Reduction of these large mechanisms is needed.
  - Reduce number of species and reactions
  - Eliminate fast time scales to reduce stiffness

Mechanism Reduction Overview

- Two major categories of mechanism reduction:
  - Skeletal reduction
    - elimination of unimportant species and/or reactions
    - typically the first step in a integrated reduction scheme
    - focus of the current work
  - Time scale-based reduction
    - Eliminate short time scales in reaction system to reduce stiffness
    - CSP, ILDM: Jacobian analysis to decouple fast and slow modes
    - QSS species and PE reactions: replace differential equations with algebraic relations to solve for concentrations of QSS species

Skeletal Reduction Methods

Skeletal reduction: removal of unimportant species and reactions to reduce mechanism size

- Sensitivity analysis (Rabitz 1983, Turányi 1990)
- CSP (Valorani 2006, 2007; Prager 2009)
- Optimization (Bhattacharjee 2003, Oluwole 2006, Mitsos 2008)
- Level of importance (Løvås 2009)
- Simulation error minimization connectivity method (Nagy 2009)
- Directed relation graph (**DRG**) (Lu 2005)
  - DRG with error propagation (**DRGEP**) (Pepiot-Desjardins 2008)
  - DRG-aided sensitivity analysis (**DRGASA**) (Lu 2007)
  - Path Flux Analysis (Sun 2009)

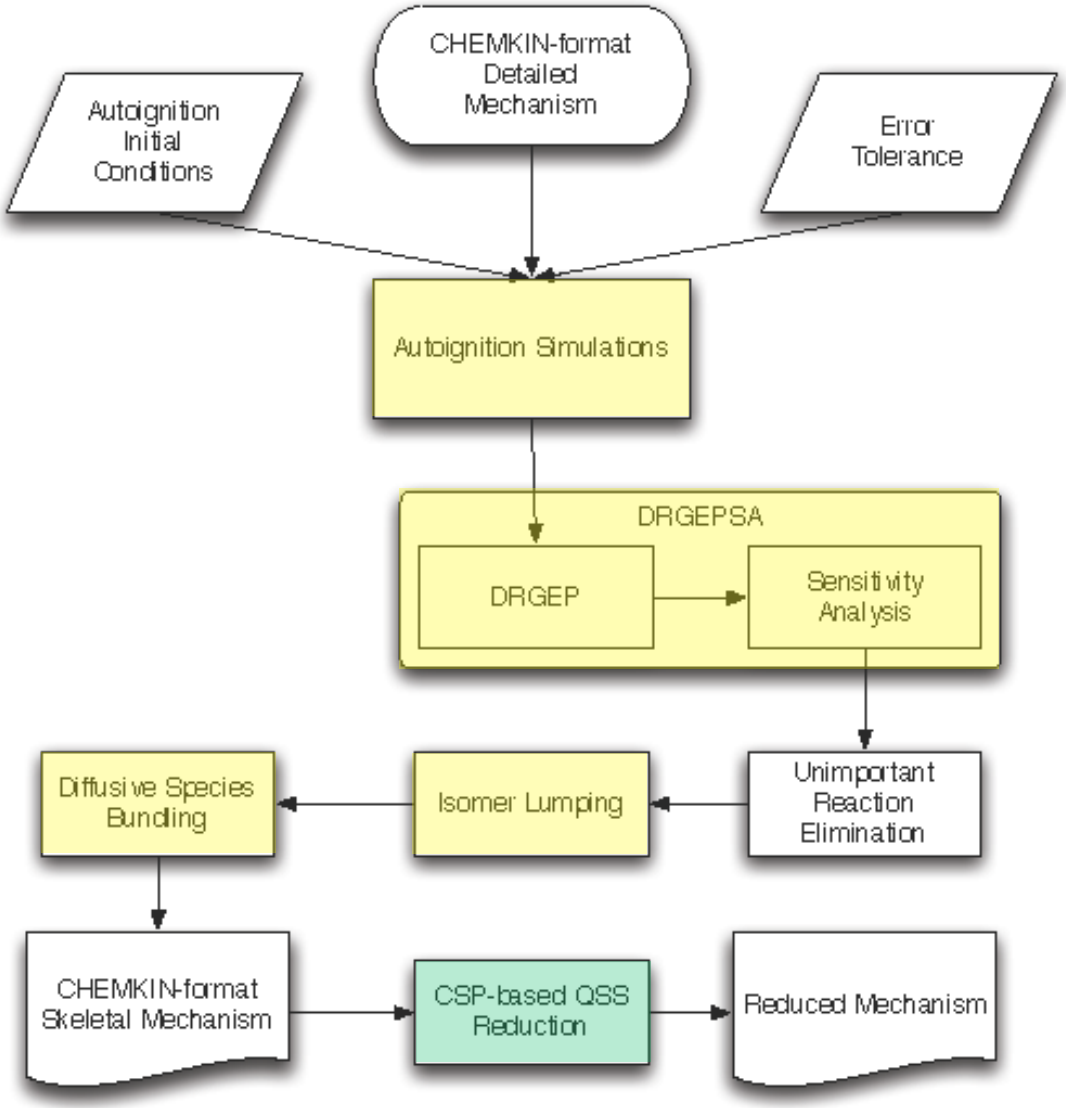
Current Approach:

- Directed Relation Graph with Error Propagation and Sensitivity Analysis (**DRGEPSA**)

Objectives

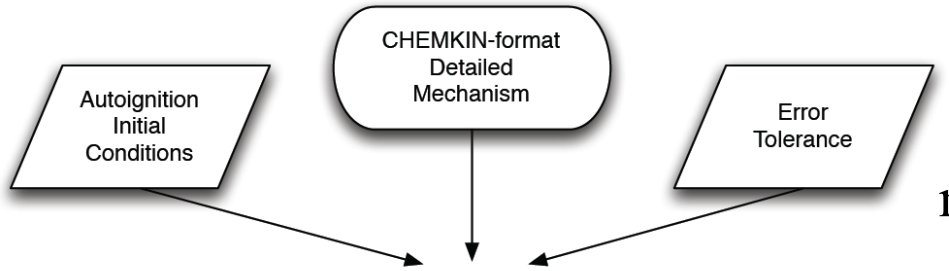
- Develop computationally efficient and robust suite for automatic generation of skeletal and reduced mechanisms at various levels of complexity with limited user input
  - Mechanism Automatic Reduction Software (MARS)
- Detailed description of skeletal reduction method DRGEPSA
- Demonstration of mechanism reduction capability using detailed LLNL mechanisms of *n*-heptane, *iso*-octane, and *n*-decane
- Demonstration of validity of *n*-decane high-temperature skeletal mechanism using perfectly stirred reactor (PSR) and laminar flame (PREMIX) simulations

Mechanism **A**utomatic **R**eduction **S**oftware (**MARS**)



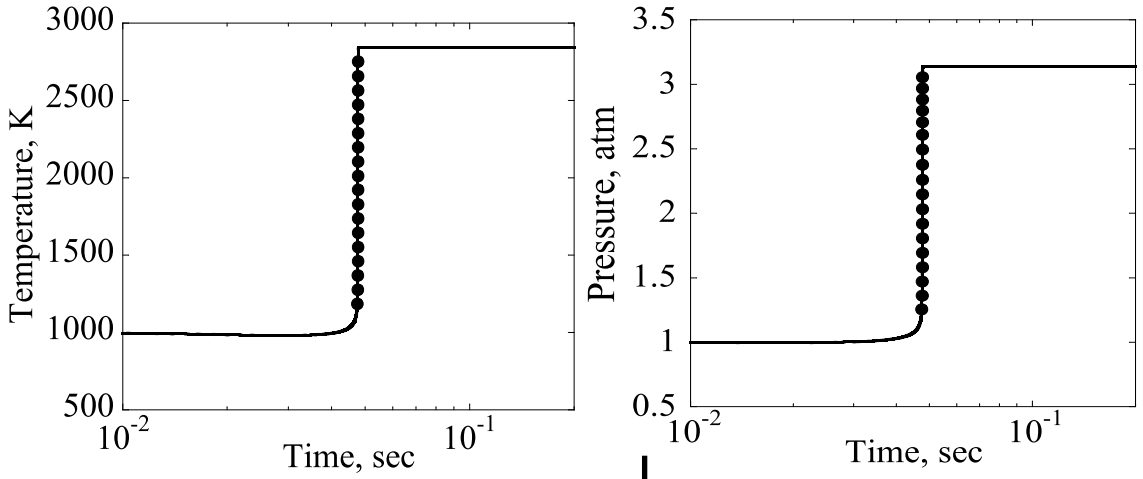
MARS/DRGEPSA

Wide Range T_0 P_0 ϕ



$$\max \frac{|\tau_{skel} - \tau_{det}|}{\tau_{det}}$$

Constant Volume Autoignition



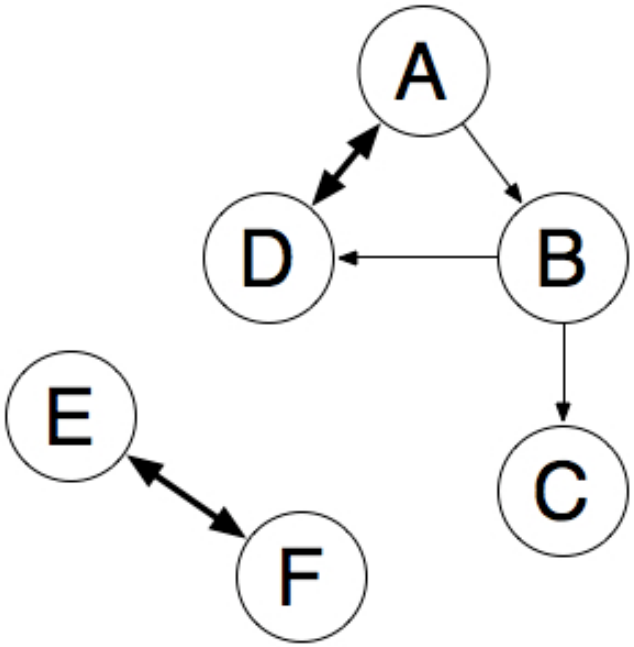
Skeletal Mechanism ← DRGEP

Final Skeletal Mechanism ← Skeletal Mechanism ↕ SA

Directed Relation Graph (DRG)

- Method used to develop skeletal mechanisms at various levels of complexity.
- Graph theory-based method to identify important species for designated target species using a normalized contribution value.
- Efficient method to identify and eliminate unimportant species.

DRG/DRGASA Method (1)



- Coupling of species determined by normalized contribution to overall production
- Directed arrow shows dependence of one species to another.

$$r_{AB}^{DRG} \equiv \frac{\left|\sum_{i=1,I} \nu_{A,i}\omega_i\delta_B^i\right|}{\left|\sum_{i=1,I} \nu_{A,i}\omega_i\right|}$$

r_{AB}^{DRG} – normalized interaction coefficient of species B to the production of species A

$\nu_{A,i}$ – stoichiometric coefficient for the i^{th} elementary reaction for species A

ω_i – production rate of the i^{th} reaction

$$\delta^i_B = \begin{cases} 1, & \text{if the } i^{th} \text{ reaction involves species B,} \\ 0, & \text{otherwise} \end{cases}$$

DRG/DRGASA Method (2)

- Species *B* where $r_{AB}^{DRG} < \varepsilon_{DRG}$ is removed from the dependent set for target species *A* (ε_{DRG} is a small value, e.g. 0.1).
- Skeletal mechanism consists of set of dependent species for designated target species (fuel, oxidizer, important pollutants, etc) based on depth first search.
- Species with $\varepsilon_{DRG} < r_{AB}^{DRG} < \varepsilon^*$ (e.g. 0.4) are then analyzed with sensitivity analysis to produce a minimal skeletal mechanism for a given error threshold.

DRGEP Method (1)

$$r_{AB} \equiv \frac{\left|\sum_{i=1,I} \nu_{A,i}\,\omega_i\,\delta^{i}{}_{B}\right|}{\max\left(P_A, C_A\right)}$$

$$P_A = \sum_{i=1,I} \max\left(0, \nu_{i,A}\,\omega_i\right)$$

$$C_A = \sum_{i=1,I} \max\left(0, -\nu_{i,A}\,\omega_i\right)$$

- Extension of DRG considering error propagation along species paths
- Identifies more unimportant species for an equivalent error
- Species B where $R_{AB} < \varepsilon_{EP}$ is removed from the dependent set for target species A

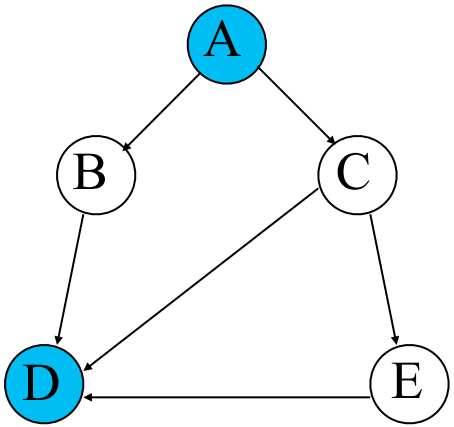
$$r_{AB,p} = \prod_{i=1}^{n-1} r_{S_i S_{i+1}}$$

$$R_{AB} = \max_{\text{all paths } p}\left(r_{AB,p}\right)$$

$r_{AB,p}$ – path-dependent interaction coefficient for path p between species A and B

R_{AB} – Overall Interaction Coefficient (OIC)

DRGEP Method (2)



$$R_{AD}^{\mathrm{DRG}} = \max\left(r_{AB}, r_{BD}, r_{AC}, r_{CD}, r_{CE}, r_{ED}\right)$$

$$R_{AD}^{\mathrm{DRGEP}} = \max\left(r_{AD,1}, r_{AD,2}, r_{AD,3}\right)$$

$$r_{AD,1} = r_{AB} \cdot r_{BD}, \quad r_{AD,2} = r_{AC} \cdot r_{CD}, \quad r_{AD,3} = r_{AC} \cdot r_{CE} \cdot r_{ED}$$

R_{AD} is the overall interaction coefficient of species D to the target species A

DRGEPSA vs. DRGASA

- Sensitivity analysis (SA) included to eliminate more unimportant species, but computationally expensive
- By using DRGEP prior to SA phase, more species can be removed than with DRGASA to produce a smaller final mechanism for the same mechanism performance.
- DRGEP alone is insufficient because the relationship between interaction coefficient and induced error in global properties is unclear for some species, requiring sensitivity analysis.

DRGEPSA Method (1)

- DRGEP produces a preliminary skeletal mechanism.
  - *Removed species*: $R_{AB} < \varepsilon_{EP}$
- Species are classified into two categories based on overall interaction coefficient:
  - *Limbo species:* $\varepsilon_{EP} < R_{AB} < \varepsilon^*$ (e.g. 0.2)
    - analyzed with SA
  - *Retained species:* $R_{AB} > \varepsilon^*$
    - retained in mechanism without analysis

DRGEPSA Method (2)

- Iterative error threshold (ε_{EP}) selection:
  - Initial low ε_{EP} used (e.g. 0.01) to generate preliminary skeletal mechanism
  - Error of skeletal mechanism:

$$\delta_{\text{skel}} = \max_{k \in \mathcal{D}} \frac{\left| \tau_{\text{det}}^{k} - \tau_{\text{skel}}^{k} \right|}{\tau_{\text{det}}^{k}}$$

  - If error is above user-defined error limit, ε_{EP} is lowered and procedure repeats
  - If error is below error limit, ε_{EP} is raised until the error reaches the limit
  - In this manner, the optimal skeletal mechanism (for given error limit) using DRGEP is generated

DRGEPSA Method (3)

- SA is performed by removing each species in the limbo category one at a time and calculating the induced error
- Species are arranged in order using:

$$\delta_B = \left|\delta_{B,\mathrm{ind}} - \delta_{\mathrm{DRGEP}}\right|$$

  - δ_{DRGEP}: error of DRGEP-generated skeletal mechanism
  - $\delta_{B,ind}$: error induced by removal of species *B*
  - Many species do not change the mechanism performance compared to the DRGEP mechanism, so using induced errors alone for ranking would be not correctly capture sensitivity
- The final skeletal mechanism is generated by removing species one at a time in order until the resulting error reaches the required tolerance level.

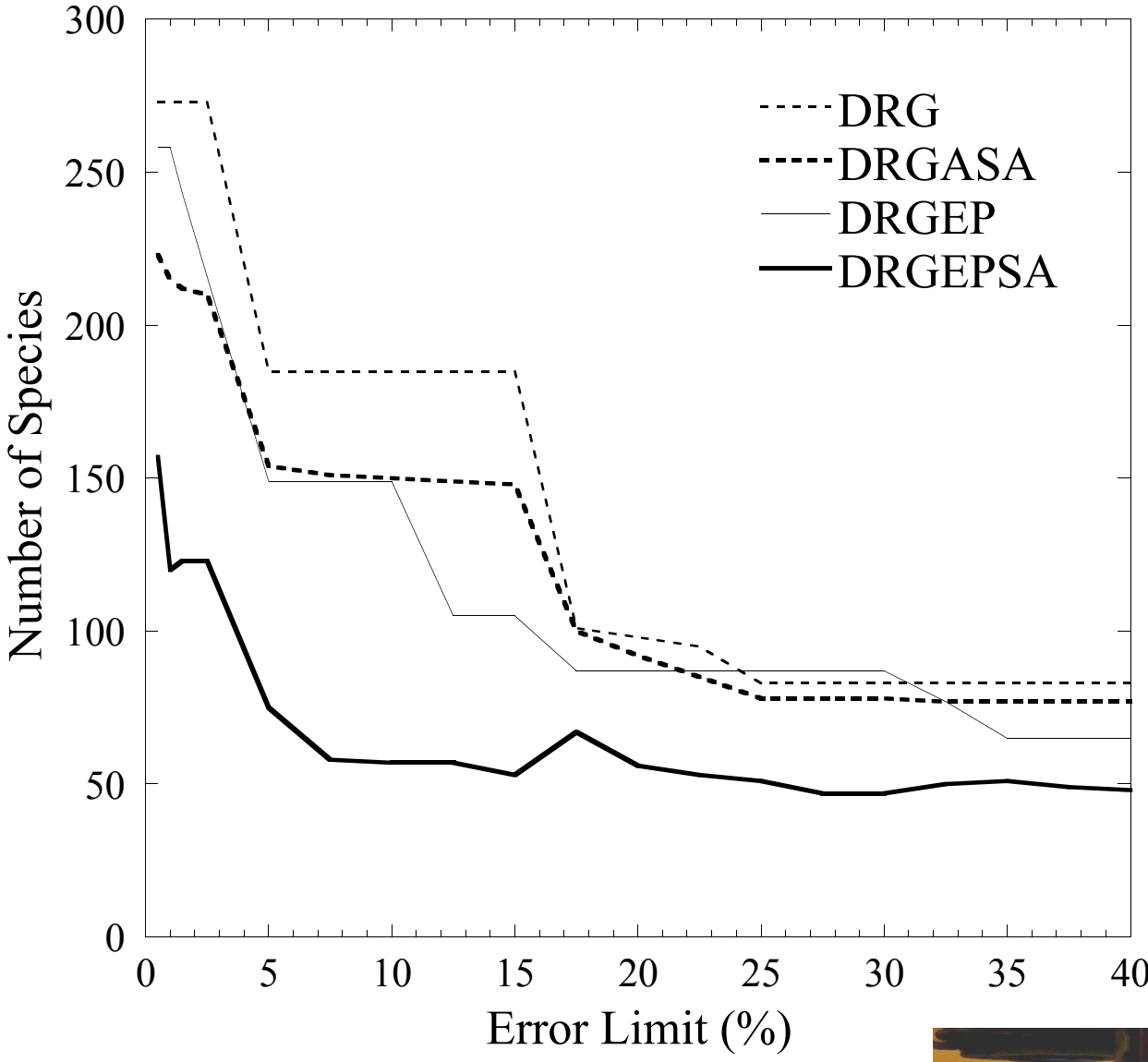
n-Heptane Preliminary Reduction (1)

Constant volume ignition of ***n*-heptane**: initial conditions 1000 K, 1 atm, and ϕ=0.5–1.5 from detailed mechanism of Curran *et al.* 1998 (561 species and 2539 reactions):

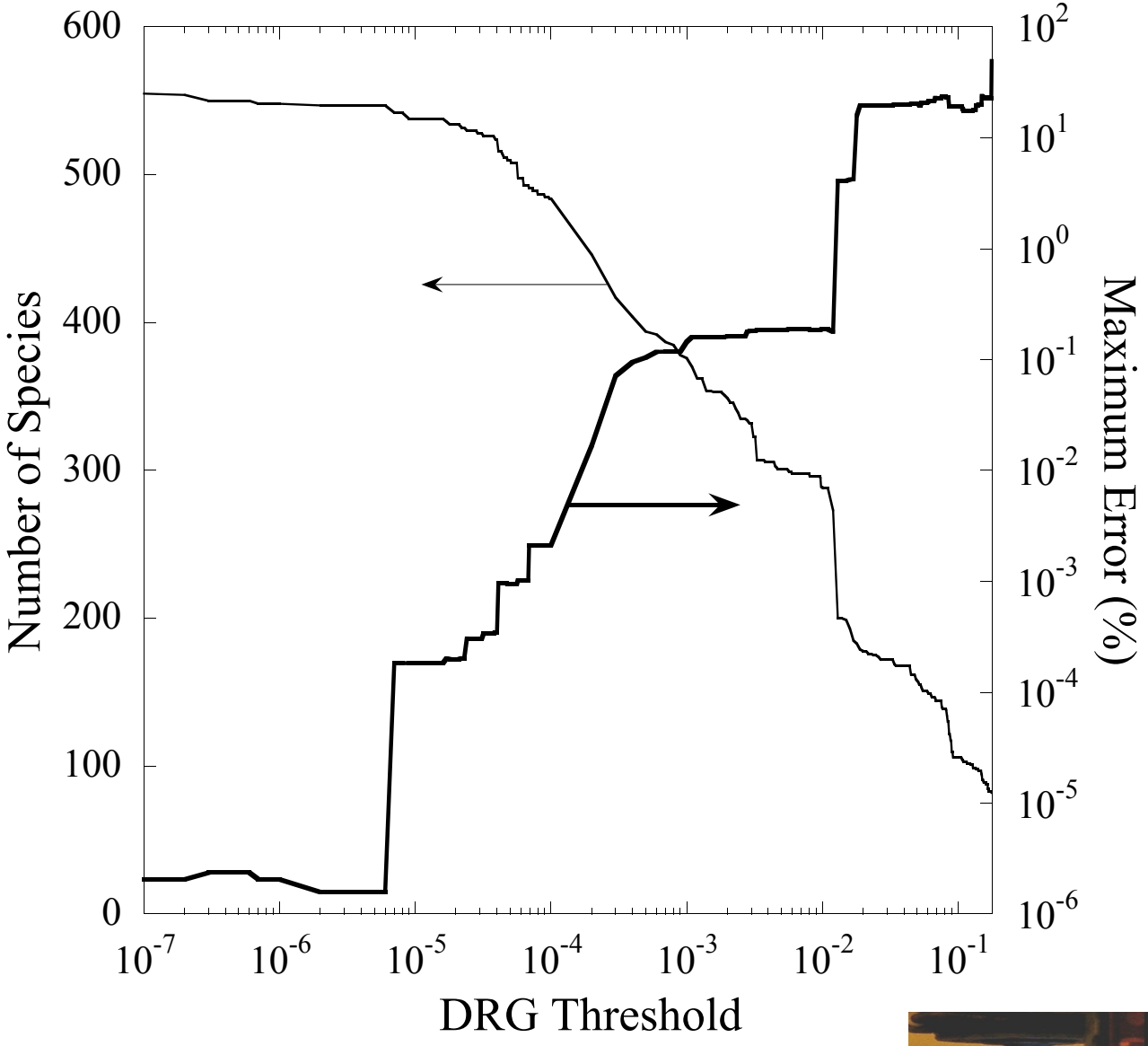
- Maximum tolerable error: 0.5-40%
- Target species: *n*-heptane, oxygen, nitrogen, H-radical

Wide range of error limits used to compare the methods at varying levels of complexity

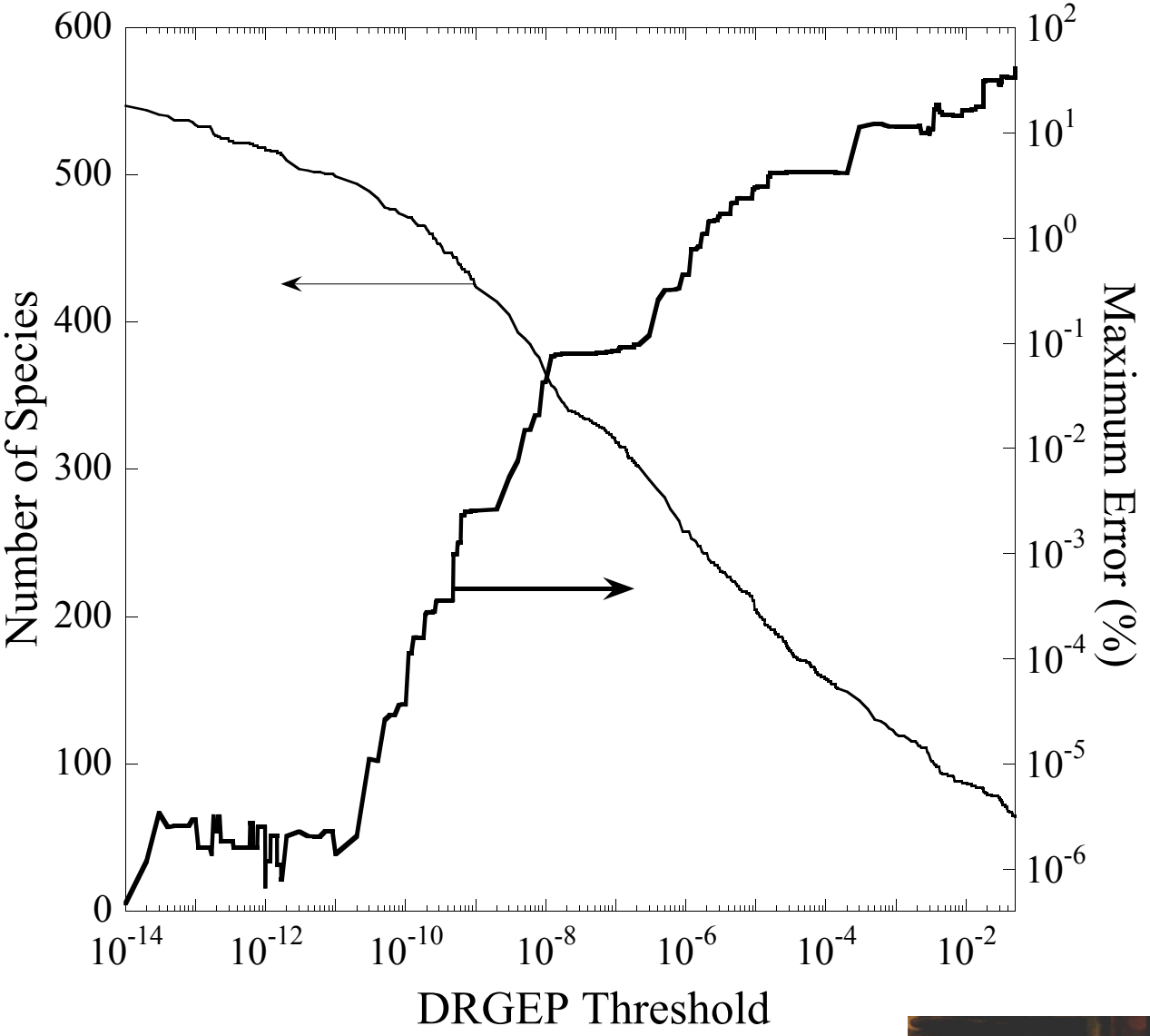
n-Heptane Preliminary Reduction (2)



n-Heptane Preliminary Reduction (3): DRG



n-Heptane Preliminary Reduction (4): DRGEP



DRGEPSA Reduction Capability Extended to LLNL Mechanisms

- *n*-Heptane
  - Detailed: 561 species and 2539 reactions
  - Skeletal: 108 species and 406 reactions
- *iso*-Octane
  - Detailed: 857 species and 3606 reactions
  - Skeletal: 165 species and 779 reactions
- *n*-Decane
  - Detailed: 2115 species and 8157 reactions (covering C_8-C_{16})
  - Skeletal: 202 species and 846 reactions
  - High-temperature skeletal: 51 species and 256 reactions

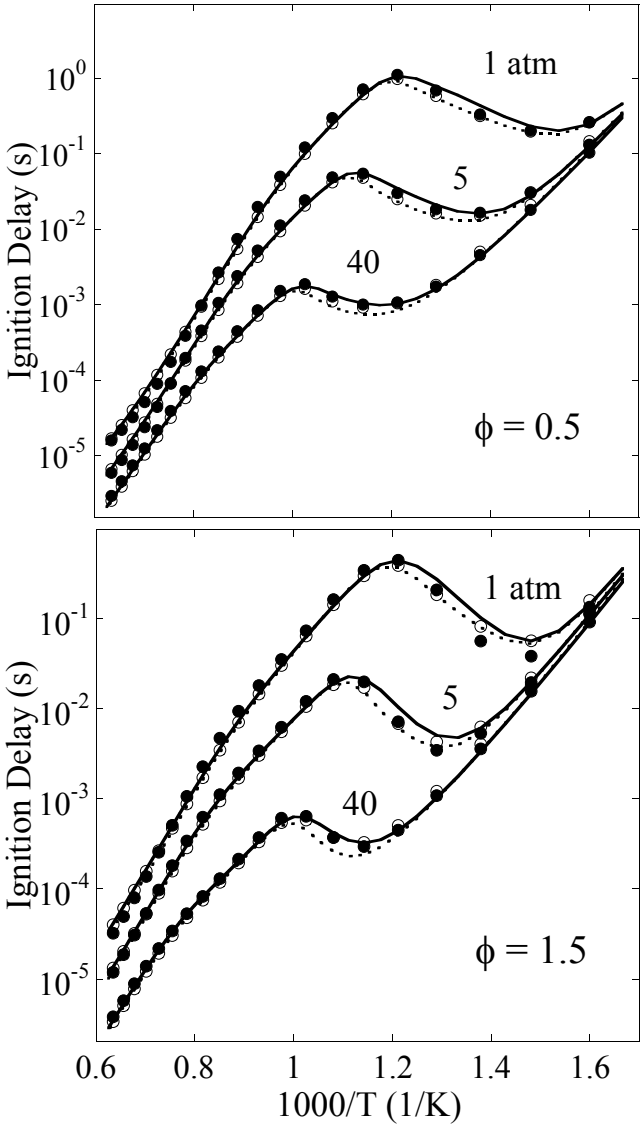
n-Heptane

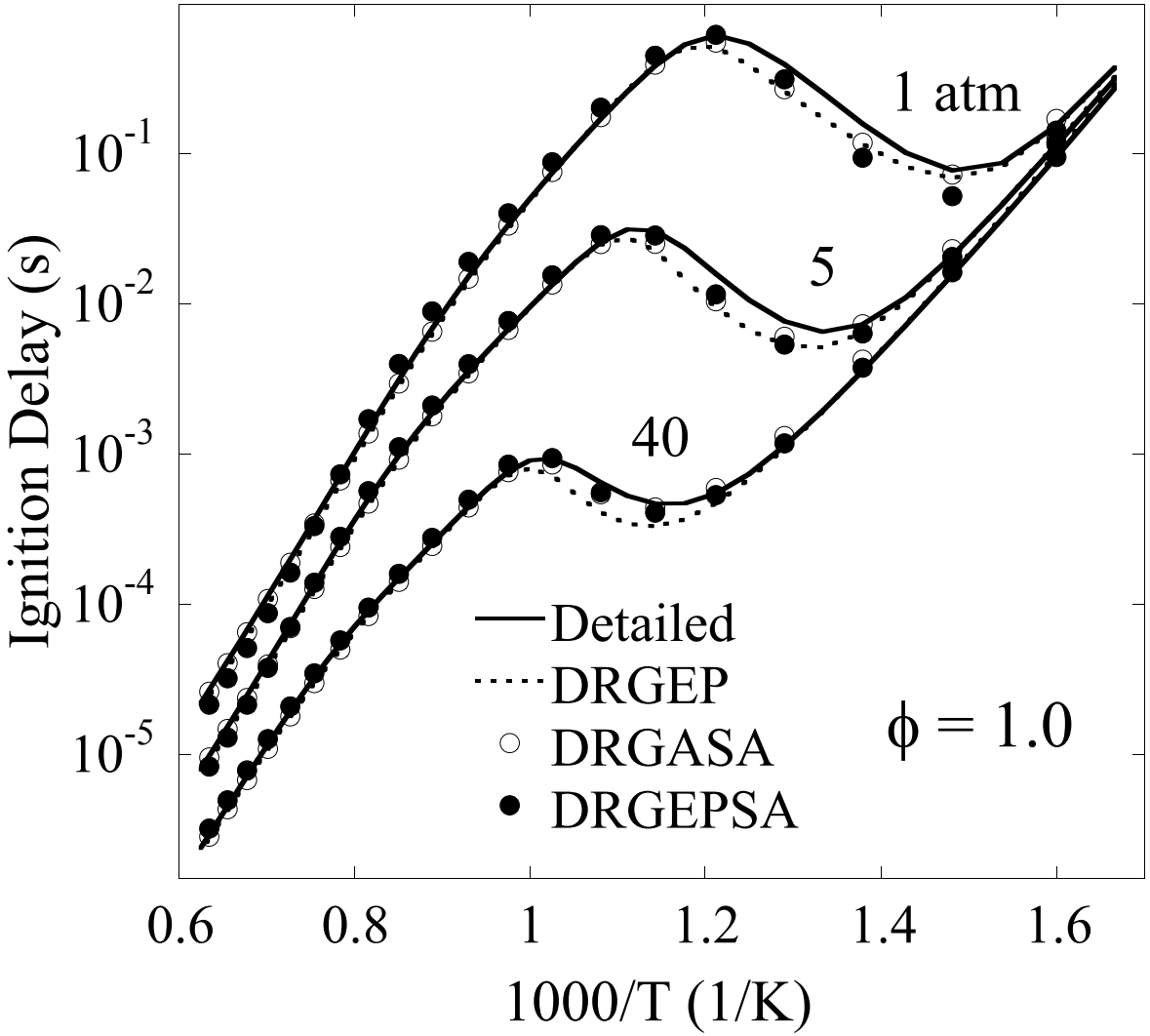
Constant volume ignition of ***n*-heptane**: initial conditions 600–1600 K, 1-20 atm, and ϕ=0.5–1.5 from detailed mechanism of Curran *et al.* 1998:

- Maximum tolerable error: 30%
- ε_{DRG}=0.16, ε_{EP}=0.01
- Target species: *n*-heptane, oxygen, nitrogen, H-radical

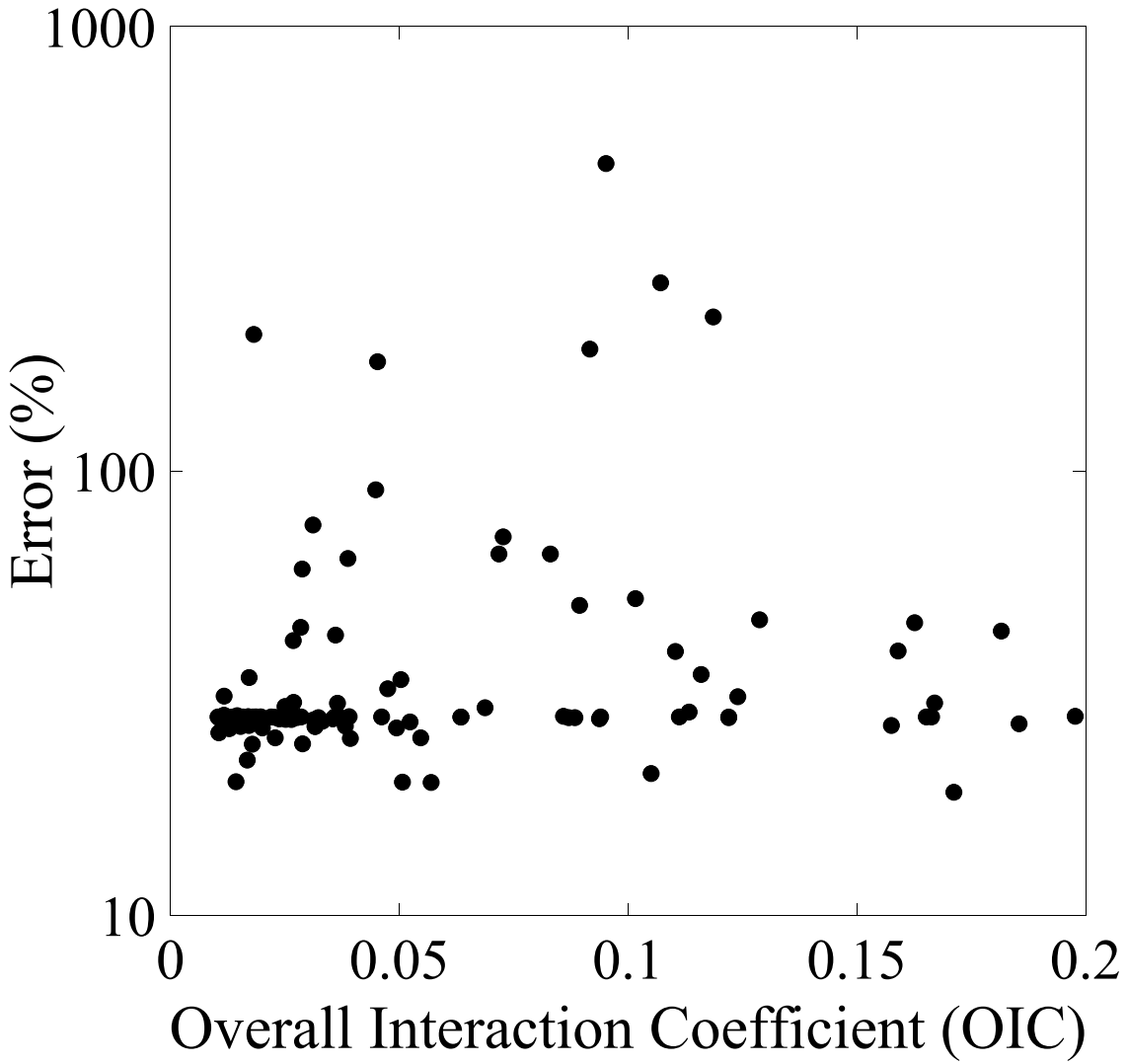
	Detailed	DRG	DRGEP	DRGASA	DRGEPSA
Species	561	211	173	153	**108**
Reactions	2539	1044	868	691	**406**
Maximum error		21%	28%	24%	27%

n-Heptane Autoignition Results





n-Heptane Limbo Species



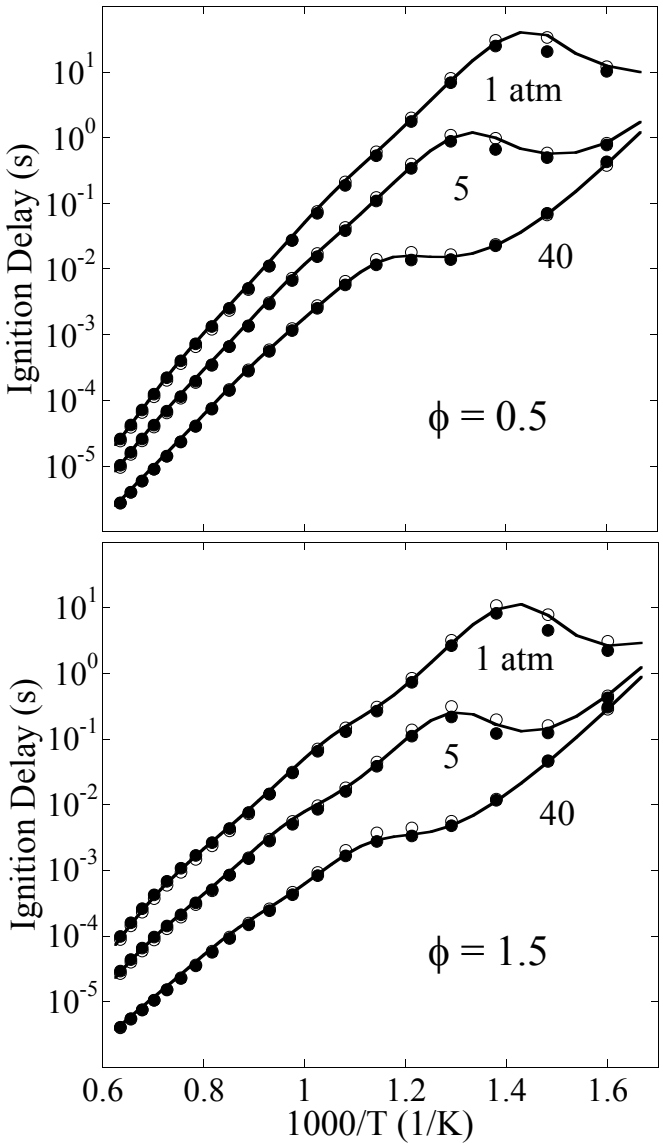
iso-Octane

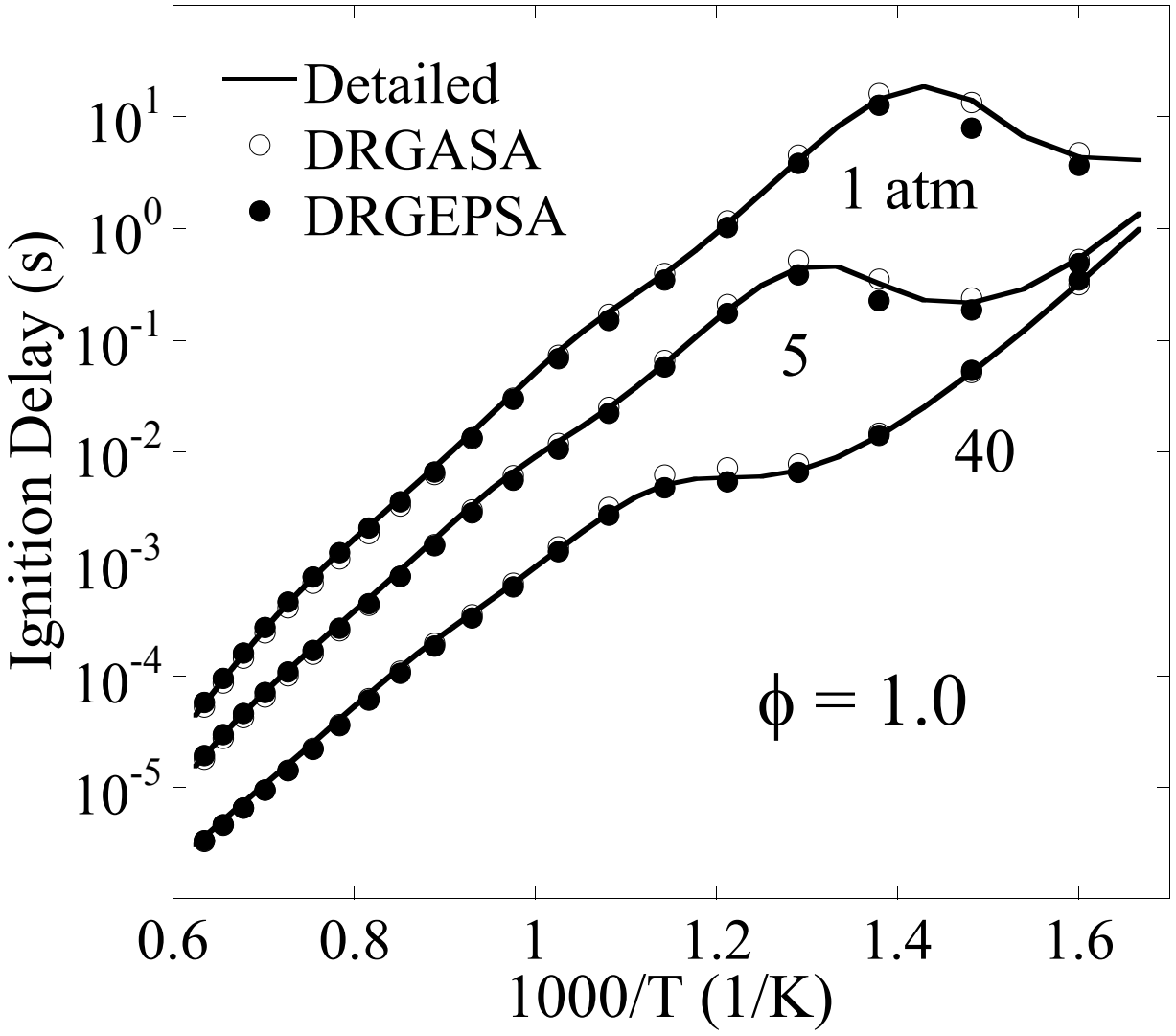
Constant volume ignition of ***iso*-octane**: initial conditions 600–1600 K, 1-20 atm, and ϕ=0.5–1.5 from detailed mechanism of Curran *et al.* 2002:

- Maximum tolerable error: 30%
- ε_{DRG}=0.15, ε_{EP}=0.004
- Target species: *iso*-octane, oxygen, nitrogen, H-radical

	Detailed	DRG	DRGEP	DRGASA	DRGEPSA
Species	857	275	232	211	**165**
Reactions	3606	722	1140	885	**779**
Maximum error		13%	15%	26%	19%

iso-Octane Autoignition Results

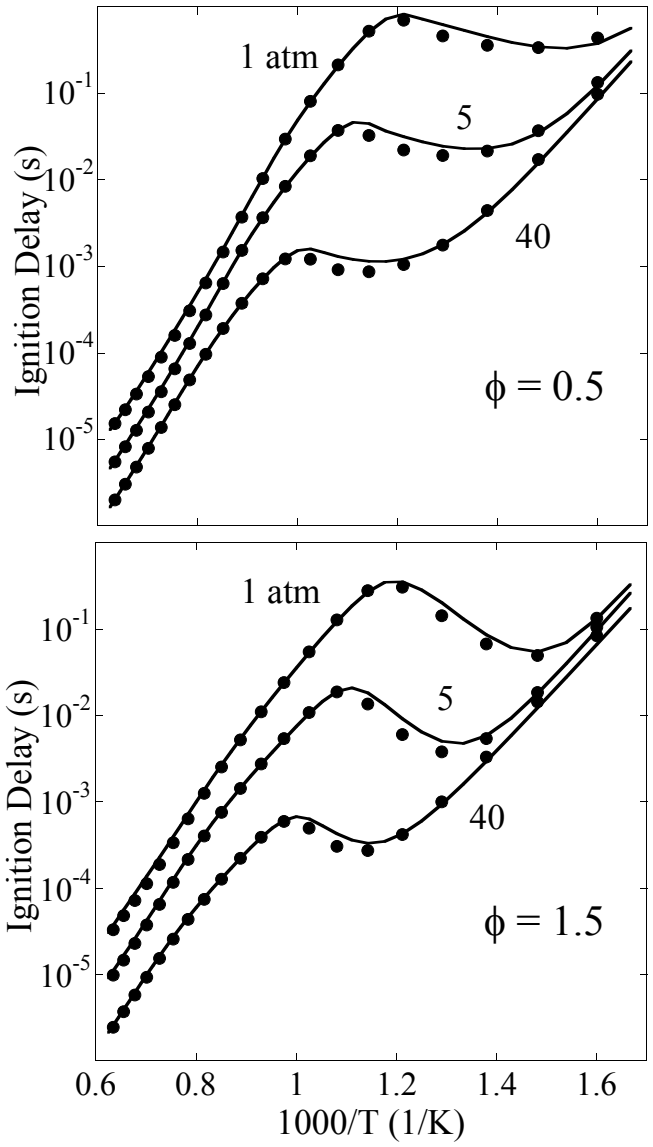


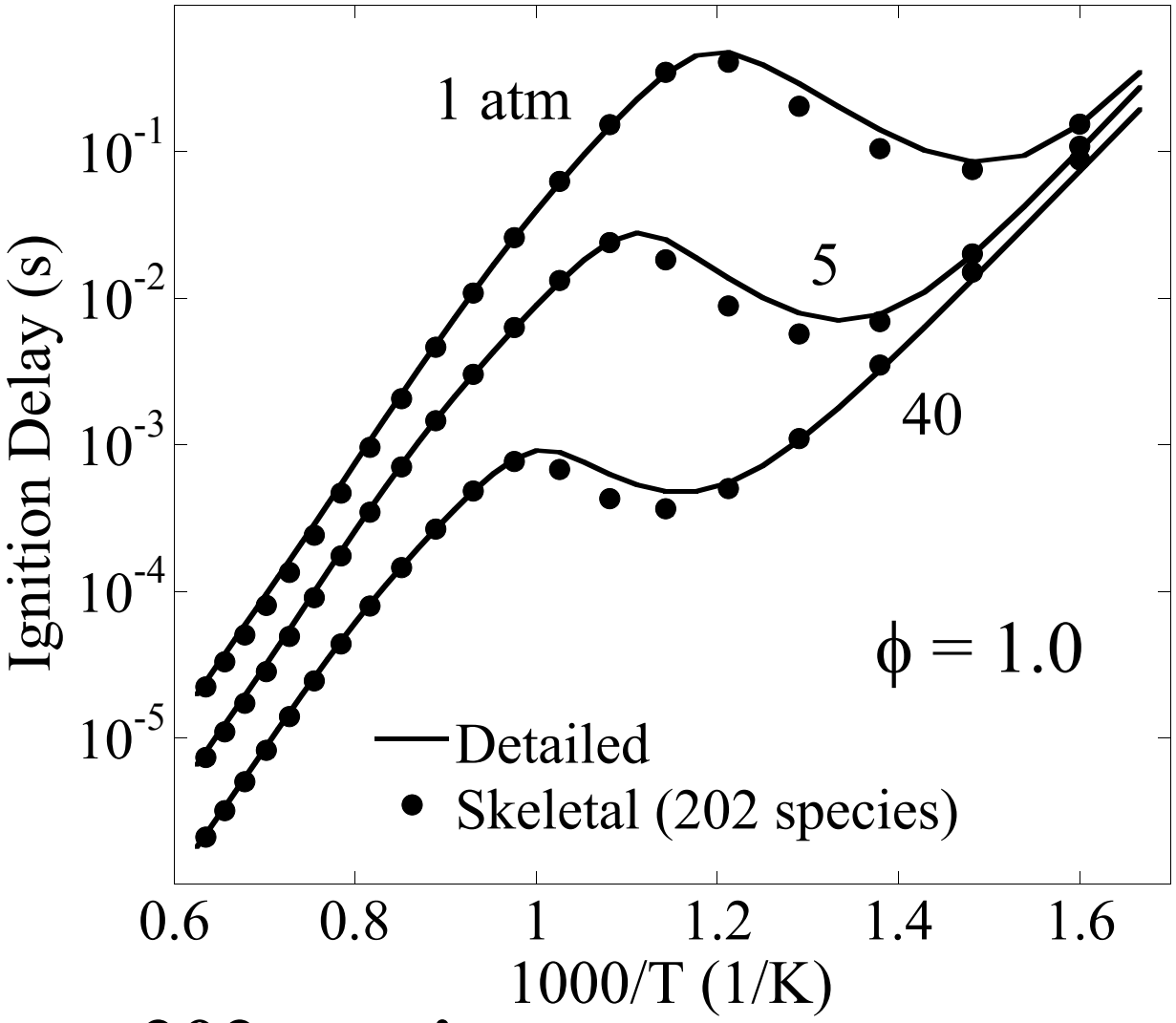


n-Decane Skeletal Mechanisms

- Two skeletal mechanisms generated from constant volume autoignition **n-decane** from mechanism of Westbrook *et al.* 2009 (2115 species, 8157 reactions):
  - Initial conditions: 600–1600 K, 1–20 atm, and ϕ = 0.5–1.5 (*comprehensive mechanism*)
    - Skeletal mechanism: **202** species, **846** reactions
  - Initial conditions: 1000–1300 K, 1.0 atm, and ϕ = 0.5–1.5 (*high-temperature mechanism*)
    - Skeletal mechanism: **51** species, **256** reactions
- Validation performed with autoignition, PSR, and PREMIX.

n-Decane Skeletal Mechanism: Autoignition Results (1)





202 species

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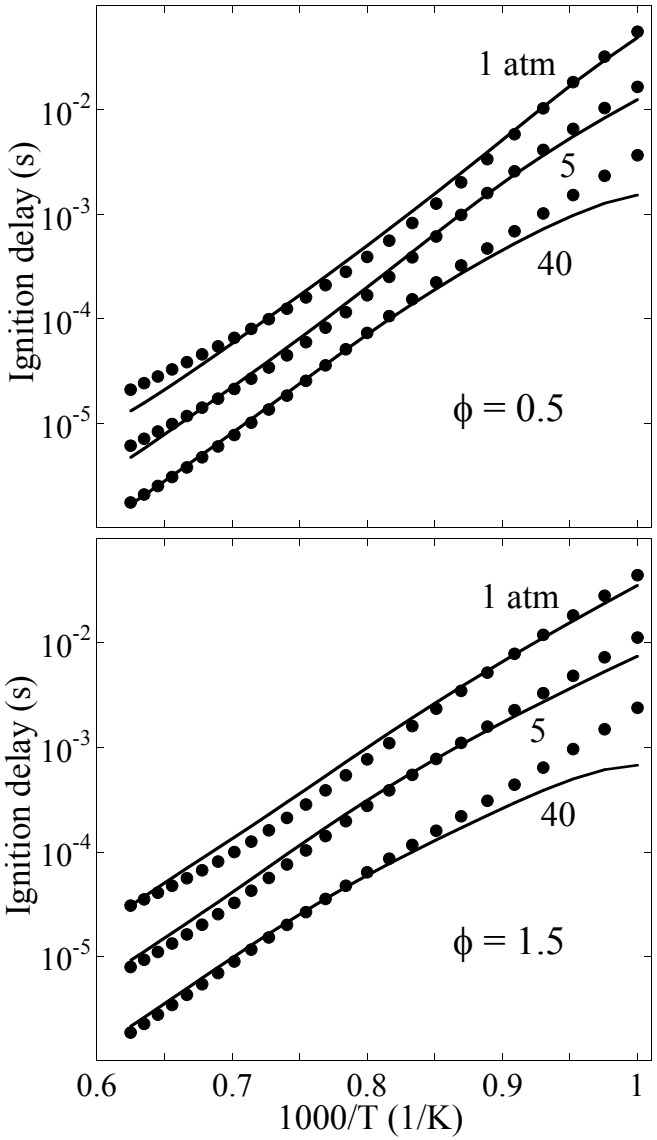
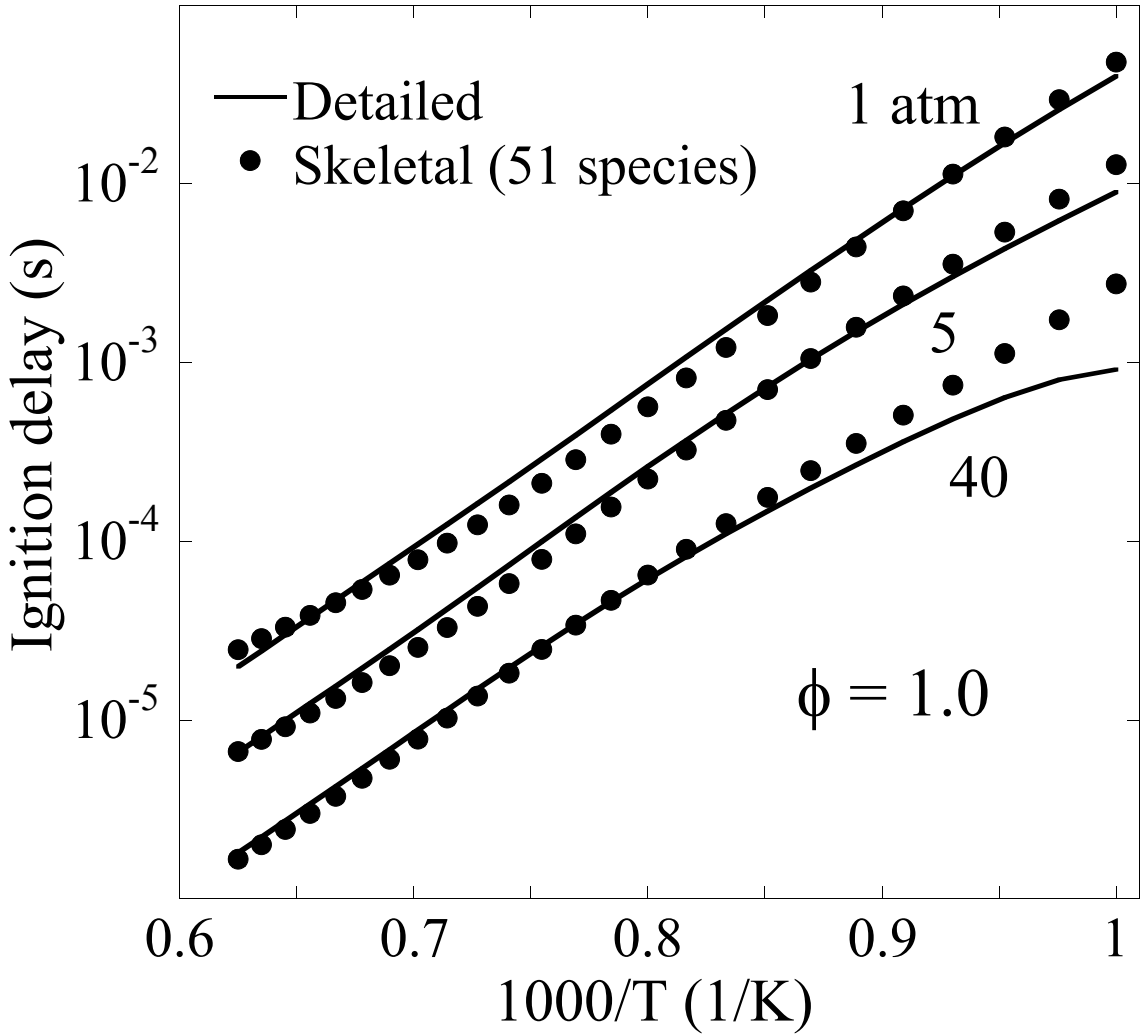
n-Decane Skeletal Mechanism: Autoignition Results (2)





51 species

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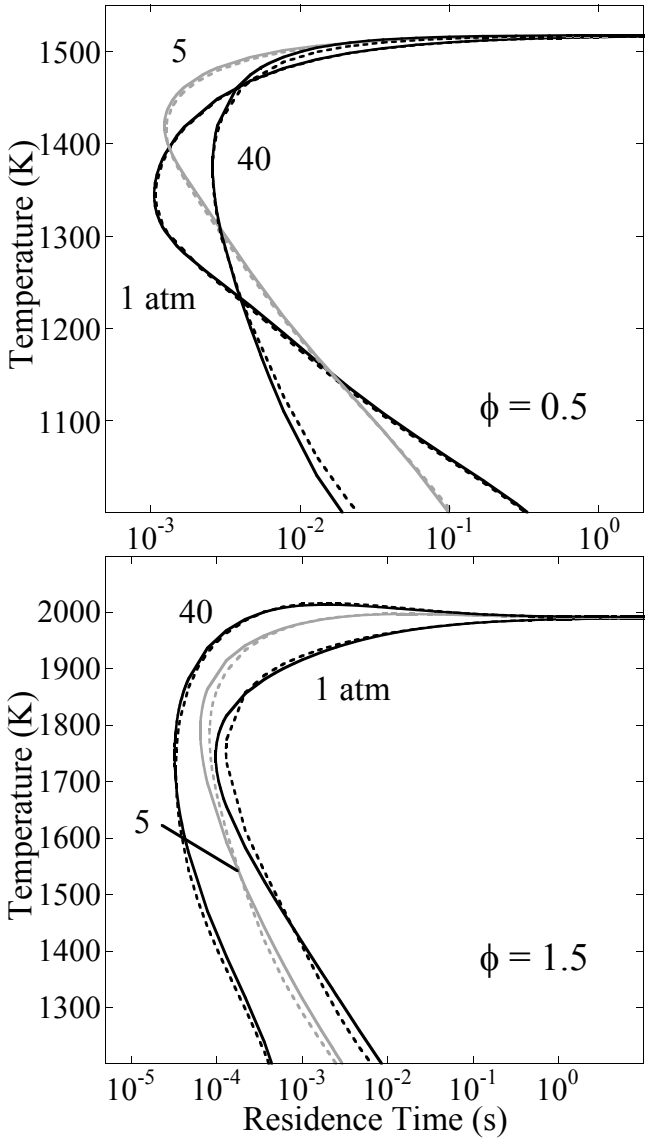
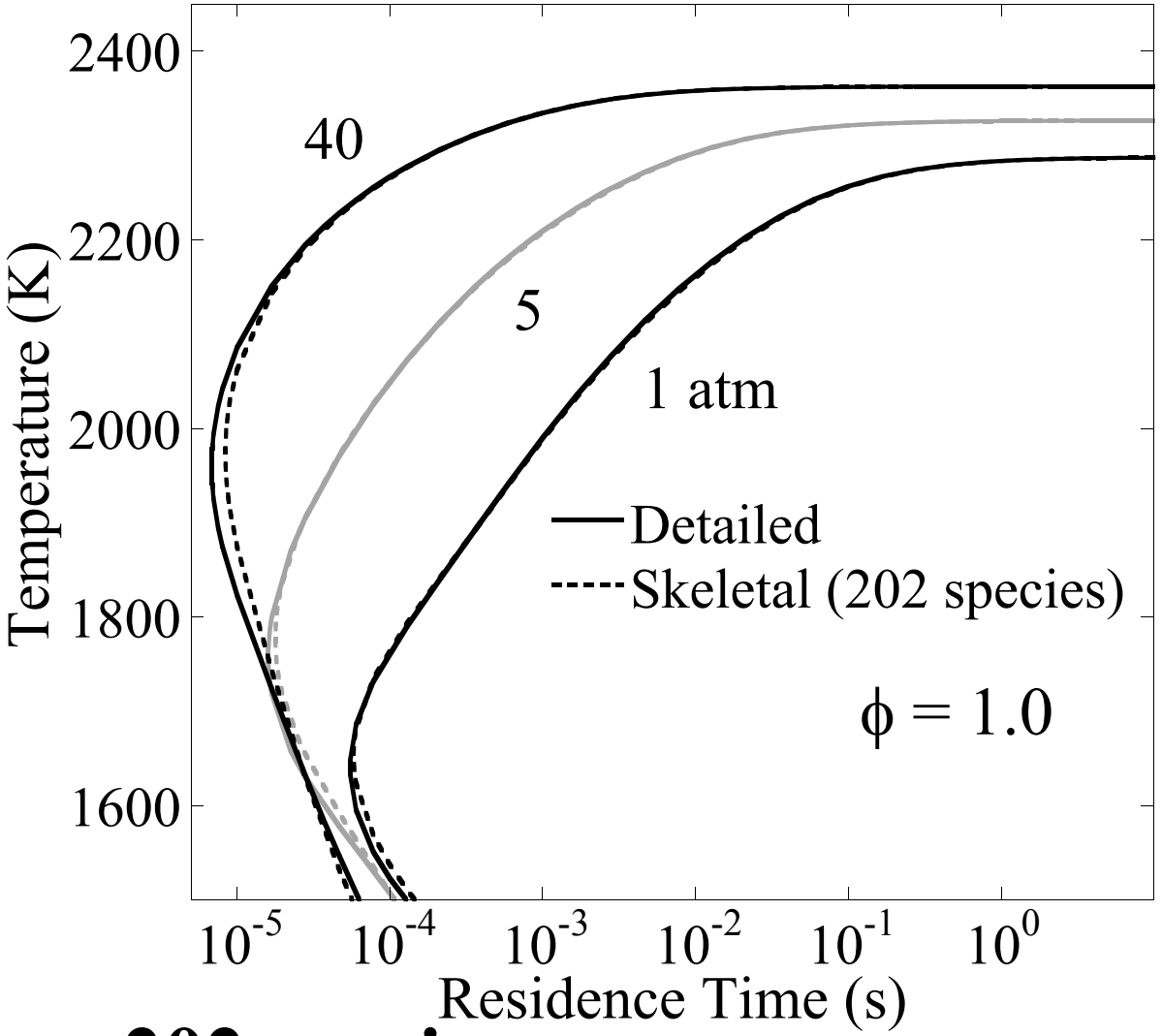
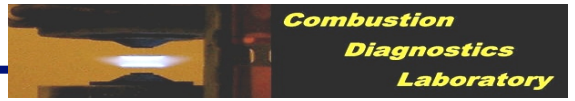
n-Decane Skeletal Mechanism: PSR Results (1)

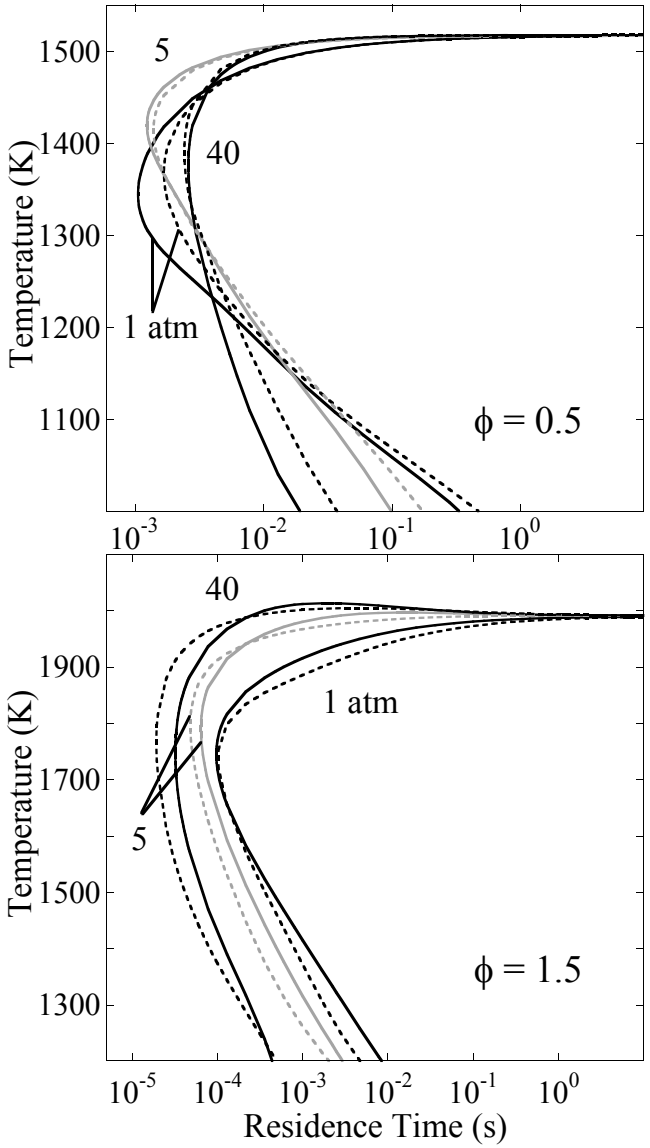


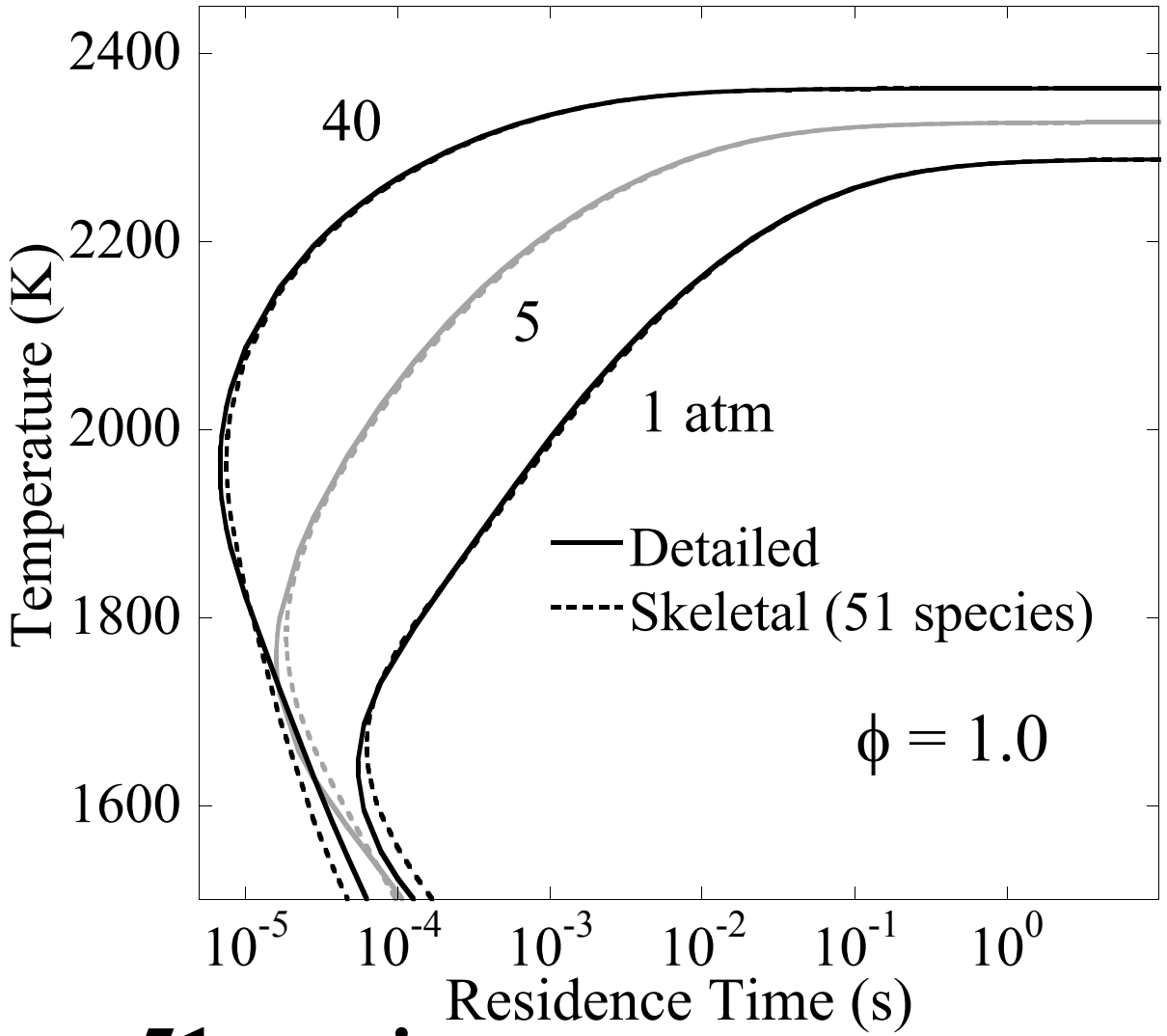


202 species

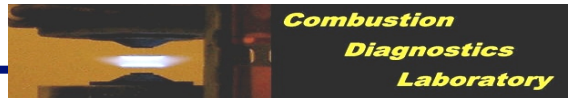


n-Decane Skeletal Mechanism: PSR Results (2)

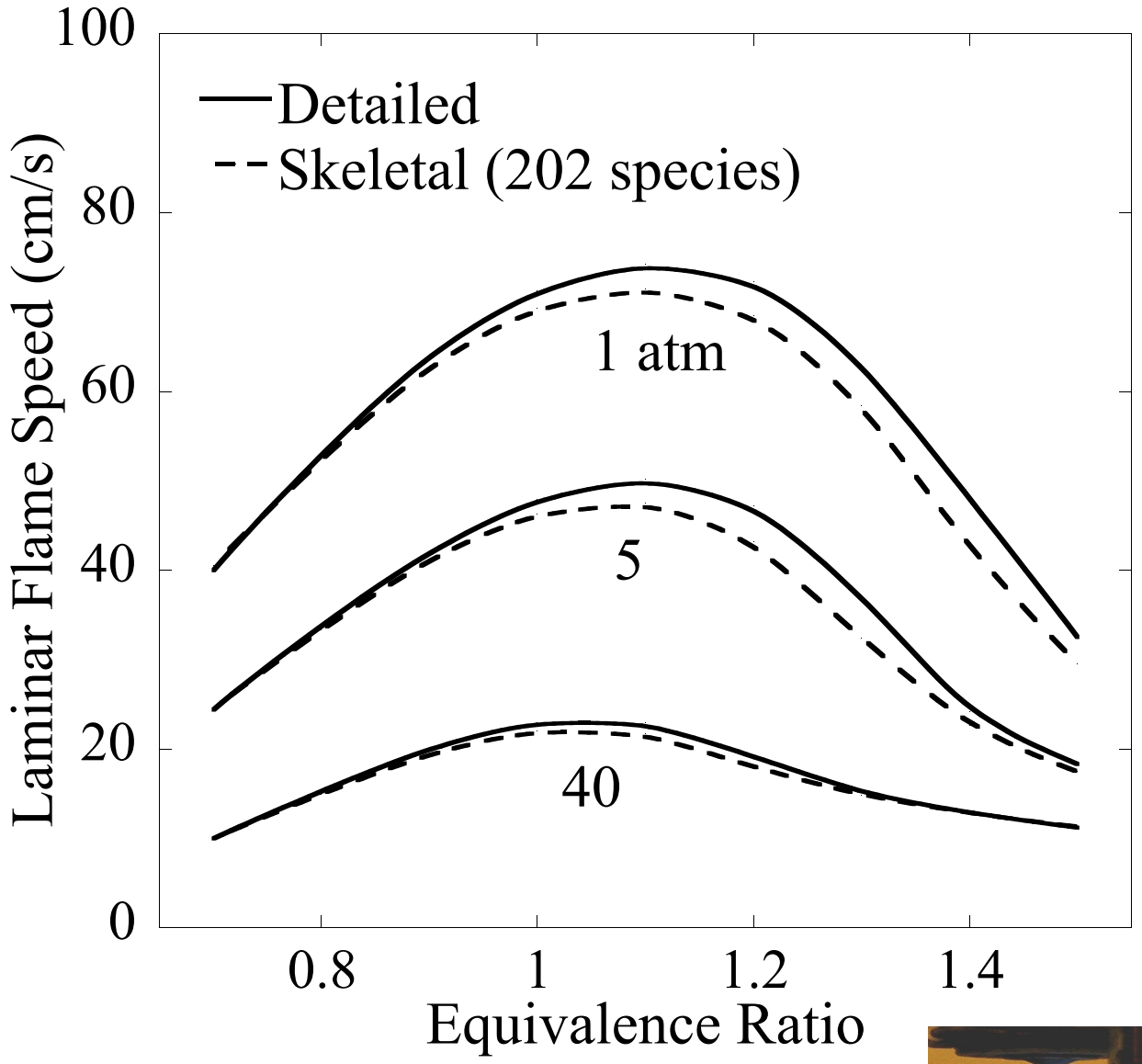




51 species



n-Decane Skeletal Mechanism: PREMIX Results (1)



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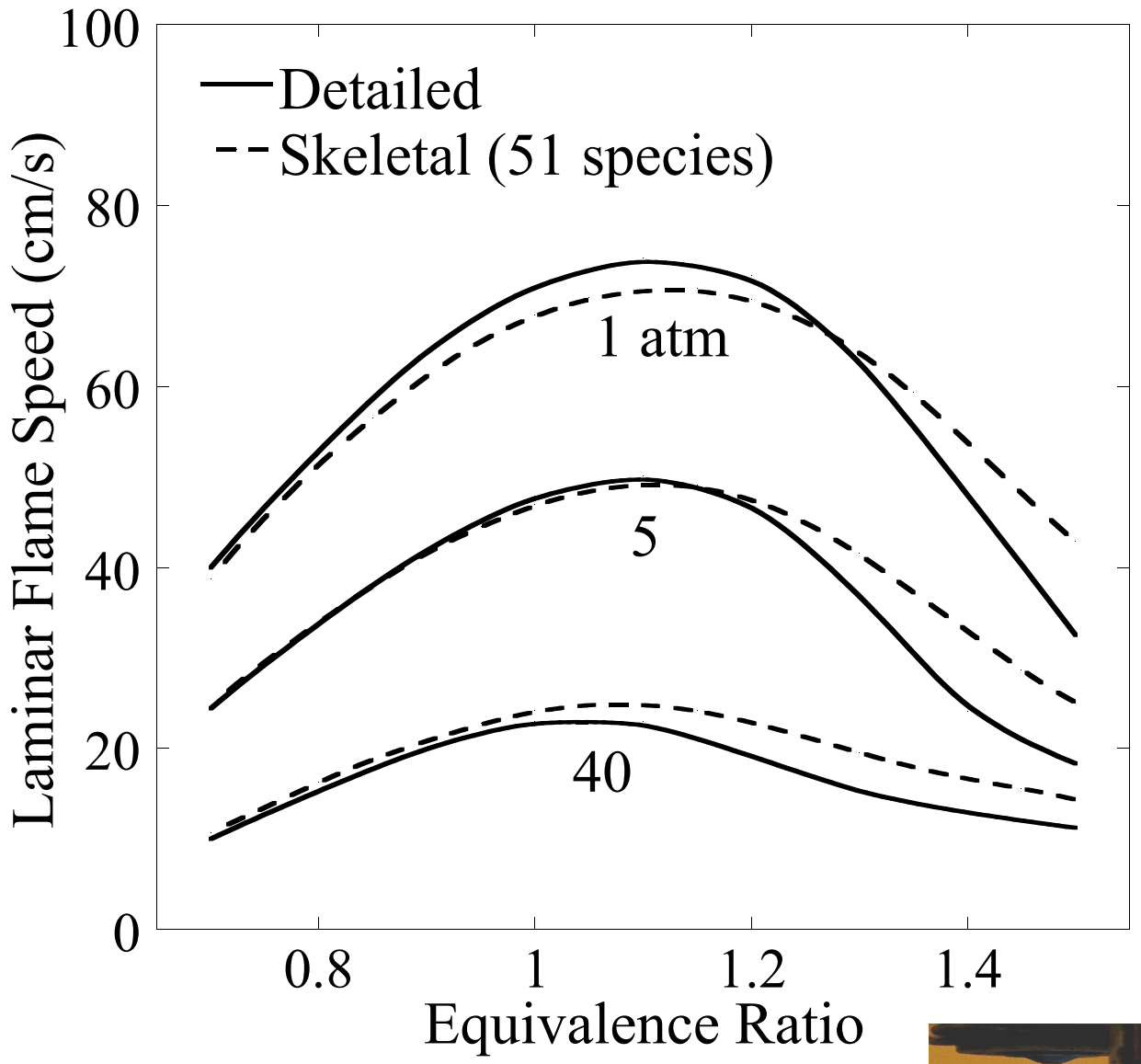
n-Decane Skeletal Mechanism: PREMIX Results (2)



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Conclusions (1)

- By combining error propagation and sensitivity analysis, DRGEPSA provides greater reduction of large mechanisms with equivalent performance compared to the DRGASA and DRGEP methods
  - Even at strict error limits, DRGEPSA generates noticeably smaller skeletal mechanisms
- DRGEPSA can be used to generate skeletal mechanisms to match the performance of large reaction mechanisms in predicting autoignition with acceptable error
- As one component of MARS package, DRGEPSA provides simple and automated method to generate skeletal mechanisms
  - Additional reduction techniques and strategies are needed to further improve the skeletal mechanisms

Conclusions (2)

- By limiting the range of validity to that desired, compact skeletal mechanisms for use in large-scale simulations can be developed
- Both *n*-decane skeletal mechanisms show good performance in external validation (PSR, PREMIX)
  - These results validate the rationale of using constant autoignition simulations for chemical kinetics data sampling and error evaluation

Future Work

- Improvements to DRGEPSA:
  - Investigate species whose importance is not well identified by DRGEP overall interaction coefficient
  - Implement smarter error threshold (ε_{EP}) selection
  - Implement smarter limbo species threshold (ε^*) selection
- Improvements to MARS:
  - Unimportant reaction elimination
  - Isomer lumping
  - Diffusive species bundling
  - CSP-based QSS reduction
    - Hybrid iterative/analytic solution for QSS species concentrations

Questions?

Acknowledgements

- Prof. Sung
- Committee members
- Dr. Kamal Kumar and CDL Staff
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