Computationally Efficient Modeling of Hydrocarbon Oxidation Chemistry

K. G. Harstad* and J. Bellan*,**
*Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 90019-8099
**Mechanical Engineering Dept., California Institute of Technology, Pasadena, CA 91125

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Outline

- Background
- Our previous work
  - chemistry modeling consistent with turbulence modeling
  - concept → finding of a self similarity for n-heptane oxidation
  - *a priori* modeling
  - *a posteriori* assessment
- Recent results
  - further evaluation of the concept → finding of quasi-linear relationships for two major species for n-heptane oxidation
  - identification of model further simplification
  - identification of the process through which modeling can be further refined
- Summary and conclusions
- Future work

Background

- Necessity to reduce the computational cost of chemistry in simulations of turbulent combustion

- Some existing chemistry reduction schemes:
  - reduction of detailed mechanisms to a few reactions and species
  - reduction of detailed mechanisms to 'representative' reactions past C_4 hydrocarbons using species lumping
  - piecewise implementation of solution mapping (PRISM)
  - *in-situ* adaptive tabulation (ISAT)
  - intrinsic low-dimensional manifold (ILDM)
  - computational singular perturbation (CSP)
  - directed relation graph (DRG) reduction

Making chemistry modeling framework consistent with turbulence modeling

Turbulence modeling

1. Exact solution computable: Direct Numerical Simulation (DNS), but it is too costly for practical computations

2. Reduced modeling: solve differential equations only for energetically important scales and model the other scales (Large Eddy Simulation (LES))
- find models
- test to see how they fit the neglected scales (*a priori* analysis)

3. Conduct LES using the model(s) for the neglected scales and see how well one recovers the exact solution (*a posteriori* analysis)

Our chemistry modeling

1. Start with exact set of elementary reactions, e.g. LLNL database, which is too costly for practical computations

2. Reduced modeling: solve differential equations only for energetically important (and pollutant, if of concern) species and model other species
- find models
- test to see how they fit the modeled species (*a priori* analysis)

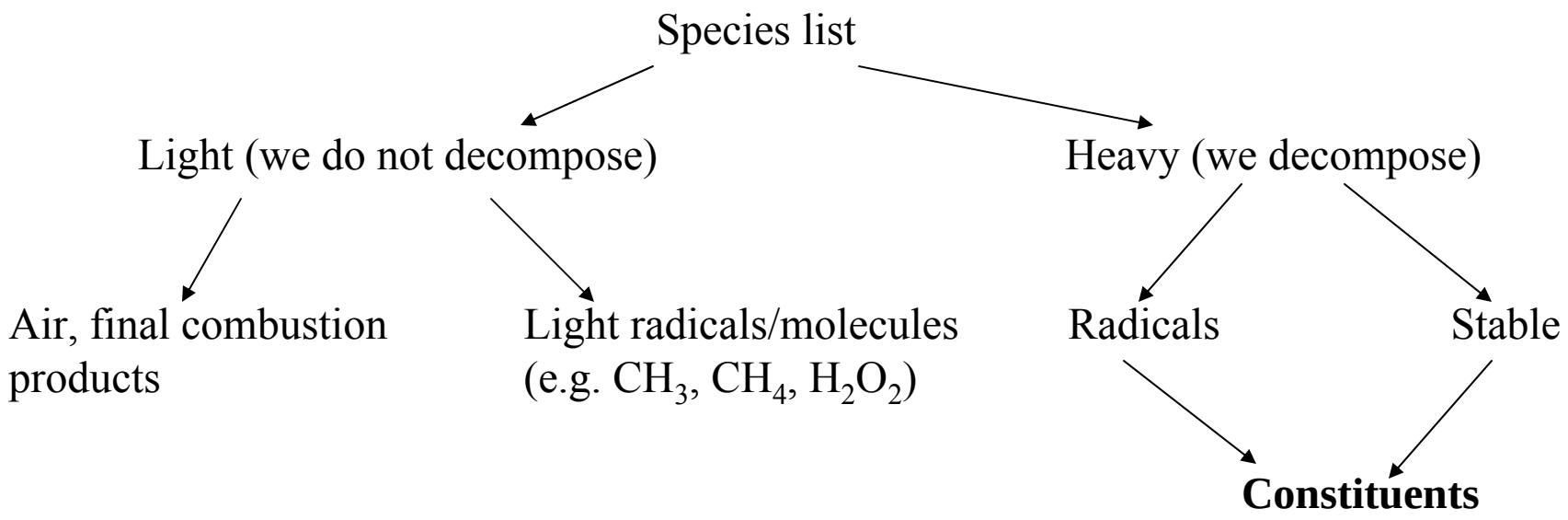
3. Conduct simulations using the model(s) for the approximated species and see how well one recovers the set of elementary reactions (*a posteriori* analysis)

Further similarities between turbulence and chemical reduction

- In the reduction process
  - The scales containing most motion-related energy are retained in LES and the other scales are modeled in turbulence
  - The scales containing most thermodynamic/kinetic-related energy are retained as progress variables in the kinetic reduction and the other scales are modeled

- The modeling consists in providing mathematical forms to fit the approximated-scale behavior. This is a major departure from current reduction schemes.

A priori model: The concept of a base



For general alkane or alkene with air:

The base = Light species + Constituents
(26) (13)

Remove NOx, C, C2, N2 and N at this preliminary stage, and then,

The base = Light species + Constituents
(20) (13)

A priori model: Concept

Facts

1. Plots of the heats of combustion for alkanes and for alkenes having a C double bond at the molecular chain end have a linear variation with the C number, *n*.

2. At fixed *T*, the species C_p vary linearly with *n*.

Implications

- Heats of combustion and C_p's may be considered obtainable by summing those of constituent radicals CH_2, CH_3 and C_2H_3 that form these hydrocarbons.

- For $n \geq 3$, species may be decomposed into constituent radicals. This is consistent with group additivity theory.

Group additivity and constituents

- Starting point akin to, but different from, typical chemical group additivity

Group additivity
- interactions with adjacent groups
- interactions with non-adjacent groups
- accounts for steric effects

Constituents
- only interactions with adjacent groups
- only first order (compositional) effects

- Focus is on
  - comprehensiveness
  - accuracy
  - relative simplicity

- Our process is different from lumping
  - we are decomposing ALL heavy species
  - a constituent may span the entire species set of heavy species
  - we can recover the individual constituent molar fraction in the ensemble of constituents

The base

1. Inspection of the LLNL kinetics shows that a subset of the light species is quasi-steady (i.e. gain and loss balance within 5% or less). These species are: O, CH, CH_2, CH_3, HO, HCO, HO_2, HC_2, C_2H_3 .

2. Examination of the global constituent mole fraction, N_c, shows that, appropriately multiplied/divided by other variables/parameters and plotted against a non-dimensionalized temperature, it has a self-similar behavior (will show).

3. Conclusion: the final base is

- N_c
- molar densities of unsteady light species: H_2O, CO_2, O_2, H, CO, H_2, CH_4, H_2O_2, C_2H_2, C_2H_4, CH_2O

Base behavior in constant-volume n-heptane combustion: framework

1. Examined data from LLNL: 160 species and 1540 reaction rates with the goal of forming non-dimensional groups of variables.

2. Systematic tests performed for p_0 from 1 to 60 bar and for equivalence ratios $\phi \in [1/8,8]$. Very time-consuming iterative process.

3. Try to reduce the problem to its essence by defining

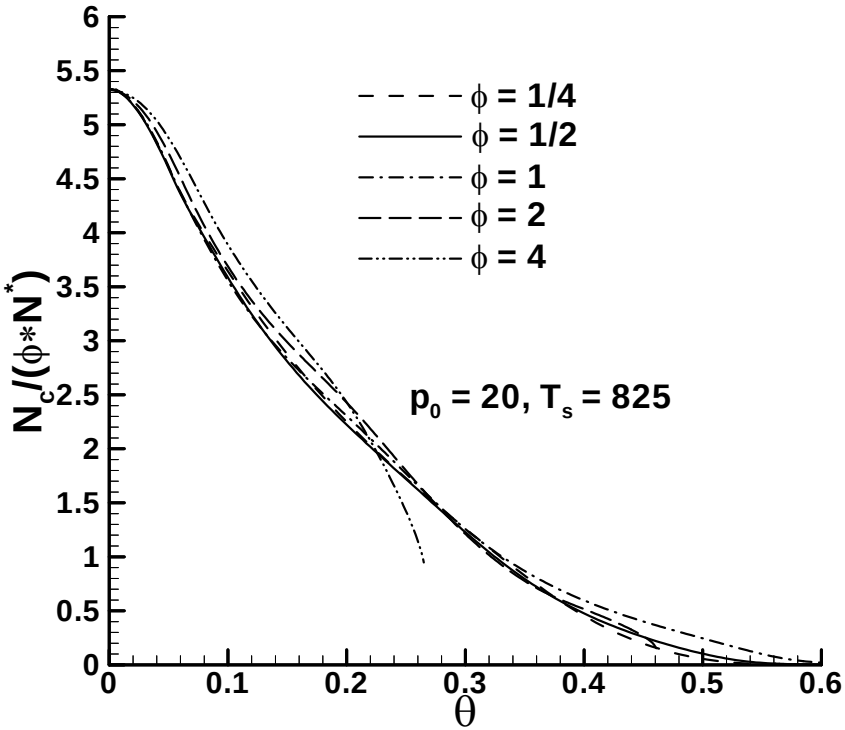
$$N_c \equiv \sum_{k=1}^{13} N_k \qquad K_c \equiv -\frac{d(\ln N_c)}{dt}$$

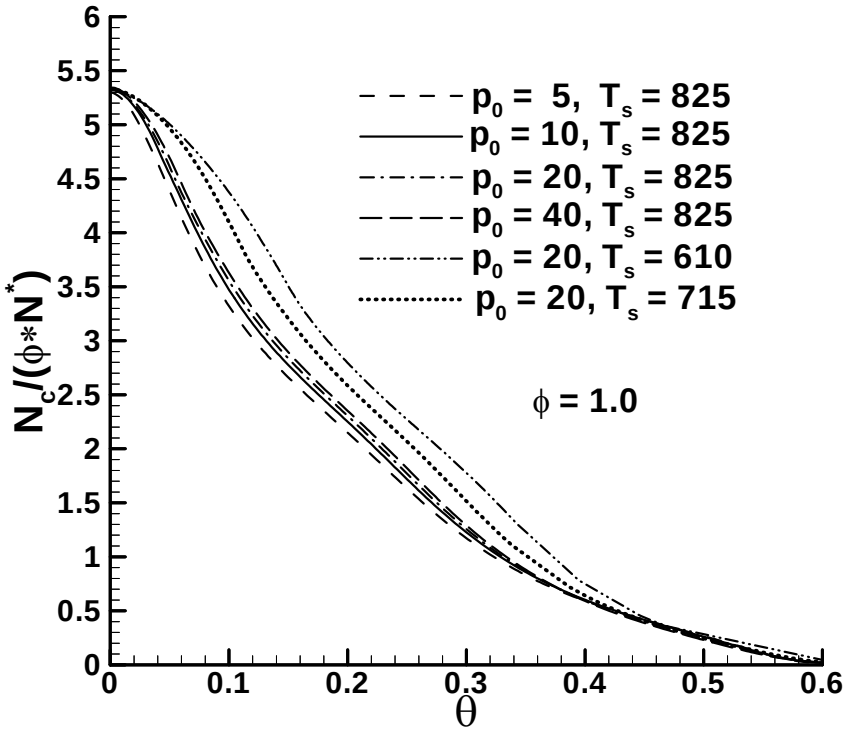
4. Non-dimensional groups of variables

$$N^* \equiv N_{N2}/N_{ref} \qquad N_{ref} = 31.5 \text{ mol/m}^3$$

$$\theta \equiv \frac{T-T_s}{T_r(\phi,N^*)}, \quad T_r \equiv 2065(N^*)^{0.06} w(\phi), \quad w(\phi) = \phi \frac{1.5+1.31\phi}{1+0.71\phi+1.1\phi^2}$$

Identification of self-similar behavior





$N_c/(\phi \times N^*)$ in mol/(m^3), p_0 in bar, T_s in K

Meaning of the N_c self-similarity

- Reduction in the dimensionality of the problem. Found a lower-dimensional manifold.

- Not to be confused with ILDM which is for species, whereas the present model is for N_c.

- The fact that the constituents rather than the heavy species are important can be directly traced to the fact that the heavy species decompose and it is the reaction of these products of decomposition that matters for the energetics.

The energetics

Energy equation:

$$\left(N_c C_{p,h} + \sum_{i \in lights} C_{p,i} N_i\right) \frac{dT}{dt} = -\sum_{i \in lights} h_i \mathcal{R}_i + N_c (R_u T_{ref}) K_h$$

where N_i is the light species mole fraction and

$$\mathcal{R}_i \equiv (dN_i/dt)_{reac}$$

$$C_{p,h} \equiv \left(\sum_{l \in heavies} C_{p,l} N_l\right)/N_c$$

$$K_h \equiv -\left(\sum_{l \in heavies} h_l \mathcal{R}_l\right) \frac{1}{R_u T_{ref} N_c}$$

$$\left(\frac{dN_i}{dt}\right)_{reac} = \left.\frac{dN_i}{dt}\right|_{lights} + \left.\frac{dN_i}{dt}\right|_{heavies}$$

$$\left.\frac{dN_i}{dt}\right|_{heavies} = N_c (KG_i - X_i KL_i)$$

The light species

Light species ensemble partitioned into two categories:

1. Species that require rate equations and are part of the base set:
H_2O, CO_2, O_2, H, CO, H_2, CH_4, H_2O_2, C_2H_2, C_2H_4, CH_2O

→ 11 species (10 for a constant-volume PSR, as H is quasi-steady)

$$\left(\frac{dN_i}{dt}\right)_{reac} = \left.\frac{dN_i}{dt}\right|_{lights} + \left.\frac{dN_i}{dt}\right|_{heavies}$$

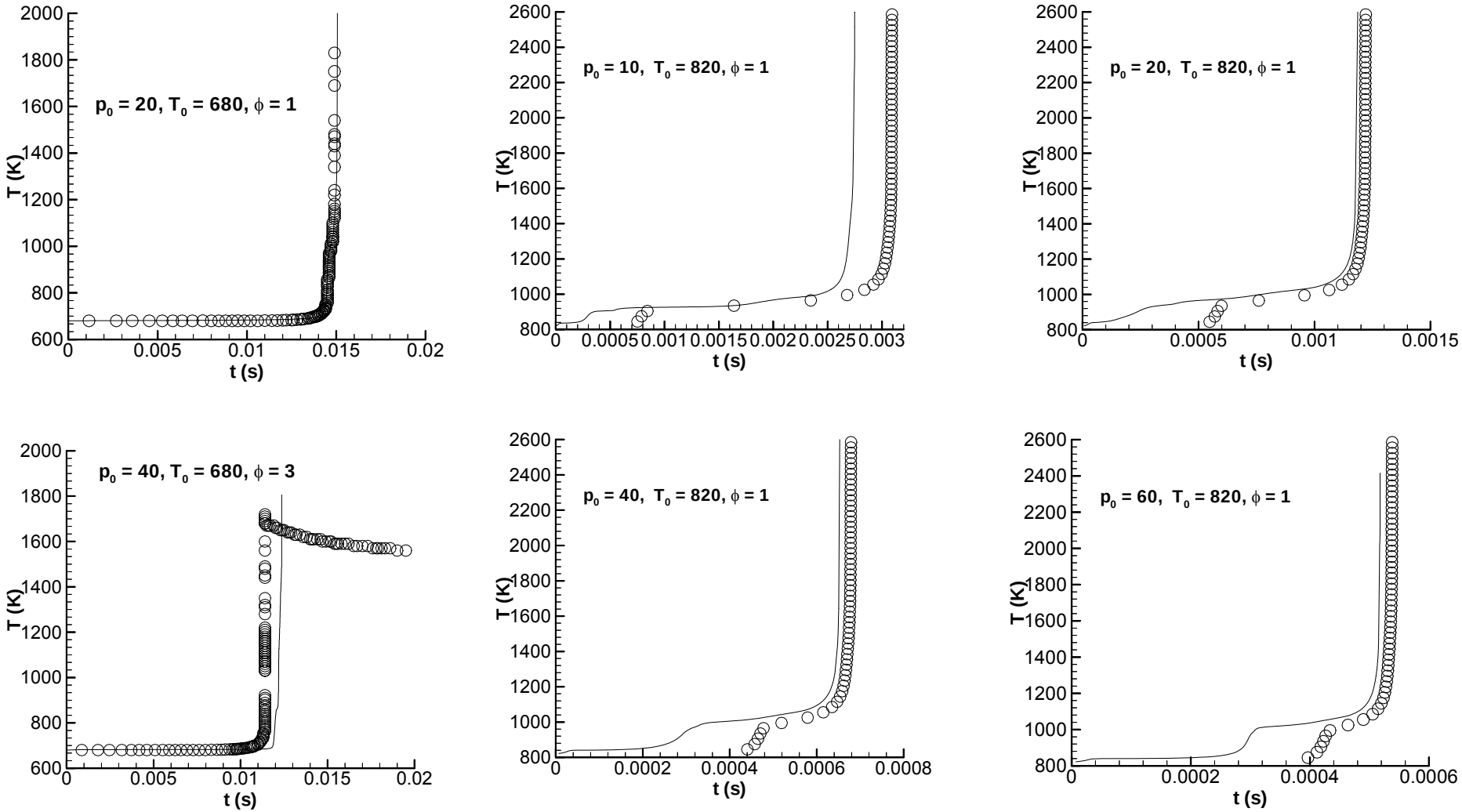
2. Species having a quasi-steady behavior that will be reproduced with curve fits for mole fractions: O, CH, CH_2, CH_3, HO, HCO, HO_2, HC_2, C_2H_3

→ 9 species

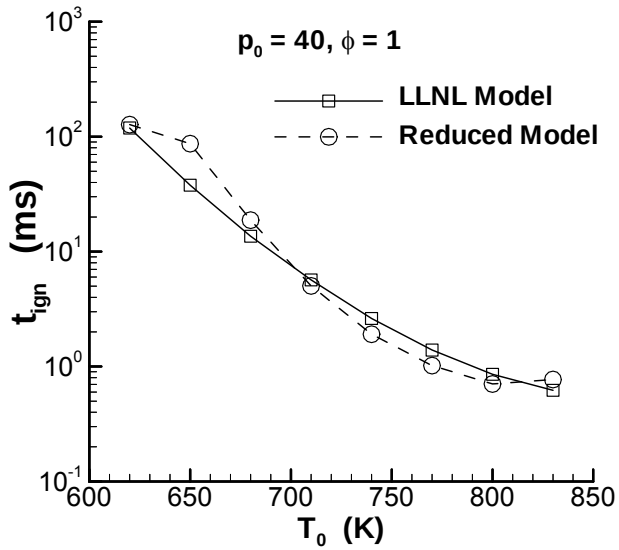
Performed *a priori* modeling

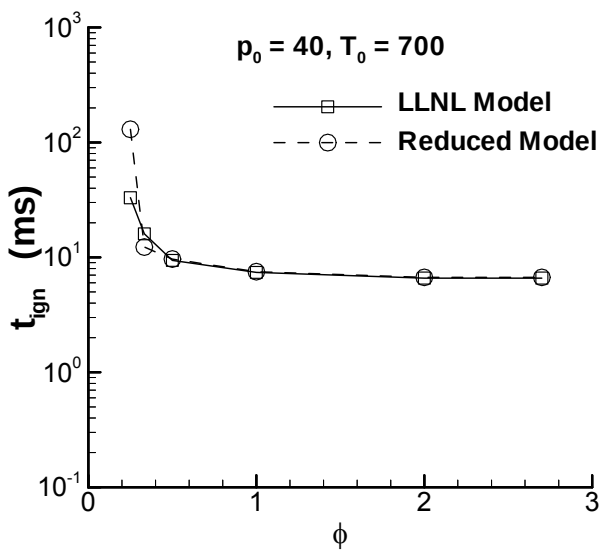
- K_c
- K_h
- KG_i
- $RL_i \equiv KL_i/KG_i$
- X_i (molar fraction of light quasi-steady species)
- All are very complex functions having two extrema over the θ regime
  - Have three distinct regimes: $\theta \ll 1$; $10^{-2} \lesssim \theta \lesssim 10^{-1}$; $\theta \gtrsim 10^{-1}$
  - Need several types of functions to model over the entire θ regime
  - Quantities K_c, K_h, KG_i and RL_i vary over seven orders of magnitude in a four-parameter space (T_0,N*, ϕ, T) → small inaccuracies in a logarithmic plot may lead to large 'local' inaccuracies

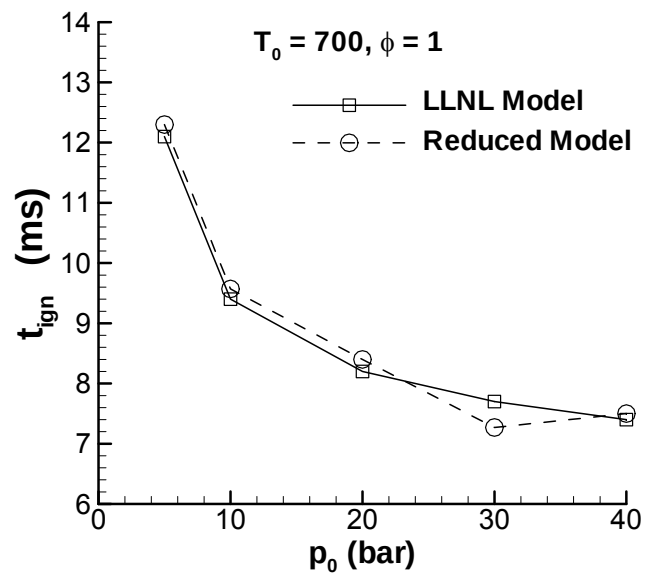
A posteriori assessment of refined *a priori* model: T evolution



A posteriori results of the refined *a priori* model: t_{ign}



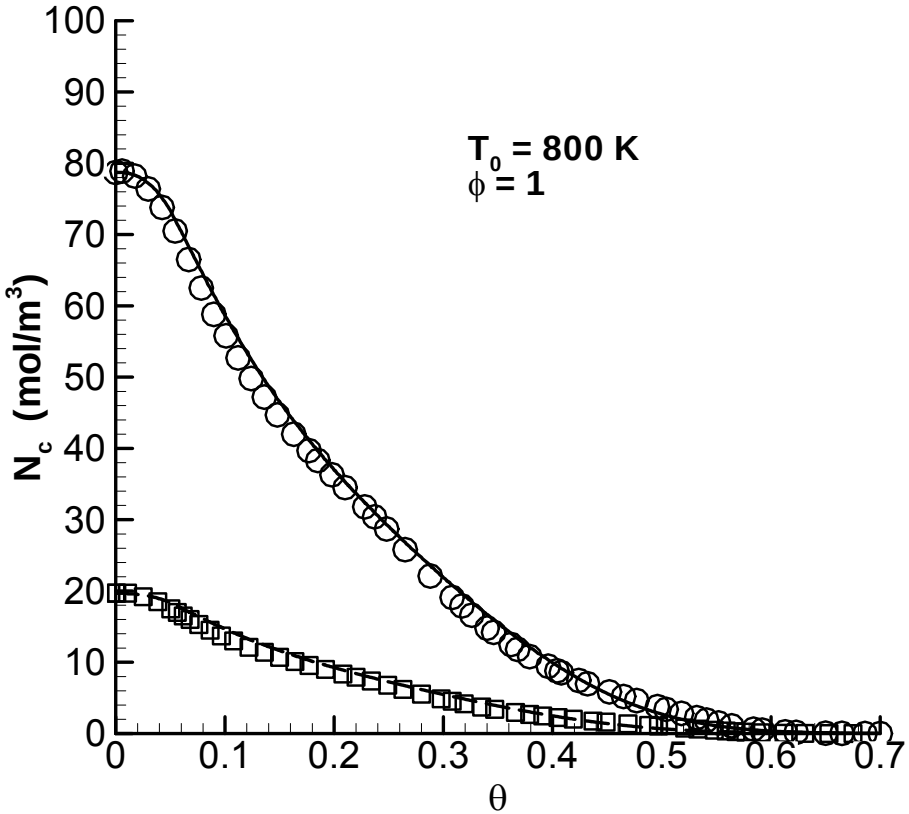


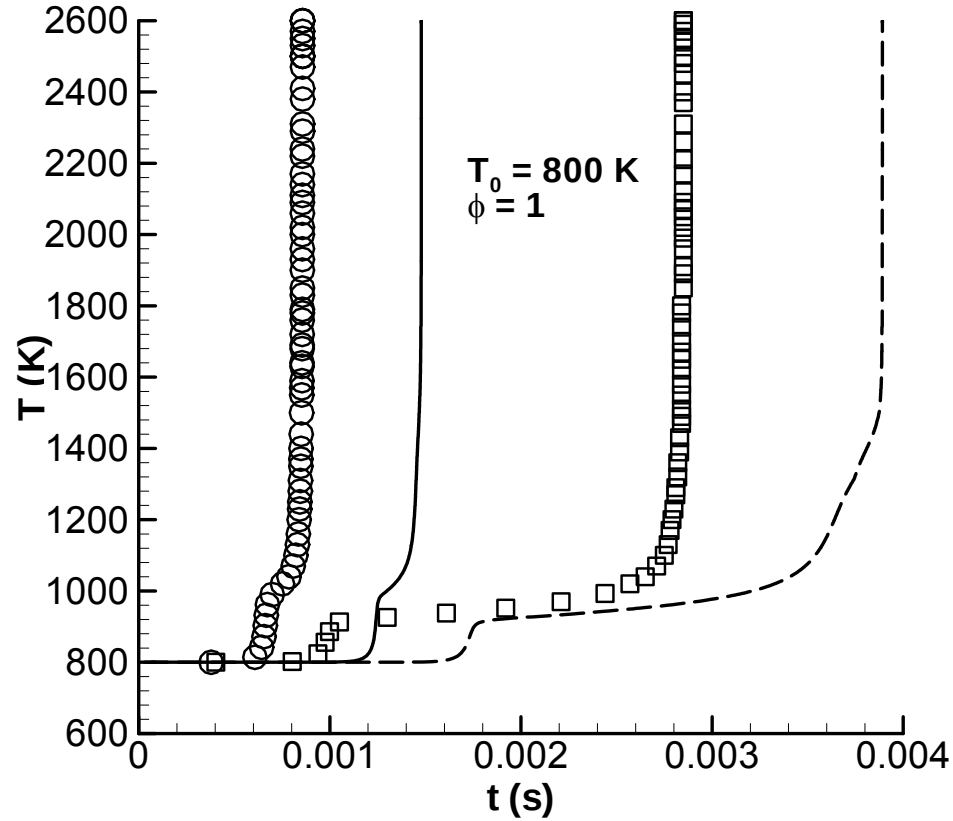


Questions!

- What determines the accuracy of the reduced model?
  - The concept? ➡ Use the concept with the functional forms provided by the LLNL template (in form of tables)!
  - The functional modeling in the *a priori* stage?
  - Both concept and functional fits?
- Where should one concentrate effort to improve the model without sacrificing the computational efficiency?
  - Important for higher order hydrocarbons, e.g iso-octane

Concept assessment with 'exact' functions from the LLNL template



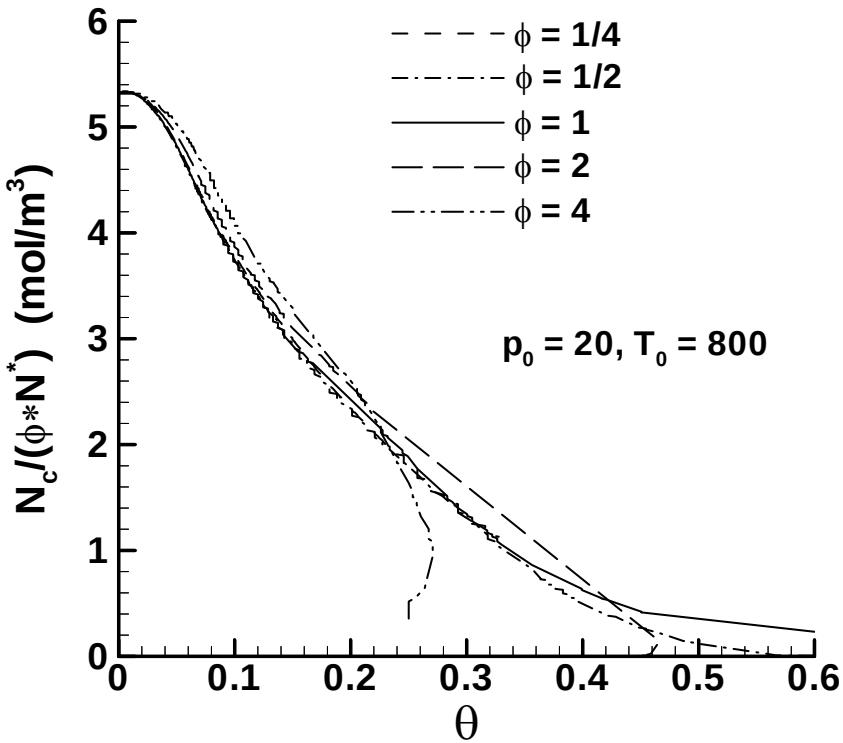


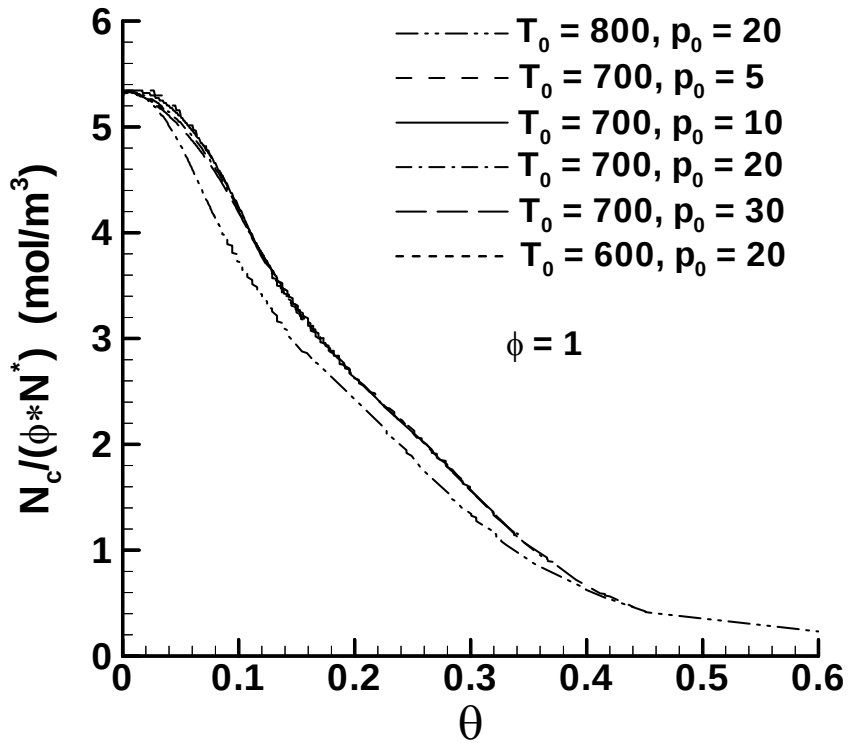
$$\theta \equiv \frac{T - T_0}{T_r(\phi, N^*)}$$

LLNL with Chemkin II: ○ ○ ○ p_0= 40 atm; □ □ □ p_0 =10 atm

Our concept with LLNL extracted functional forms: —— p_0= 40 atm; - - - - p_0 =10 atm

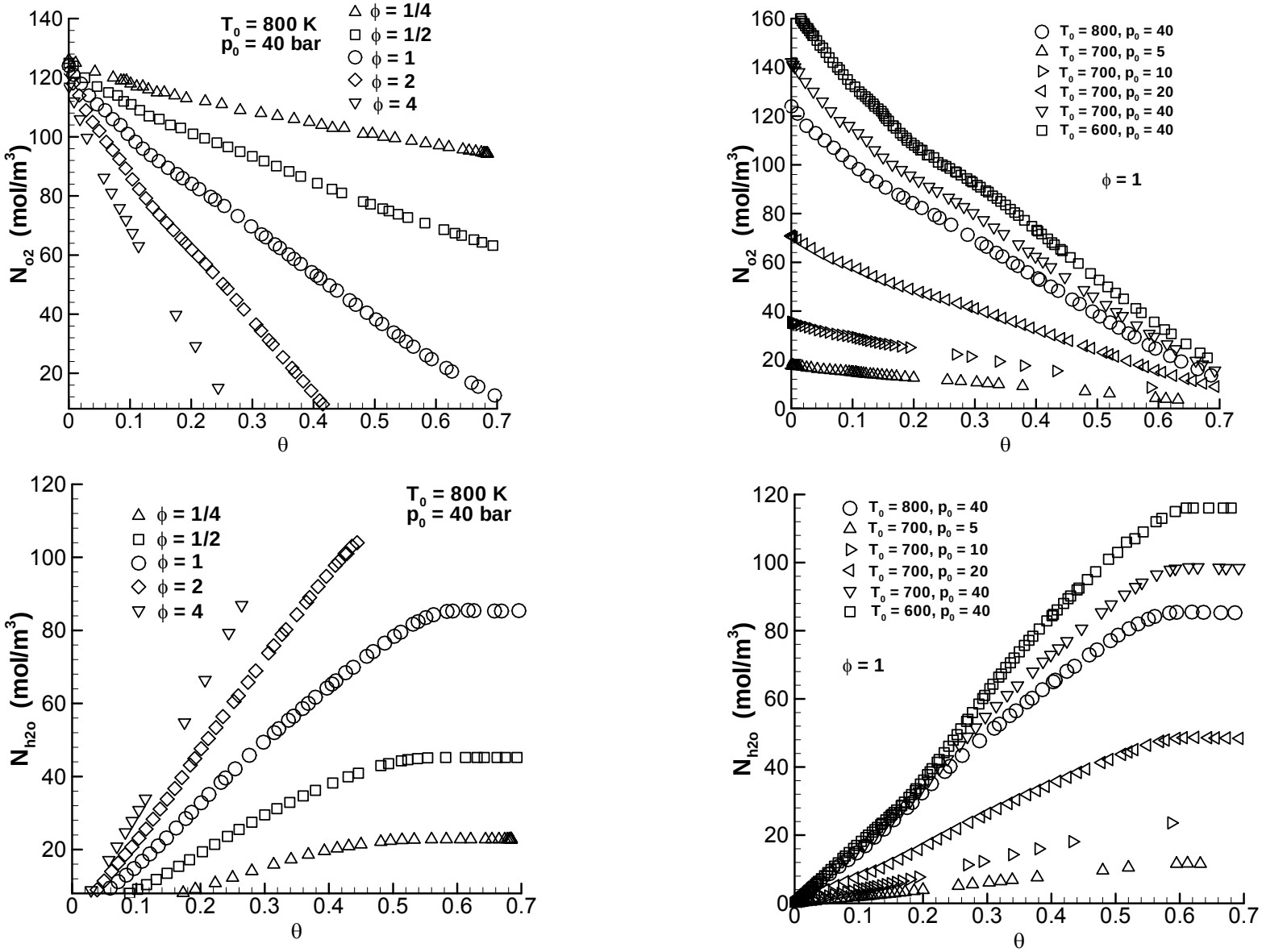
Self-similar behavior persists





$N_c/(\phi \times N^*)$ in mol/(m^3), p_0 in bar, T_0 in K

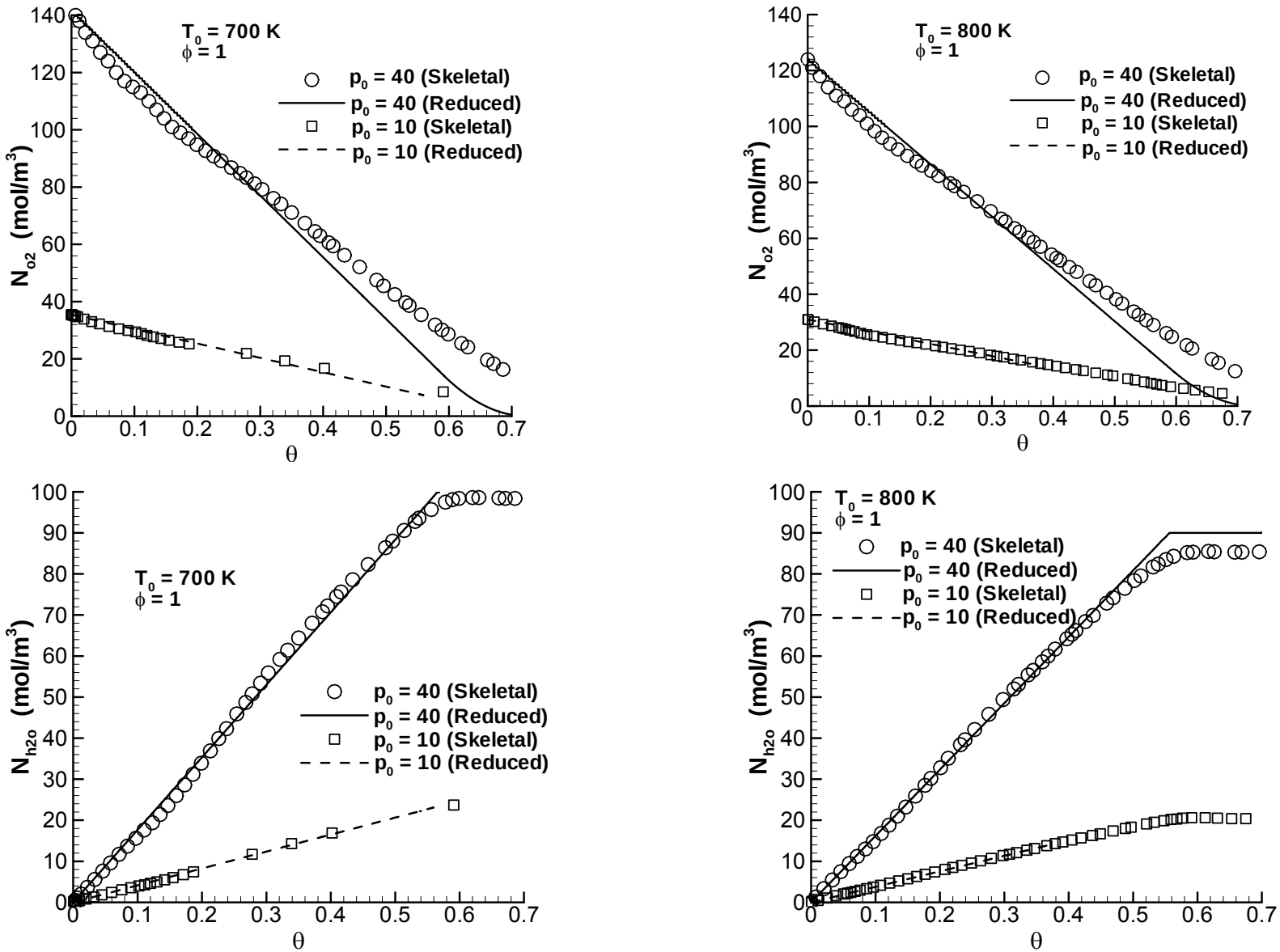
Additional benefit of concept assessment



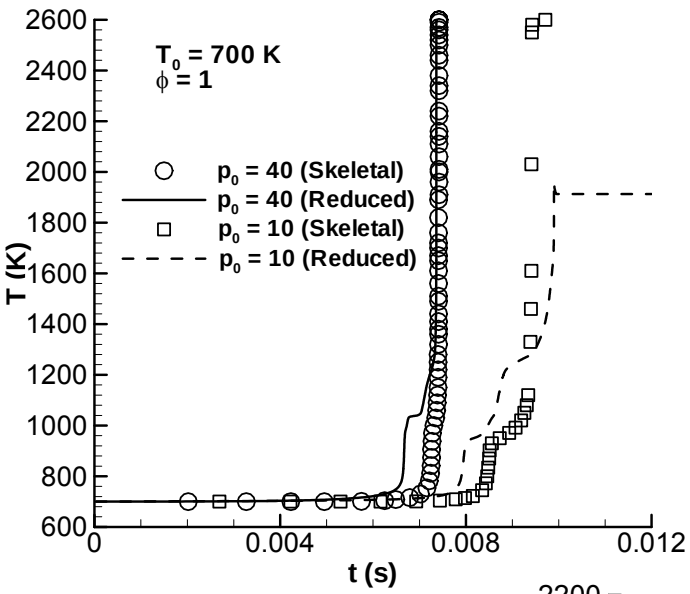
Revised reduced model

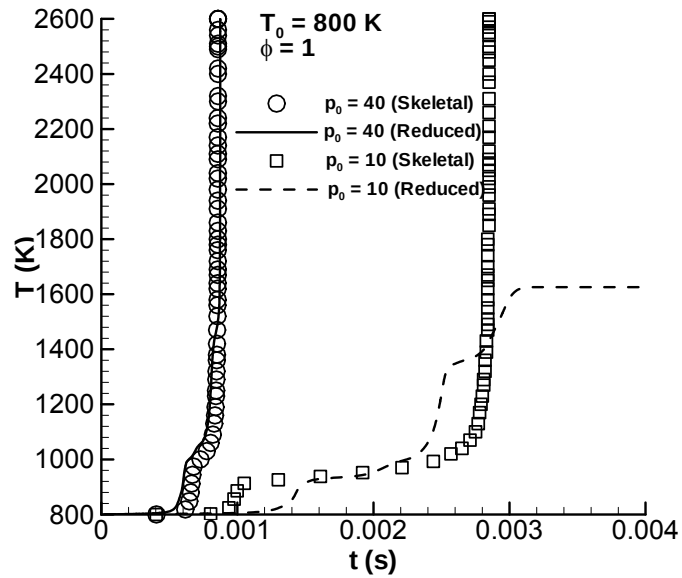
- Fit N_c rather than fitting K_c
- Revised model for K_h
  - Refined functional fit for $\theta \ll 10^{-2}$ (curve fitting improvement)
  - Modification of the initial slope w.r.t. T to capture the lost information due to mechanism reduction (modeling improvement)
- Modeling of N_{O2} and N_{H2O} as quasi-linear functions of θ
- Refined functional fit of KG_i for $\theta \ll 10^{-2}$ (curve fitting improvement)

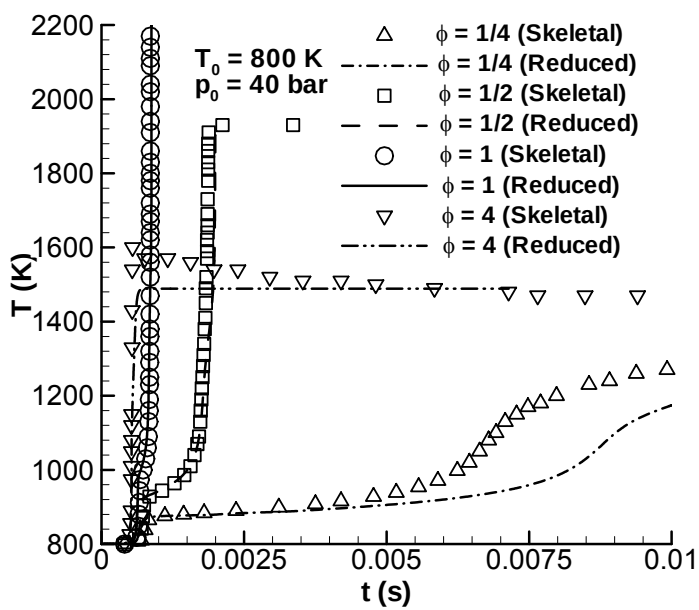
A priori modeling: functional fits for N_{O2} and N_{H2O}



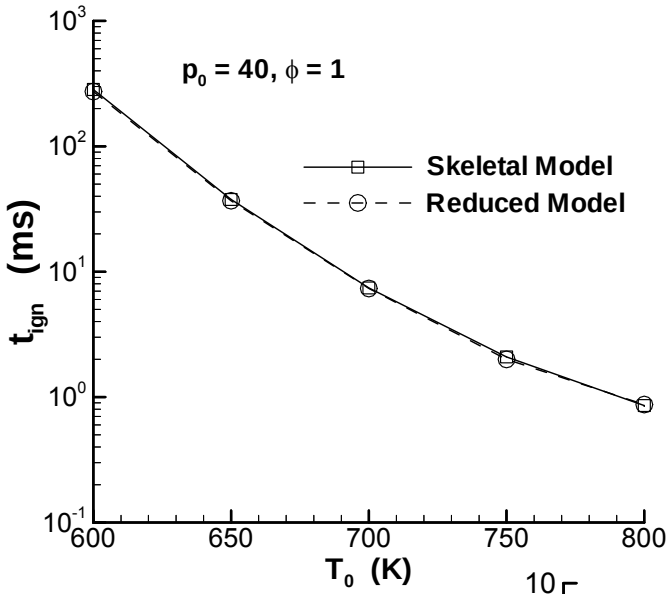
A posteriori results with revised model: T evolution

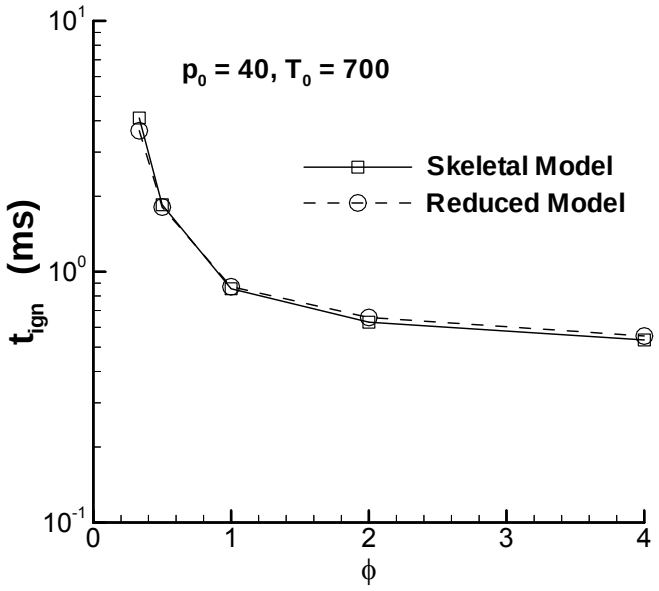


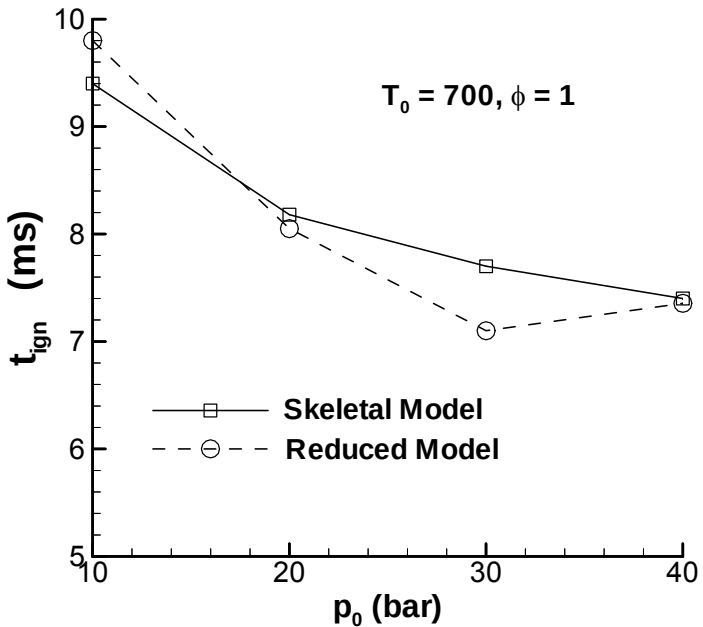




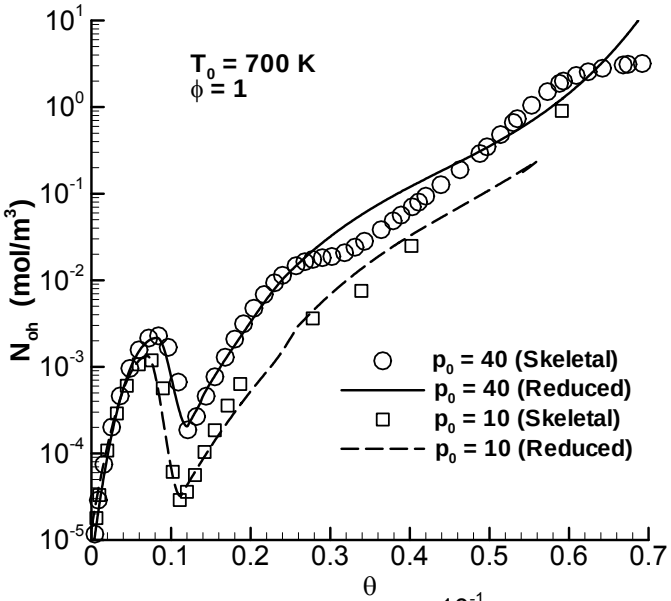
Prediction of ignition time

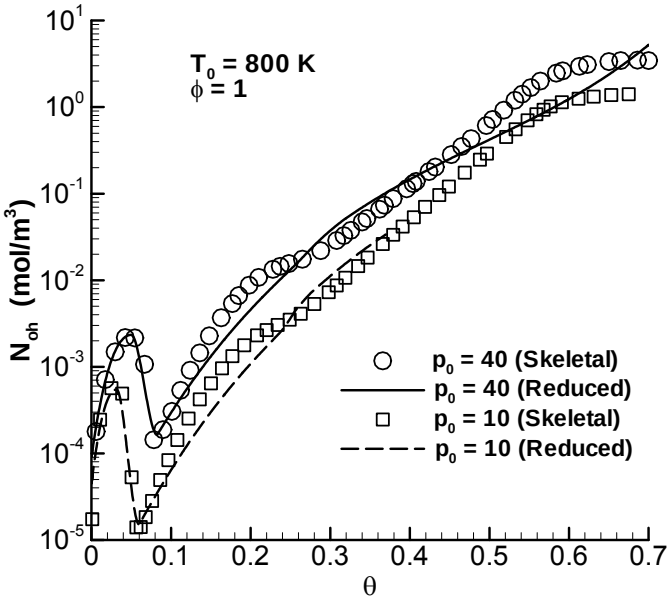


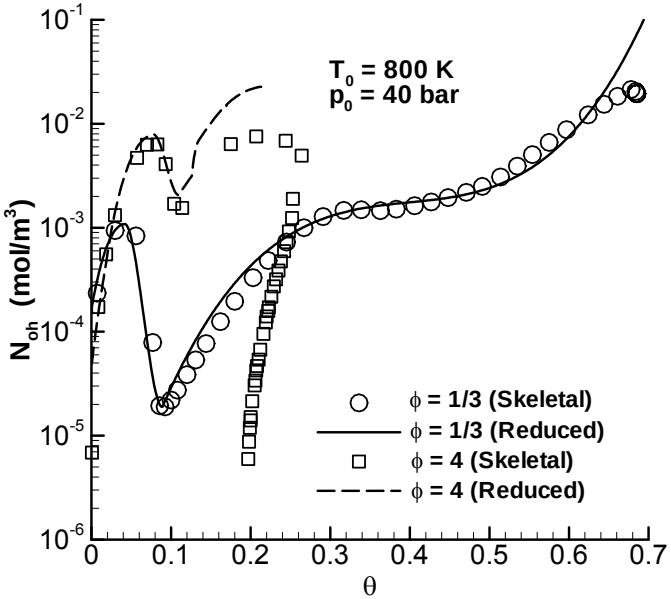




Prediction of N_{OH}







Summary and conclusions

1. Explained how our reduced kinetics modeling parallels turbulence modeling within the concept of LES: *a priori* and *a posteriori* studies.

2. Conducted decoupled concept and *a priori* model (i.e. functional fits) assessments using the LLNL template.

3. Revised our previous *a priori* model and simplified it. The revised final model has

- 9 instead of 12 ultimate species progress variables (removed N_c, N_{O2} and N_{H2O})
- 12 instead of 17 quasi-steady rate functions (removed K_c, KG_{O2}, KG_{H2O}, KL_{O2} and KL_{H2O})
- 3 added fits as function of θ (N_c, N_{O2} and N_{H2O})
- 9 curve fits for light species quasi-steady mole fractions, as in the original model
- 1 curve fit for $C_{p,h}$, as in the original model

4. Conducted an *a posteriori* assessment of the revised model study and found very good to excellent quantitative agreement for t_{ign}, T(t) and species mole fractions.

Future work

1. Enlargement to higher C alkanes is conceptually straightforward if the quasi-steady aspect is preserved because additional species do not lead to additional progress variables due to the N_c grouping

   ➡

   Extend the model to iso-octane (Remains to be seen if the present curve fits are valid for higher C alkanes or must be modified)

2. Model mixtures of hydrocarbons

3. Model flames