Introduction to Chemical Kinetics for Combustion

PART II

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Outline

- What drives combustion?
- Temperature dependency of chemical kinetic pathways (aka low T chemistry)
- Chemical kinetic model reduction and stiffness removal
- Extension to CFD: is detailed chemistry always the answer?

What drives combustion?

It is the radicals, stupid!

What drives reaction progress in combustion?

Reaction progress driven mostly by **radicals**

- The electronic configuration of an atom determines **its valence,** that is, the number of electrons in the outermost shell (highest energy levels) able to form bonds.

- A radical is formed when one of the valence electrons is not paired.

- Radicals are highly reactive and tend to react with other species to reach the more stable paired-electron configuration

Radicals drive reaction progress in combustion

Radical balance is the most important aspect

- 4 types of reactions:
  - **Initiation** reactions – Stable molecules creating radicals
    What are the initiation reactions in the heptane/air case from part I?

```
#P      78.   N-C7H16 REACTIONS
n196: N-C7H16           -> p-C4H9 + n-C3H7       { a = 3.160E+16   n = 0    E = 339.2 }

n197: N-C7H16 + H       -> 1-C7H15 + H2          { a = 7.300E+07   n = 2    E = 32.2 }
n198: N-C7H16 + H       -> 2-C7H15 + H2          { a = 3.500E+07    n = 2   E = 20.9 }

n201: N-C7H16 + OH      -> 1-C7H15 + H2O         { a = 10.560E+09   n = 1.1    E = 7.6 }
n202: N-C7H16 + OH      -> 2-C7H15 + H2O         { a = 5.200E+09    n = 1.3 E = 2.9 }

n209: N-C7H16 + HO2     -> 1-C7H15 + H2O2        { a = 1.790E+13   n = 0    E = 81.2 }
n210: N-C7H16 + HO2     -> 2-C7H15 + H2O2        { a = 13.400E+12   n = 0   E = 71.2 }

n217: N-C7H16 + O2      -> 1-C7H15 + HO2          { a = 5.500E+13   n = 0    E = 205.2 }
n218: N-C7H16 + O2      -> 2-C7H15 + HO2          { a = 8.000E+13   n = 0   E = 199.3 }
```

Radicals drive reaction progress in combustion

Radical balance is the most important aspect

- 4 types of reactions:
  - **Initiation** reactions – Stable molecules creating radicals
  - **Chain-branching reactions** – more radicals in reactants than in products
    Example
  - **Chain-Propagating** reactions – Same number of radicals on both sides
    Example
  - **Chain-breaking/terminating** reactions – Fewer radicals in reactants than in products
    Example

Radicals drive reaction progress in combustion

- **Most important** radicals for combustion:

  and in specific conditions,

- O is different from the others:

- They play similar roles in the kinetics due to fast shuffling reactions

$$O + H_2 \rightleftarrows OH + H$$
$$OH + H_2 \rightleftarrows H_2O + H$$
$$OH + OH \rightleftarrows H_2O + O$$

Radicals drive reaction progress in combustion

- Most important **chain-branching reaction**

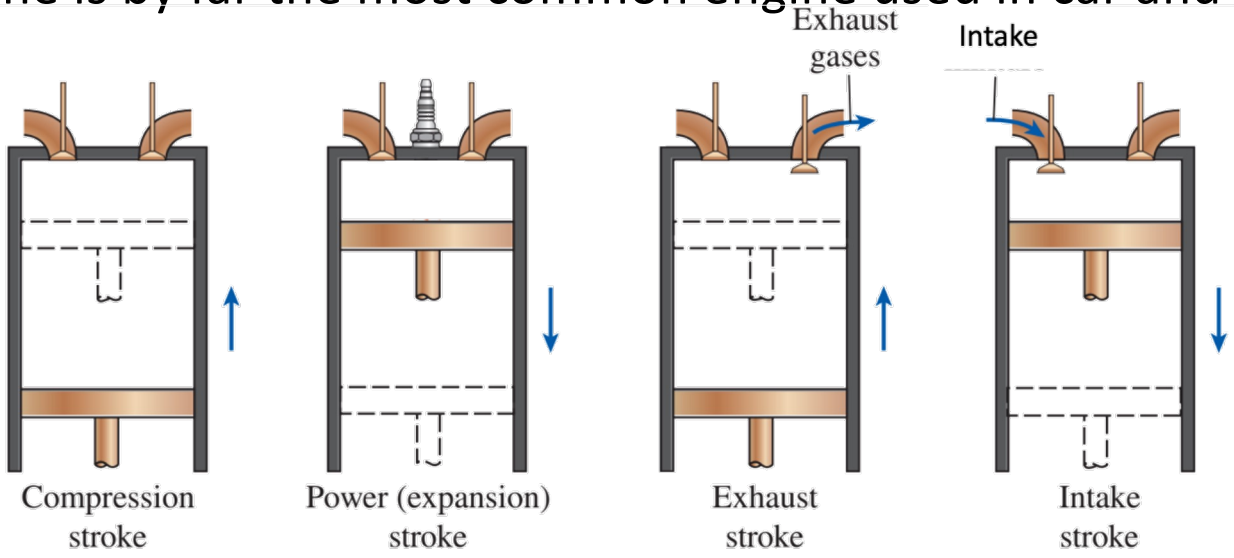
- Very significant reaction for **chain-breaking:**

Chemical kinetics pathways are strong function of the temperature

Quick overview of low temperature chemistry

Application: Internal combustion engines

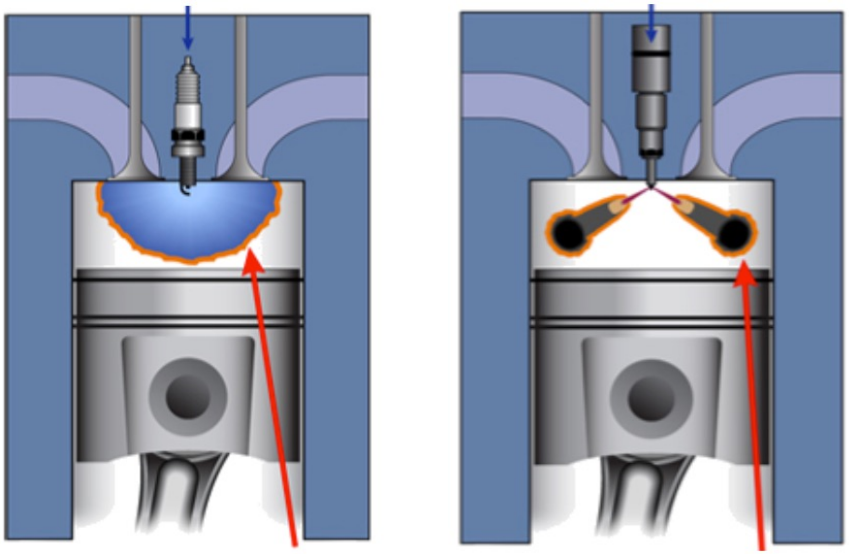
- 4-stroke engine is by far the most common engine used in car and trucks



Spark-ignition (gasoline)

- Pre-vaporized fuel and air during intake
- Timing of combustion through spark
- Premixed flame propagation

Low emissions



Compression-ignition (diesel)

- Only air during intake
- Timing of combustion through fuel injection
- Autoignition and mixed mode of combustion

High emissions

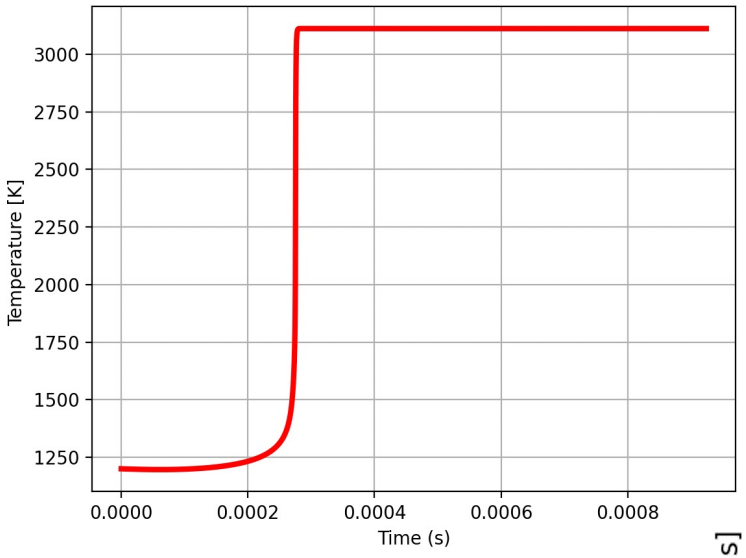
Application: Internal combustion engines

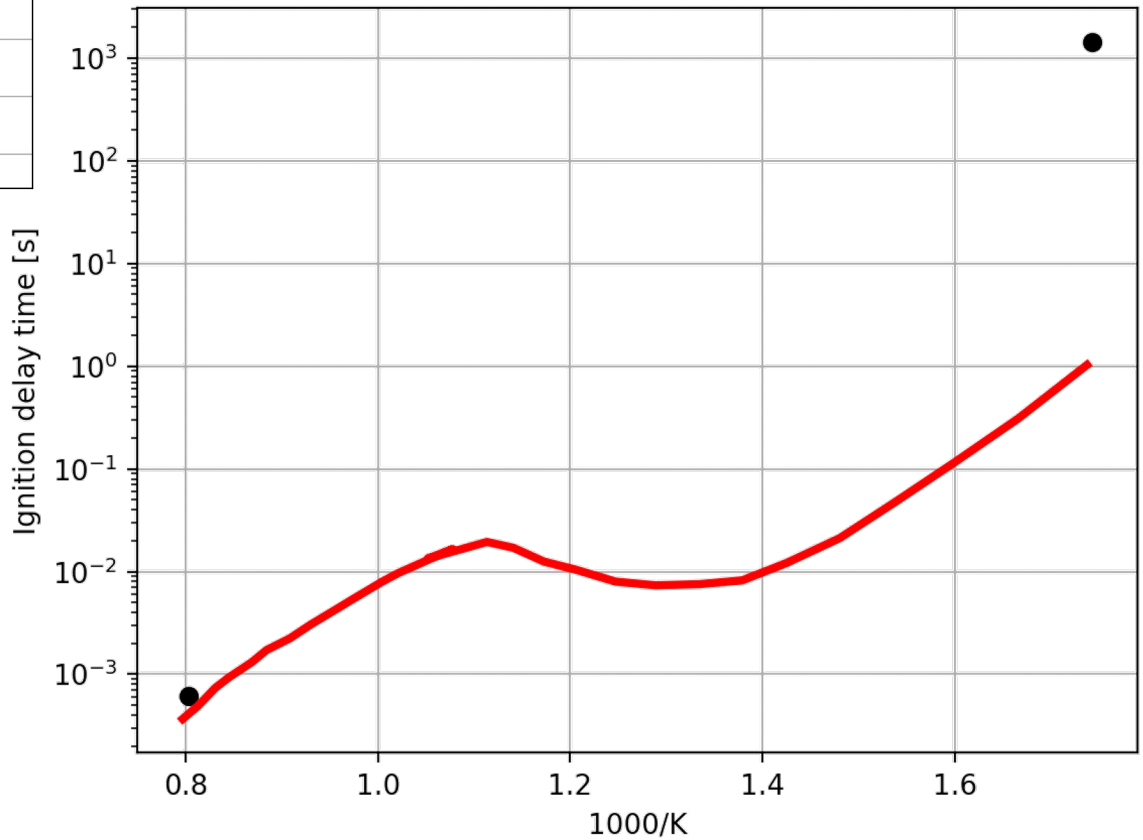
- Thermal efficiency related to compression ratio
- Typical compression ratios:

- What happens if you put gasoline into a pure ethanol engine (both SI)?
  - Vaporization is not the same, issue with cold start
  - Global reaction VERY different, you would be injecting way too much gasoline and burning very rich
  - Flame speeds not the same: ignition time advance (when spark plug goes off) would be off
  - Spark plugs, oxygen sensors, catalytic converters would be in trouble
  - Octane number is very different: high risk of knocking! Fuel/air mixture auto-ignites before flame gets to it, creating undesirable pressure peaks

Ignition delay time and its temperature dependency

Temperature profile for heptane/air





Heptane auto-ignition at high temperature

- Initiation reactions

- As soon as there is some H in the system, favorite chain-branching reaction starts cranking radicals

- Fuel radicals are short-lived: most favored reaction involves breaking the chain into small pieces

- Once the HC fragments are small enough, oxidation starts, creating C-O bonds, removing hydrogen

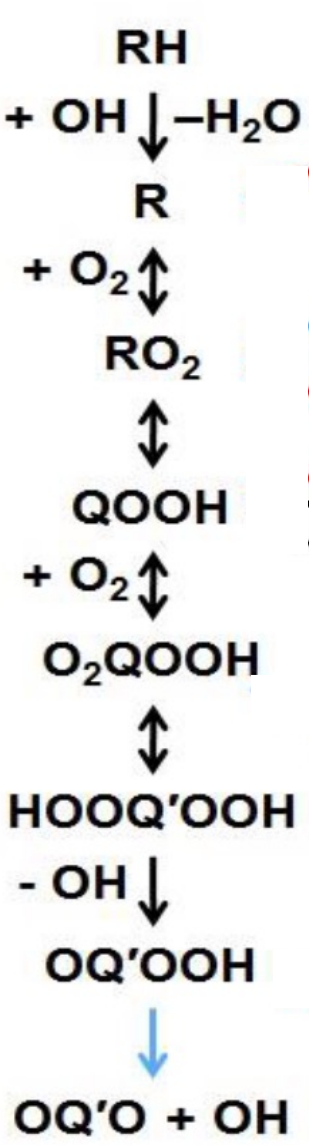
- At the end, CO is fully oxidized to CO_2 nearly exclusively through

At high temperature, fuel quickly breaks down to small fragments and C-O bonds are formed on C1-C2 species

- **Most fuels behave the same**
- **Very good understanding of the chemistry and associated rates**

Heptane auto-ignition at low-temperature

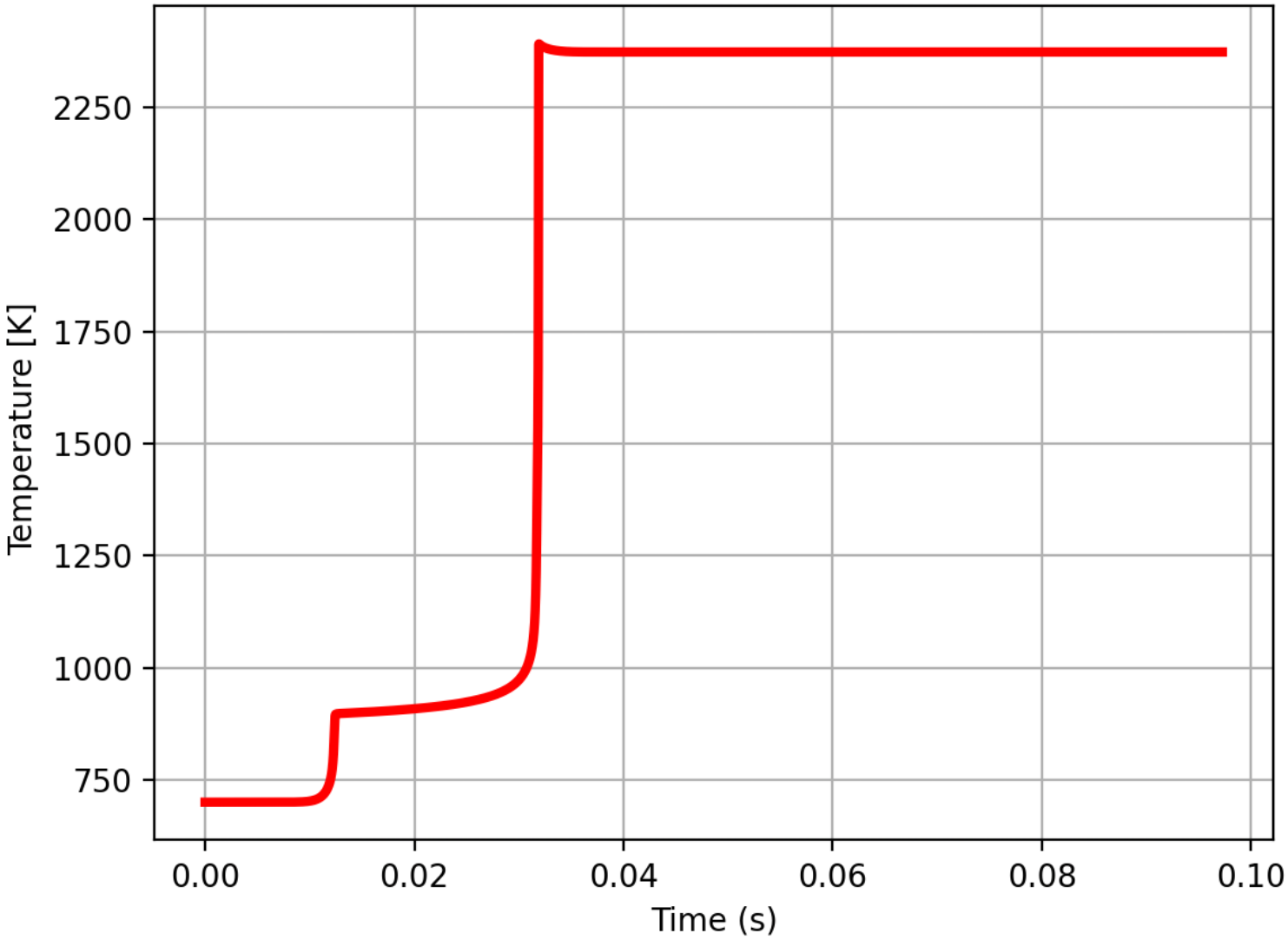
- Initiation starts the same. However, unimolecular breakdown of the fuel molecule is not favored anymore: fuel radical is long-lived



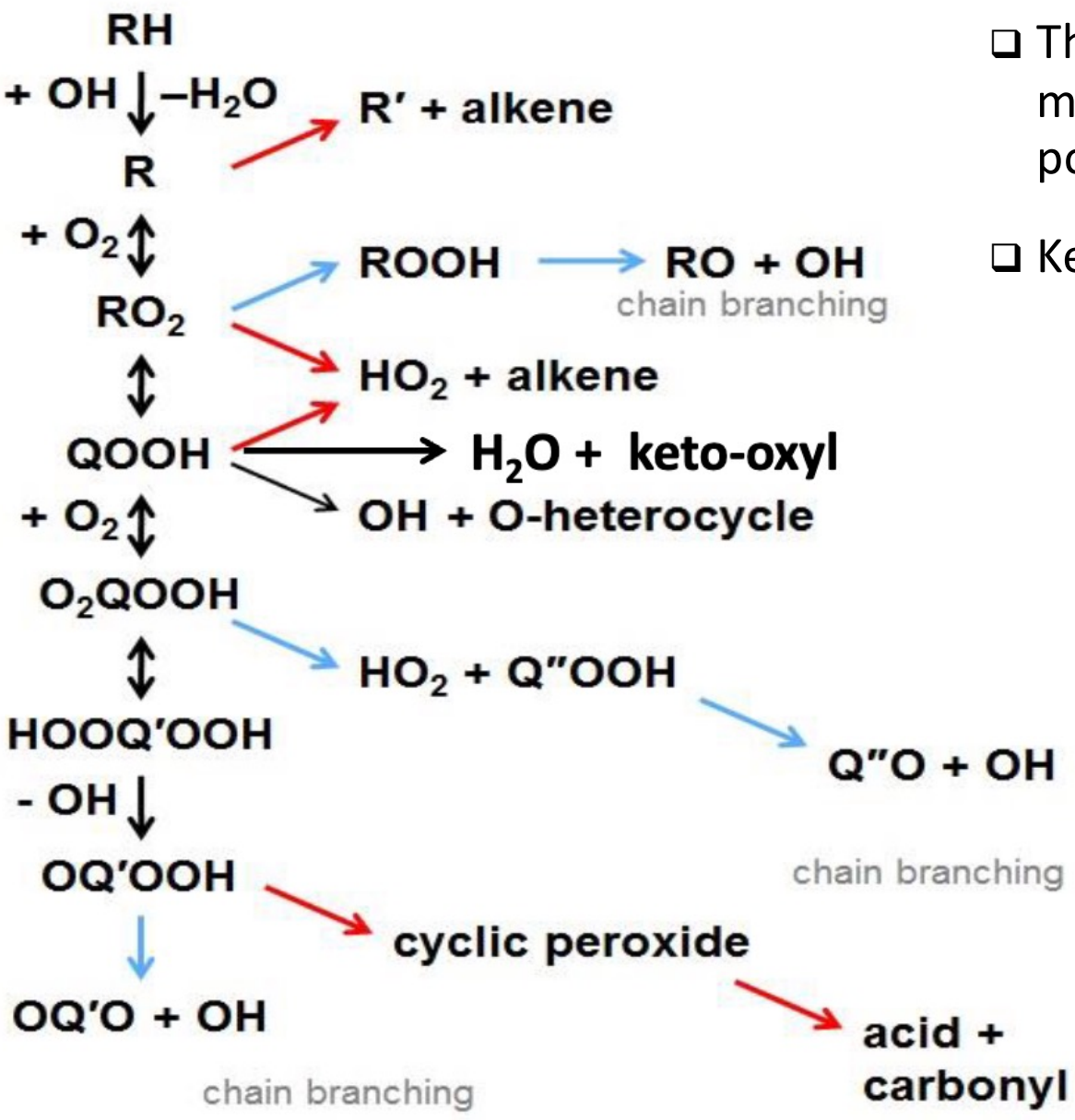
Zador, Taatjes & Fernandes, adapted by Green

Heptane auto-ignition at low-temperature

- Temperature profile is quite specific



Heptane auto-ignition at low-temperature

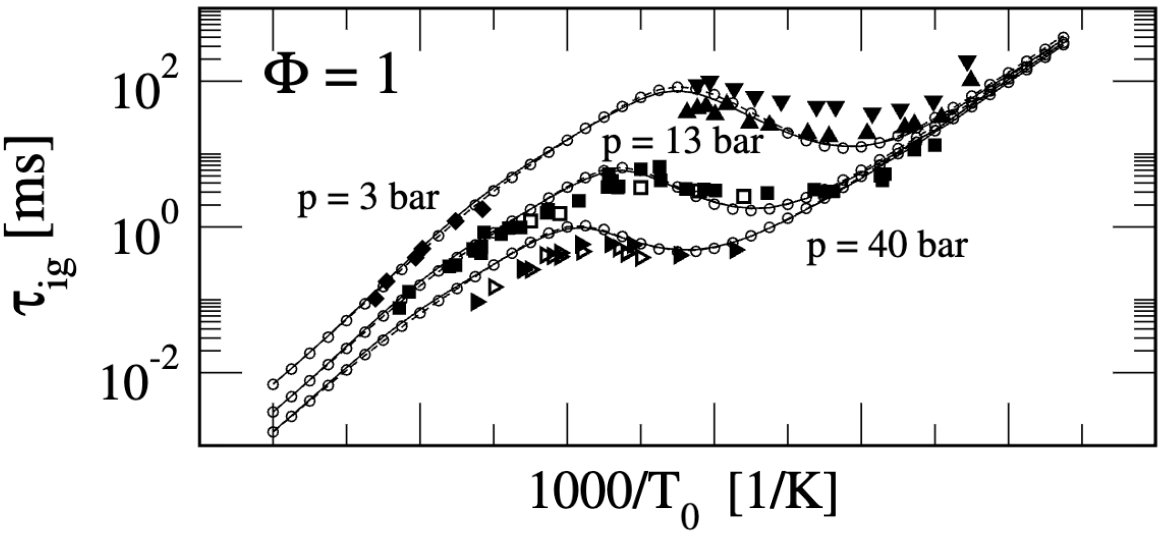


- The actual chemistry is much more complicated, with many potential side channels
- Key challenge:

Overall, reasonably well understood

Zador, Taatjes & Fernandes, adapted by Green

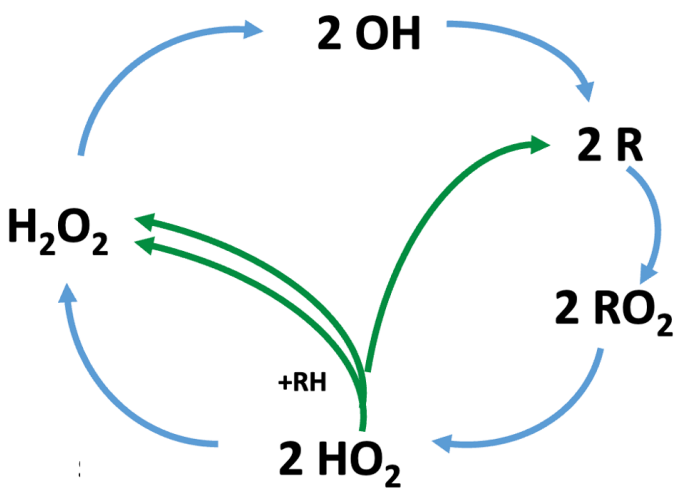
Heptane auto-ignition at medium temperatures



- In an intermediate range of temperature, there is a **kinetically favored** kinetic pathway that is
  - More efficient at igniting than the high temperature pathway (unimolecular decompositions need lots of energy to proceed)
  - Less efficient at igniting than the low temperature pathway (OH is getting replaced by some other radical)

Heptane auto-ignition at medium temperatures

- At medium T, the fuel radical is very slow at breaking down
  - O_2 has its chance! But when R and O_2 combine, they do not result in RO_2
  - In addition, our favorite chain branching reaction gets side lined
  - HO2 still creates a chain-branching cycle



Moderately well understood, less so than the other regimes

Reproduced from W. Green, MIT

When detailed chemistry is too detailed

Sometimes it is…

Numerical simulations

- **What we want**: couple kinetics info with real-world combustion, which is virtually always turbulent
- **What we can do** with detailed chemistry given the number of variables: a few simple laminar configurations
  - **Homogeneous systems (no transport terms)**
    - Isochoric adiabatic reactor
    - Isobaric adiabatic reactor
  - **One-dimensional systems**
    - Freely propagating laminar flame
    - Burner stabilized laminar flame
    - Counterflow diffusion flame
  - **Idealized reactors**
    - Partially stirred reactor: homogeneous at the macro level, heterogeneous at the micro level to mimic molecular diffusions when testing kinetic models

Far cry from actual turbulent configurations!

Numerical simulations

- Number of variables limit detailed numerical solutions to a few simple laminar configurations

Isochoric adiabatic reactor

- Governing Equations

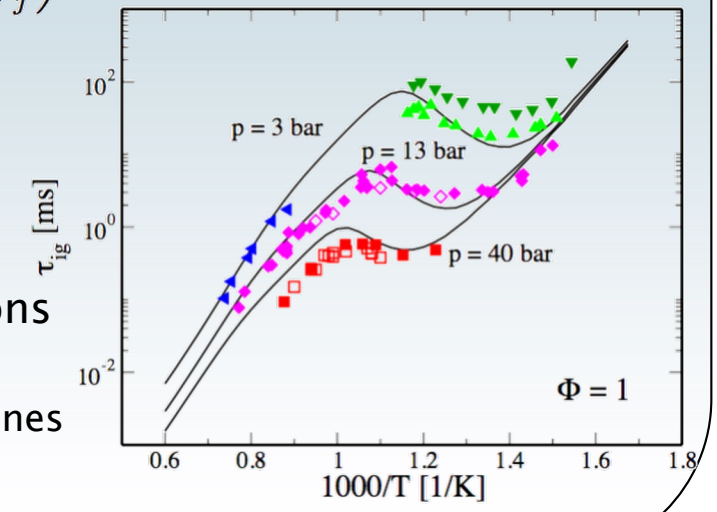
$$\rho \frac{dY_j}{dt} = W_j \omega_j$$

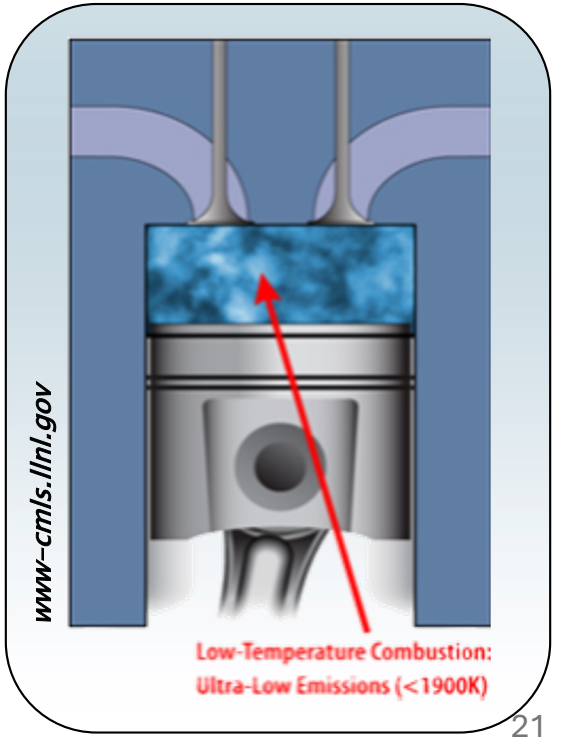
$$\rho \left(c_p - \frac{R}{W} \right) \frac{dT}{dt} + \sum_{j=1}^{n} \left(h_j - \frac{R}{W_j} \right) W_j \omega_j = 0$$

$$P = \frac{\rho R T}{W}$$

- Type of information
  - Ignition delay time
- Experimental configurations
  - Shock tube
  - rapid compression machines

n–heptane/air





Numerical simulations

- Number of variables limit detailed numerical solutions to a few simple laminar configurations

Isobaric adiabatic reactor

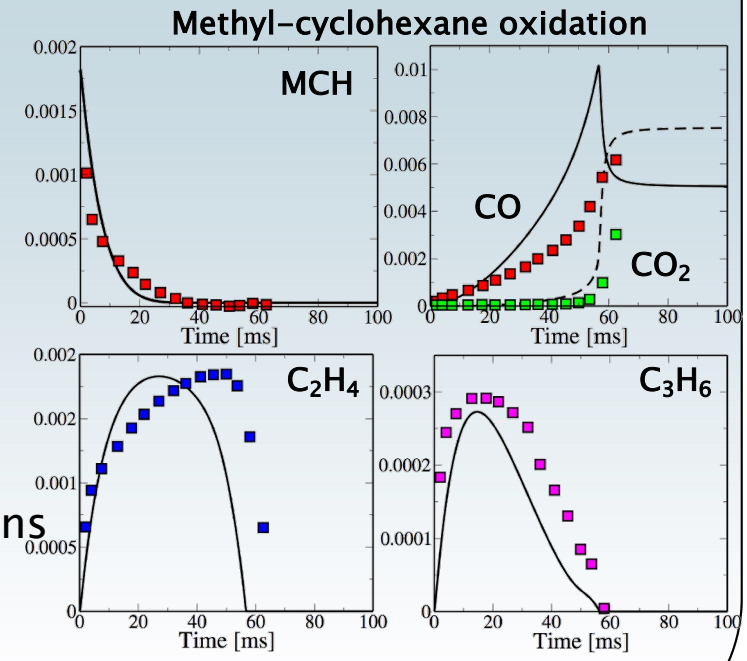
- Governing Equations

$$\rho \frac{dY_j}{dt} = W_j \omega_j$$

$$\rho c_p \frac{dT}{dt} + \sum_{j=1}^{n} h_j W_j \omega_j = 0$$

$$\rho = \frac{PW}{RT}$$

- Type of information
  - species concentrations
- Experimental configurations
  - Plug Flow Reactor (PFR)
  - Diluted or lean mixtures



Numerical simulations

- Number of variables limit detailed numerical solutions to a few simple laminar configurations

Propagating laminar flame

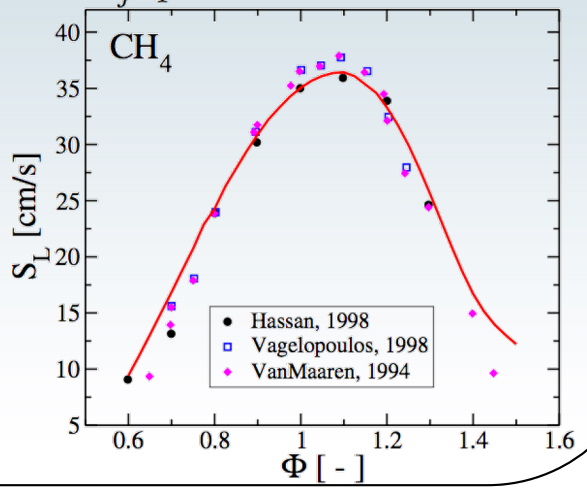
- Governing Equations

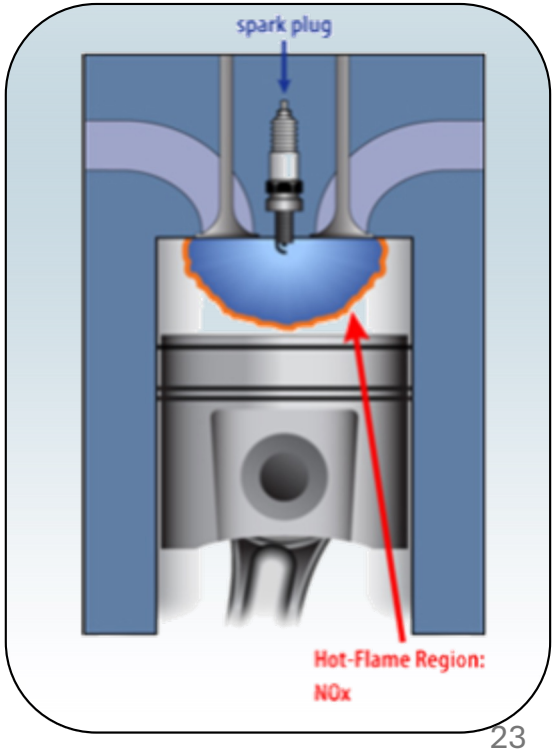
$$\rho V = \text{const}$$

$$\rho V \frac{dY_j}{dy} + \frac{d}{dy}\left(\rho Y_j v_j\right) = W_j \omega_j$$

$$\rho V \frac{dT}{dy} - \frac{d}{dy}\left(\lambda \frac{dT}{dy}\right) + \frac{d}{dy}\left(\rho Y_j v_j C_{p_j} \frac{dT}{dy}\right) + \sum_{j=1}^{n} h_j W_j \omega_j = 0$$

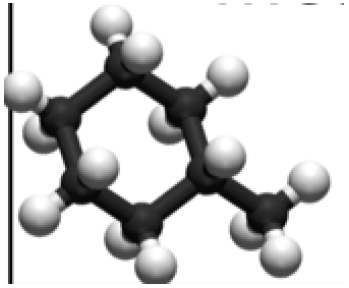
- Type of information
  - Laminar burning velocity
- Experimental configurations
  - Combustion bomb

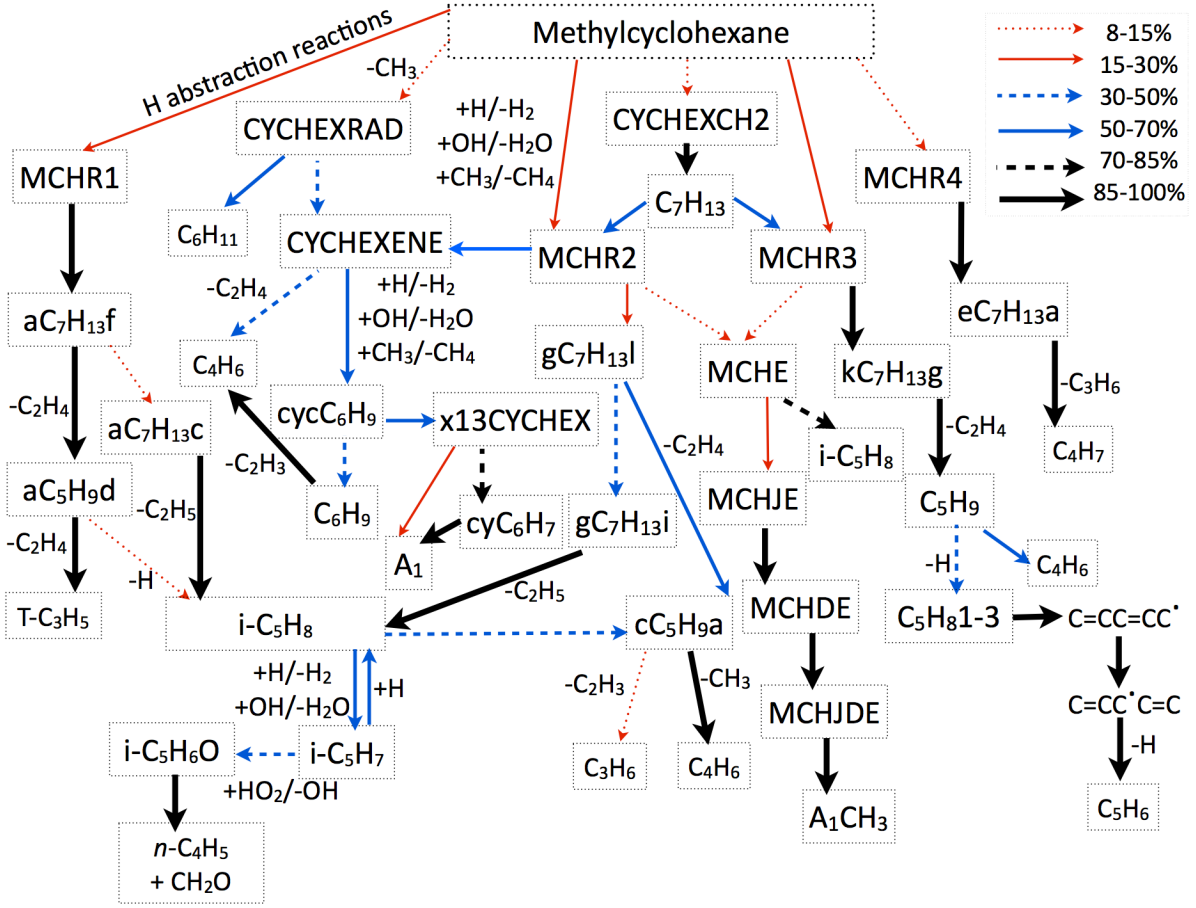




Chemical model reduction

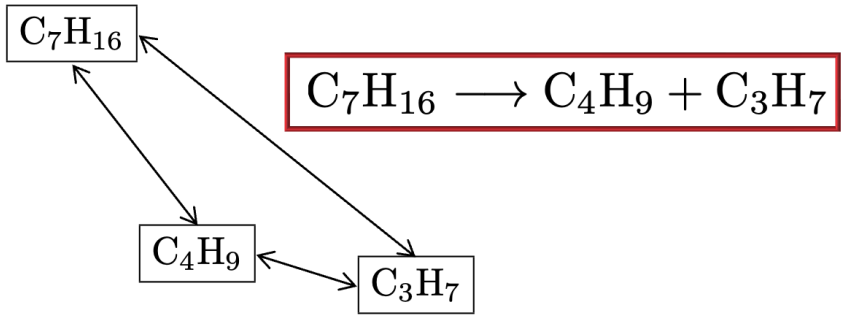
- Chemical kinetic mechanism is a network, from which we want to extract the most important connections for some conditions of interest





Chemical model reduction

- View reaction mechanism as kinetic network, well represented as a directed graph



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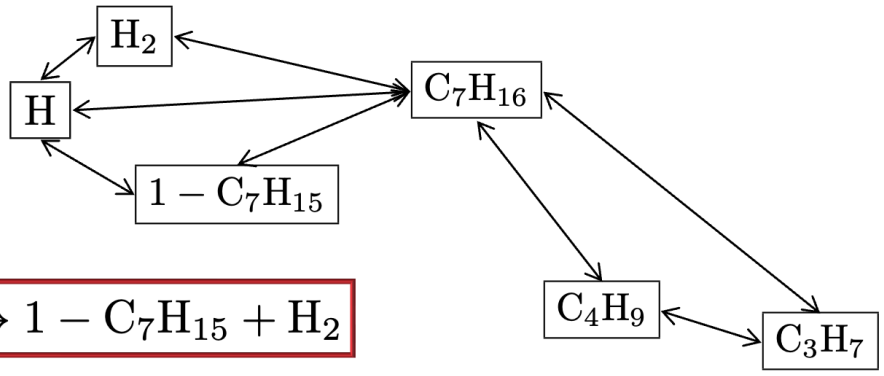
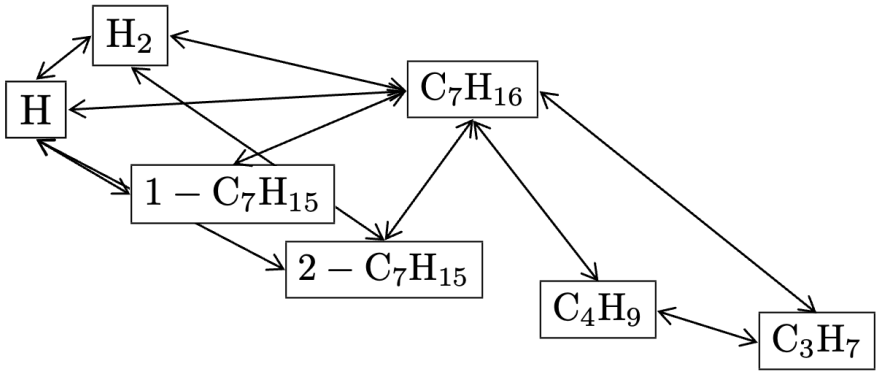


$$C_7H_{16} + H \longrightarrow 1 - C_7H_{15} + H_2$$

Chemical model reduction

- View reaction mechanism as kinetic network, well represented as a directed graph



$$C_7H_{16} + H \longrightarrow 2 - C_7H_{15} + H_2$$

Chemical model reduction

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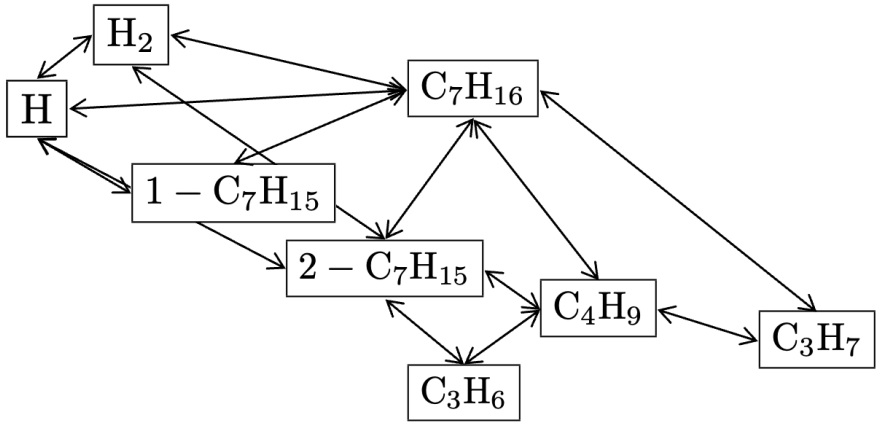
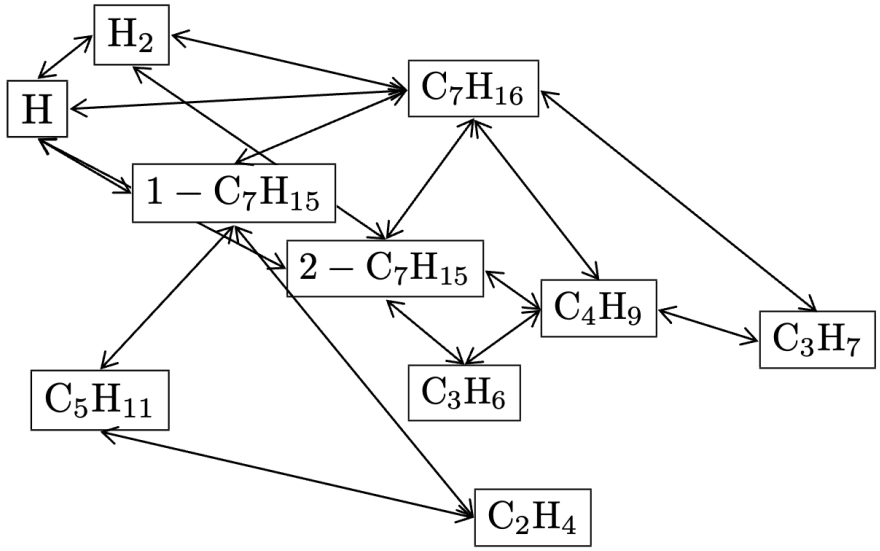


$$2 - C_7H_{15} \longrightarrow C_4H_9 + C_3H_6$$

Chemical model reduction

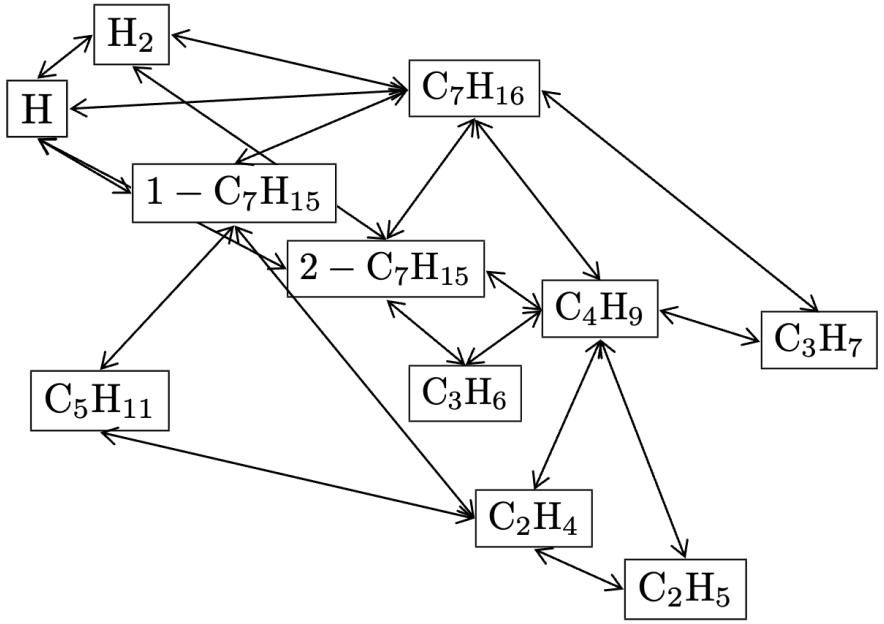
- View reaction mechanism as kinetic network, well represented as a directed graph



$$1-C_7H_{15} \longrightarrow C_5H_{11} + C_2H_4$$

Chemical model reduction

- View reaction mechanism as kinetic network, well represented as a directed graph



$$C_4H_9 \longrightarrow C_2H_5 + C_2H_4$$

Chemical model reduction

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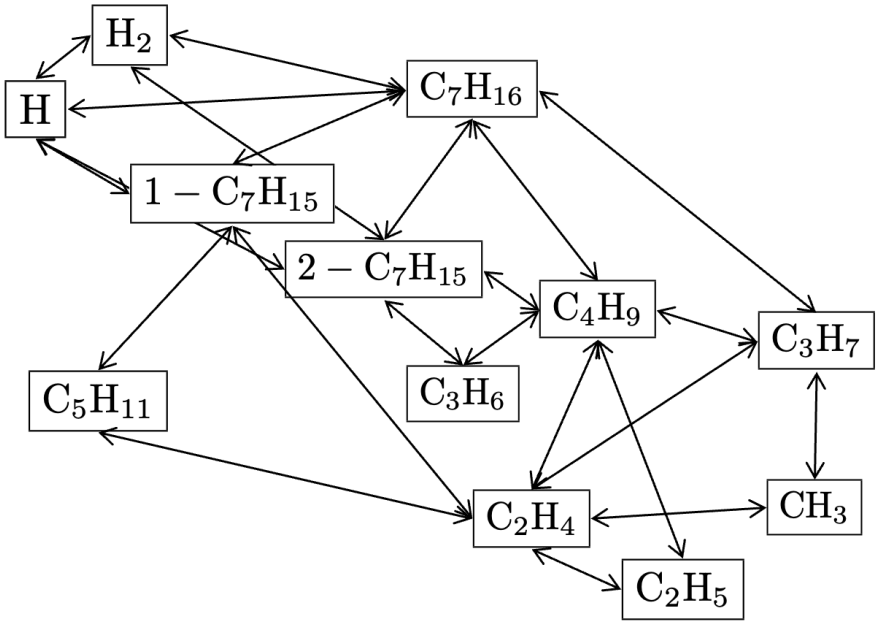

$$C_3H_7 \longrightarrow C_2H_4 + CH_3$$

Chemical model reduction

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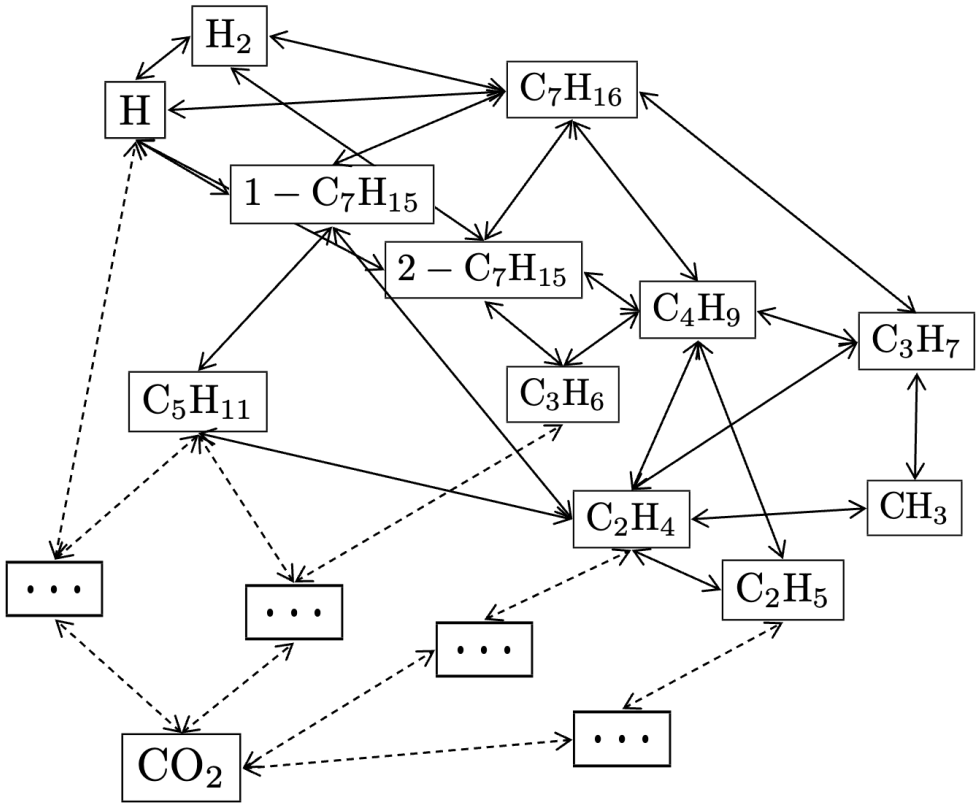
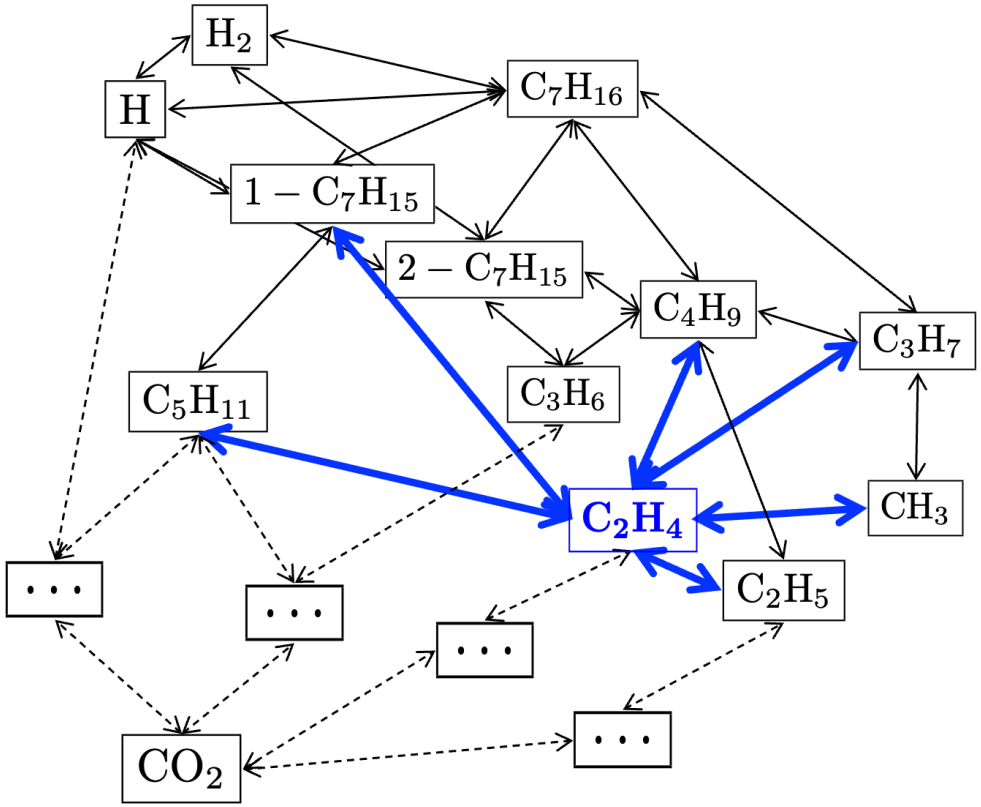


Directed Relation Graph family of techniques

- **Species reduction**: Identify nodes to remove, along with their connections



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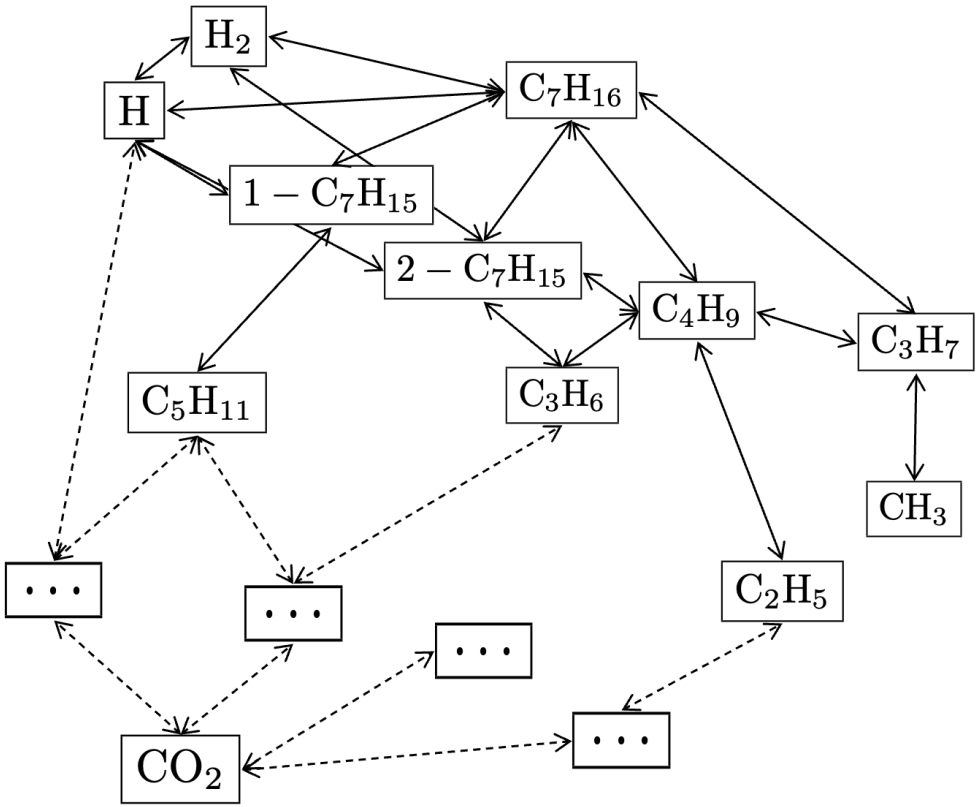

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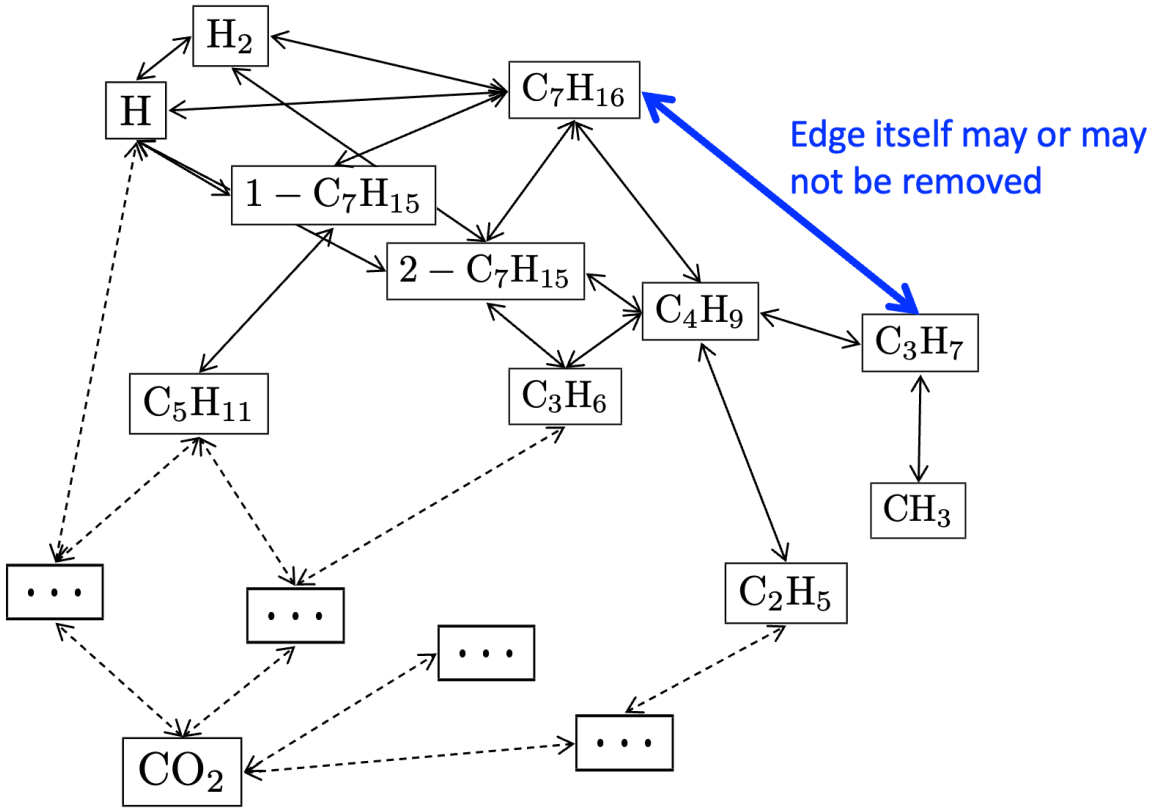
- **Species reduction**: Identify nodes to remove, along with their connections
- **Reaction reduction**: Identify edge contributions to remove



Directed Relation Graph family of techniques

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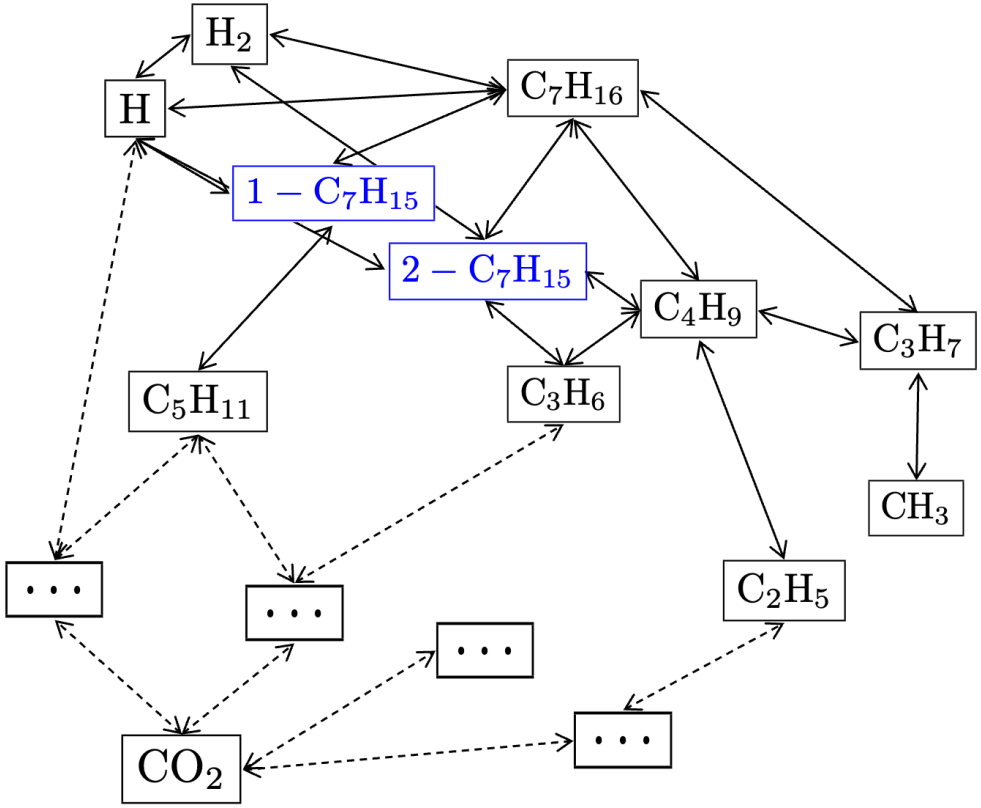
- **Isomer Lumping**: Merge nodes



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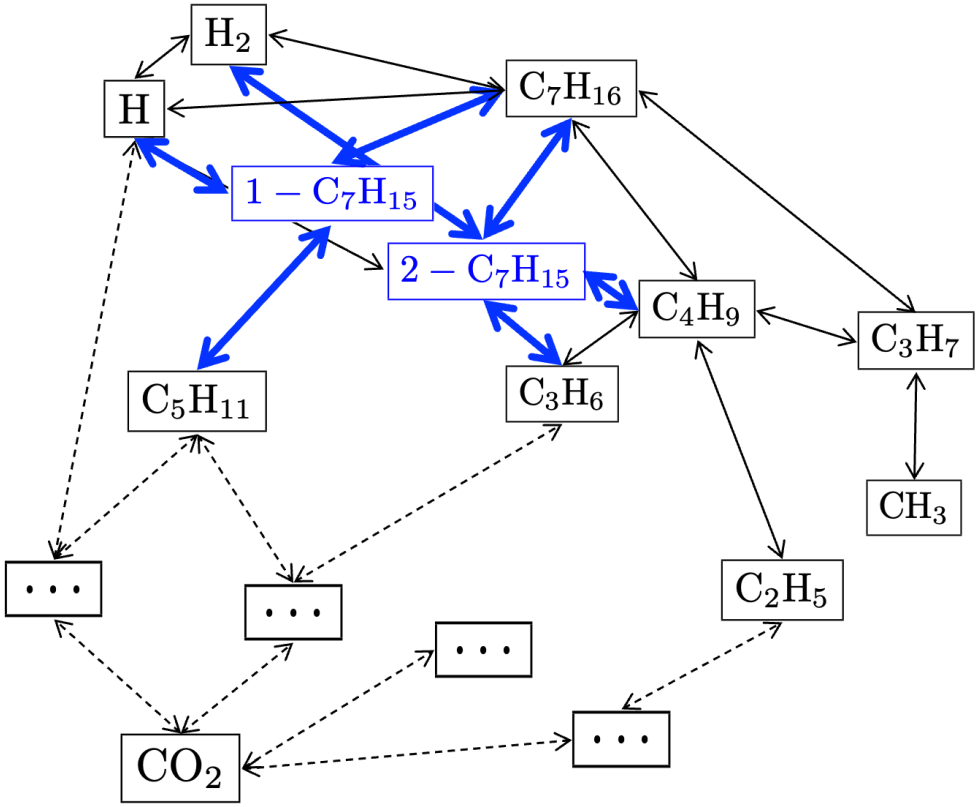

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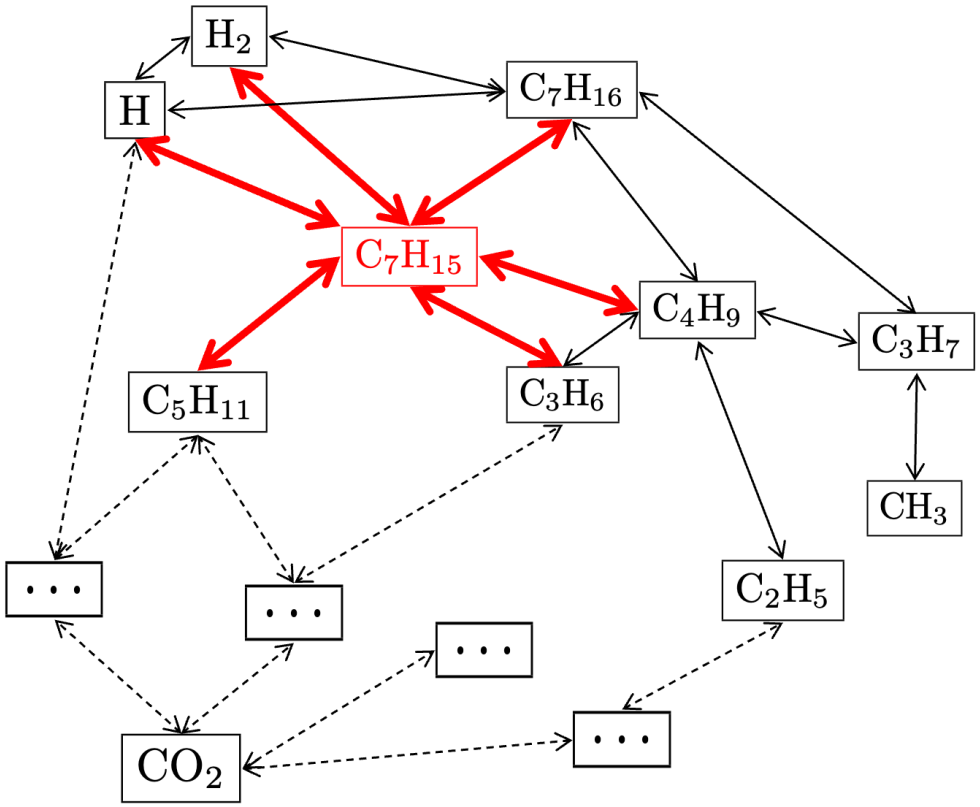
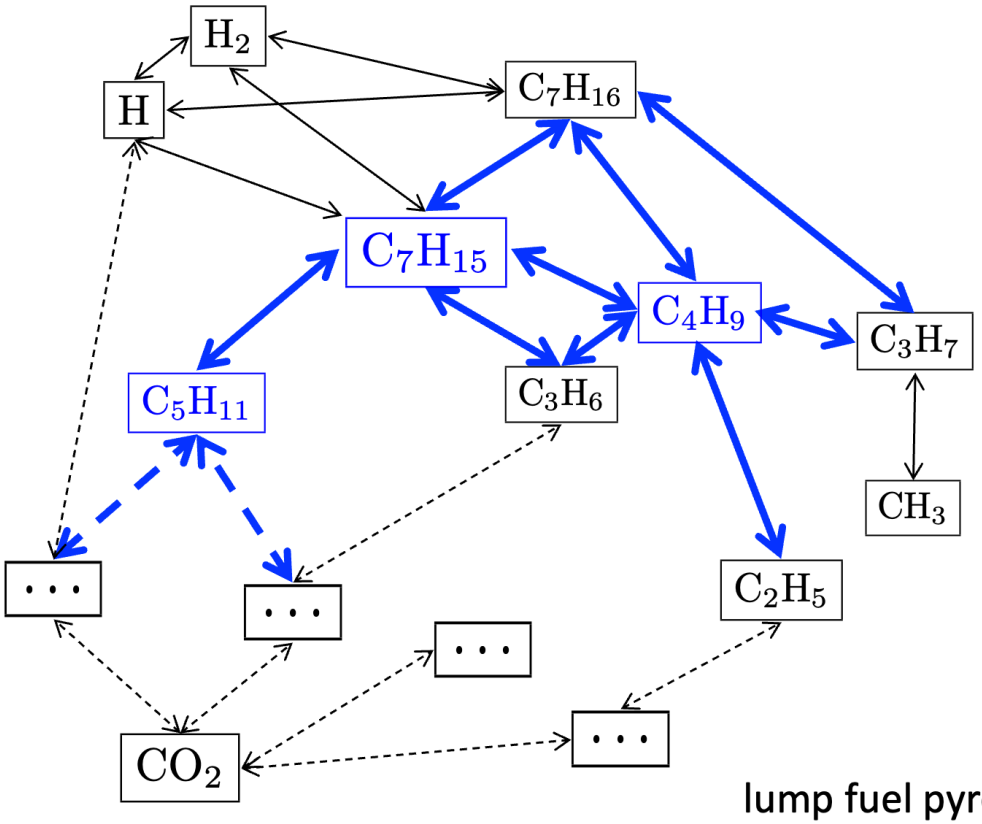


Directed Relation Graph family of techniques

- **Species reduction**: Identify nodes to remove, along with their connections
- **Reaction reduction**: Identify edge contributions to remove
- **Isomer Lumping**: Merge nodes
- **Path lumping**: collapse entire sections of the network



Example:
lump fuel pyrolysis pathway up to C3

Directed Relation Graph family of techniques

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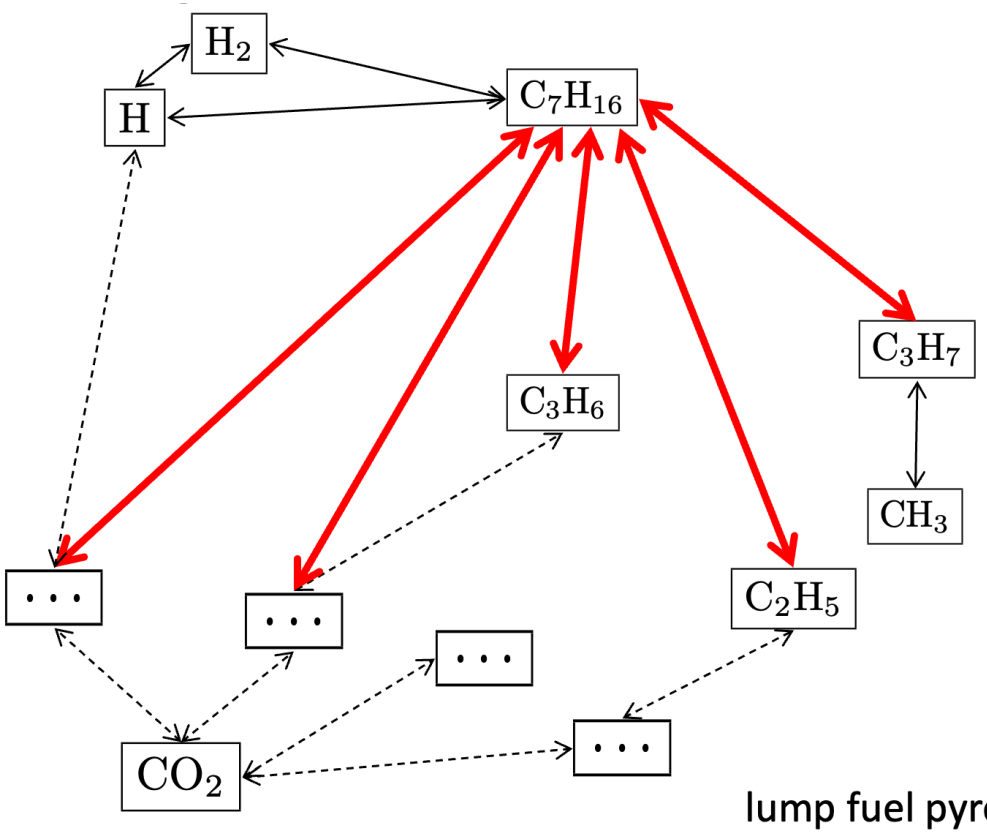

Example:
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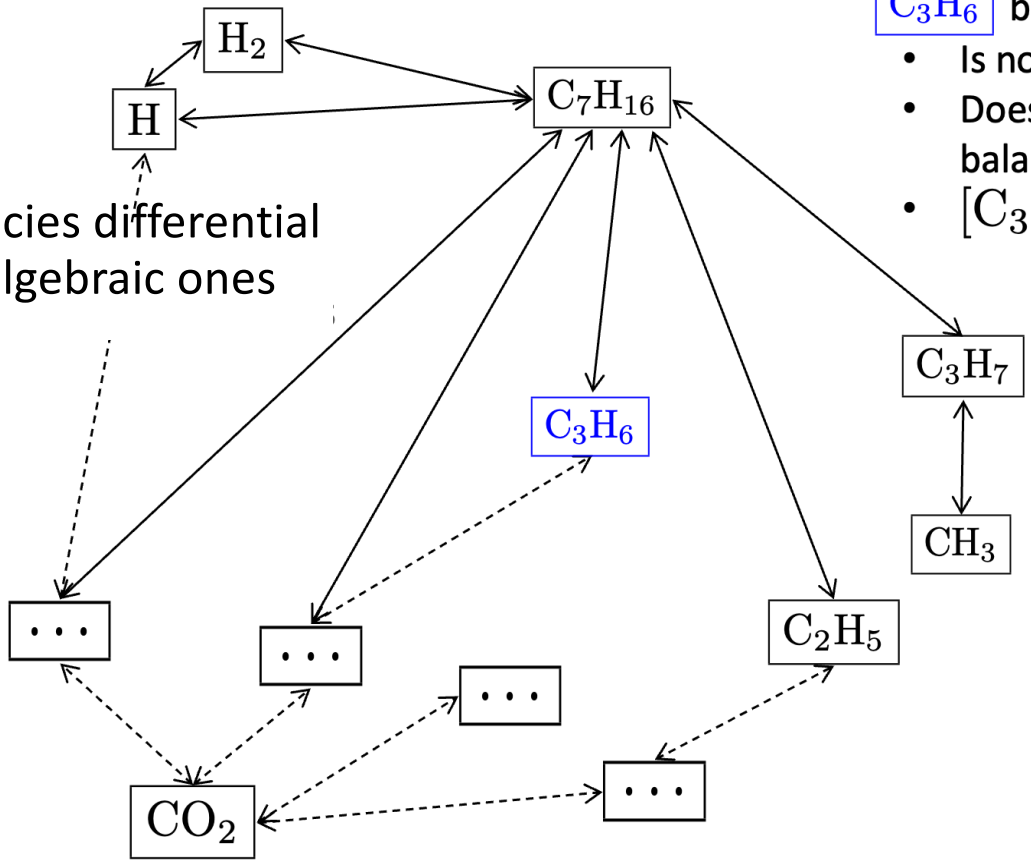
- **QSS**: replace species differential equations with algebraic ones



C_3H_6 becomes a fictitious species

- Is not transported
- Does not contribute to mass balance
- $[C_3H_6] = f\left([S_i]_{i \notin \text{qss}}\right)$

Directed Relation Graph family of techniques

- **Species reduction**: Identify nodes to remove, along with their connections
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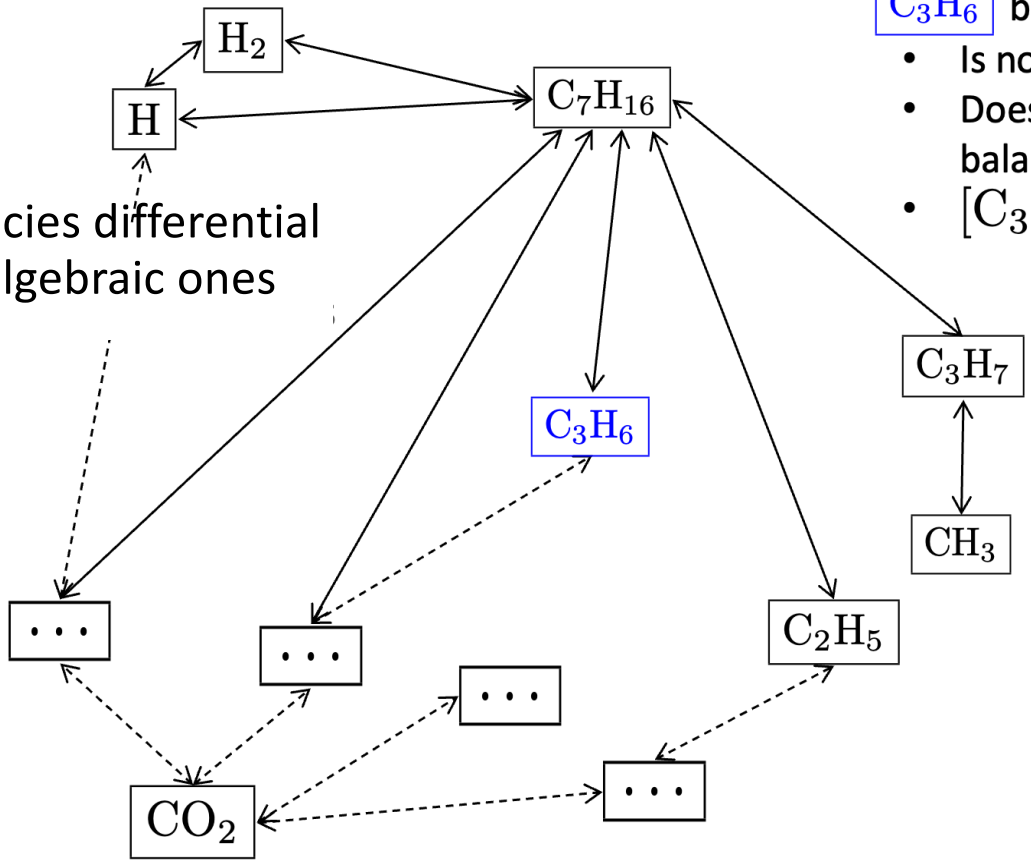
- **Isomer Lumping**: Merge nodes
- **Path lumping**: collapse entire sections of the network
- **QSS**: replace species differential equations with algebraic ones
- **Projection/ML** techniques



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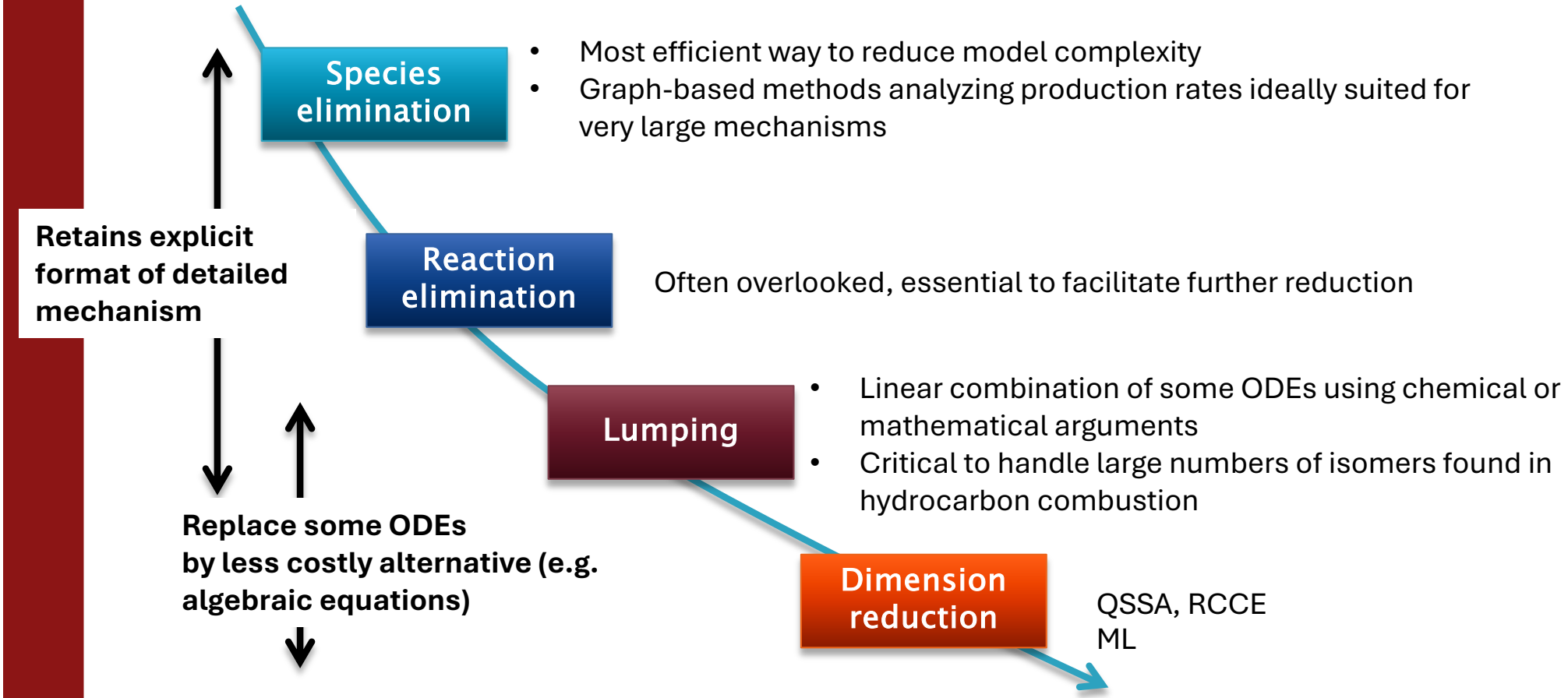
Chemical model reduction

- **Objective**: simplify the coupled set of ODEs describing the temporal evolution of a spatially homogeneous mixture of chemical species or simple 1D flames



Example – Jet fuel surrogate

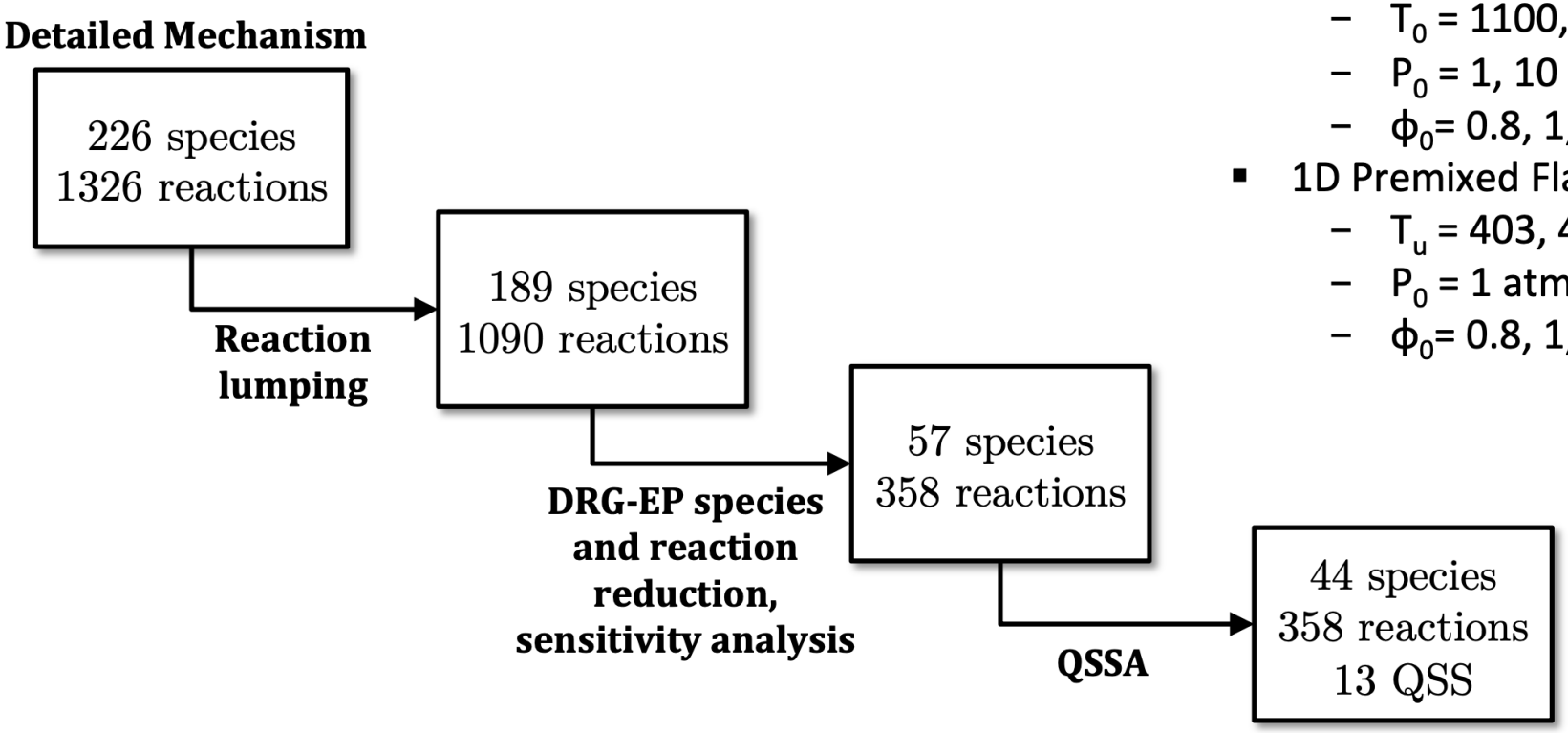
	Jet-A (POSF 4658)	Jet Fuel Surrogate
Formula	$C_{10.2}H_{19.9}$	$C_{9.4}H_{18.4}$
Molecular weight [g/mol]	142±5	131
H/C ratio	1.957	1.95
CN	47.1±0.3	56.5
TSI	21.4	14.1
Composition (vol %)		
Aromatics	20%	15.8% m-Xylene
Paraffins	60%	58.5% n-Dodecane
Napthalenes	20%	25.7% methyl-cyclohexane

Chosen based on mechanism availability, component classes in jet fuel

Initial composition formulated to match H/C, CN, TSI, MW

Final composition optimized against Jet-A flame speeds and ignition delay times

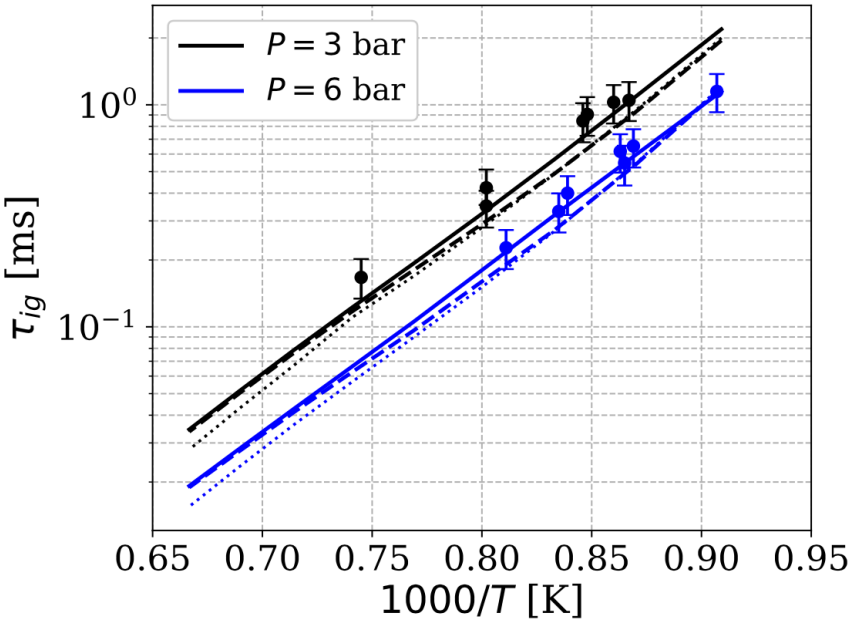
Example – Jet fuel surrogate



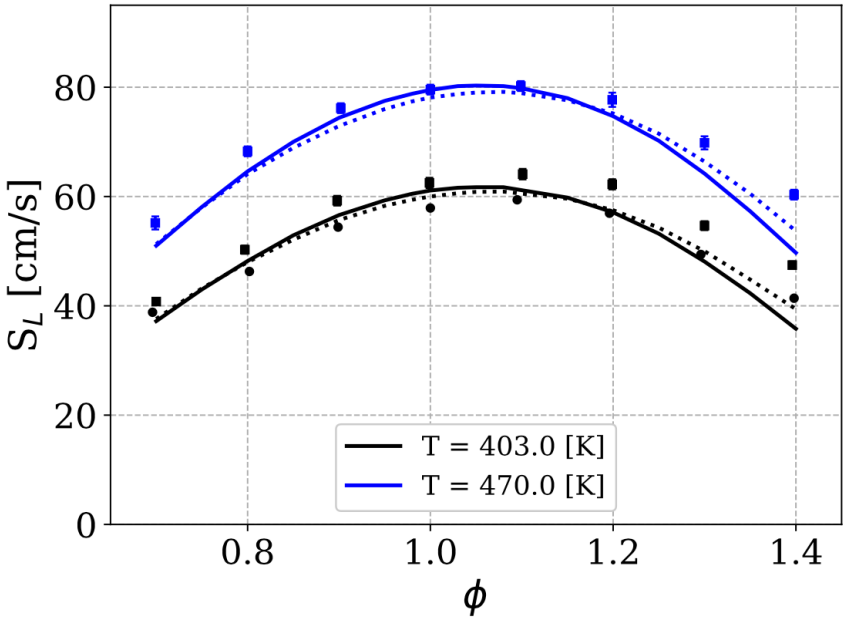
Reduction cases

- 0D Isochor Auto-Ignition
  - T_0 = 1100, 1300, 1600K
  - P_0 = 1, 10 atm
  - ϕ_0= 0.8, 1, 1.3
- 1D Premixed Flame
  - T_u = 403, 470K
  - P_0 = 1 atm
  - ϕ_0= 0.8, 1, 1.3

Example – Jet fuel surrogate



Ignition delay times in an isochor reactor at $\phi_0 = 1$ compared to experimental results with Jet-A[1,2,3].

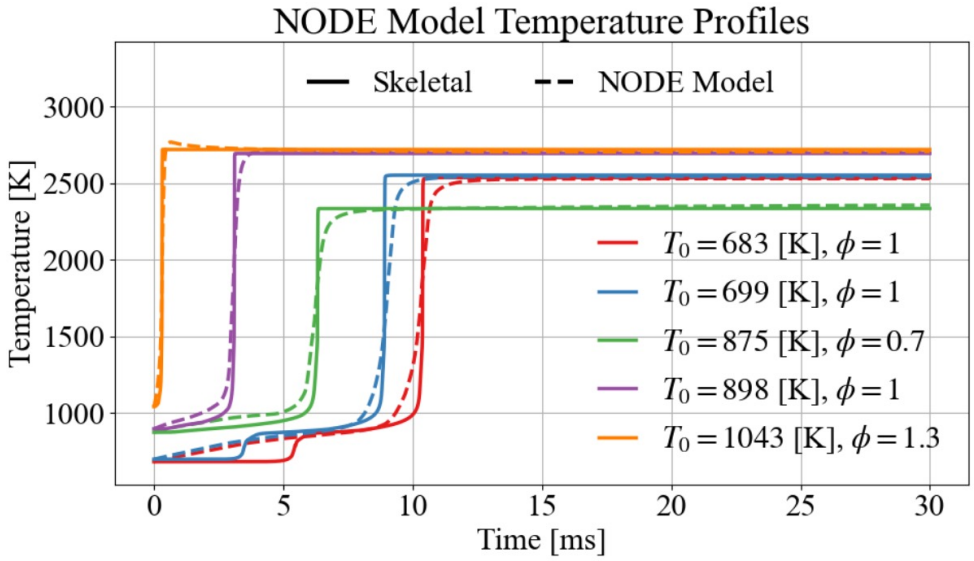


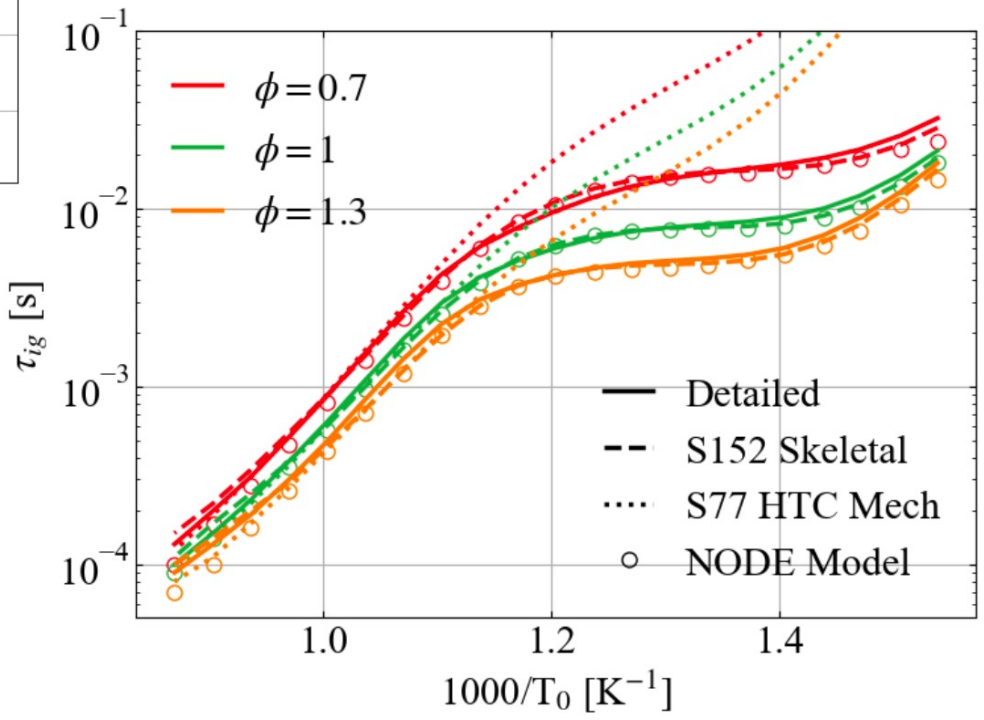
Laminar flame speeds at atmospheric pressure compared to experimental results with Jet-A[1,2].

■ ● = experiments
—— = detailed,
—— = lumped,
------ = 44 species QSS

[1]*Zhu, Y. et al. Proc. Combust. Inst. 2015.*
[2]*Dean, A. et al. Proc. Combust. Inst. 2007.*
[3]*Wang, H. et al. Fuel. 2012.*

Example with ML – SAF





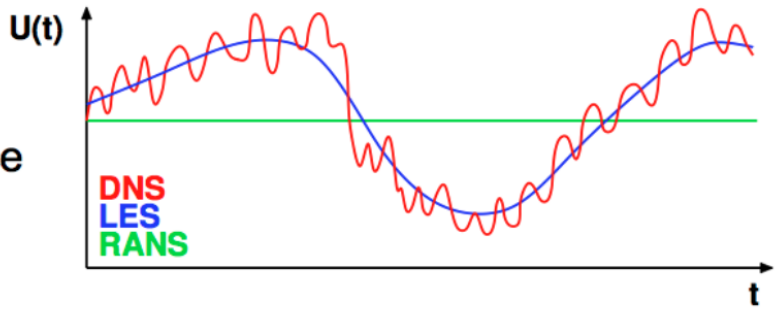
Ignition delay time well predicted with only 6 latent variables over a wide range of conditions compared to 152 species using the state-of-the-art skeletal reduction technique

Chemical kinetics and CFD simulation of turbulent combustion

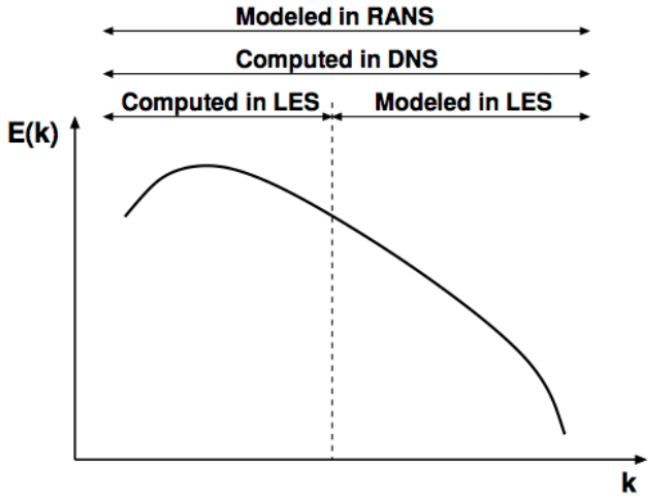
A good model is the **simplest model** that contains the physics we care about

Numerical frameworks to simulate turbulence

- Direct Numerical Simulation (DNS)
  - Resolve all flow scales directly
  - No need for physical model of turbulence
  - Very high cost

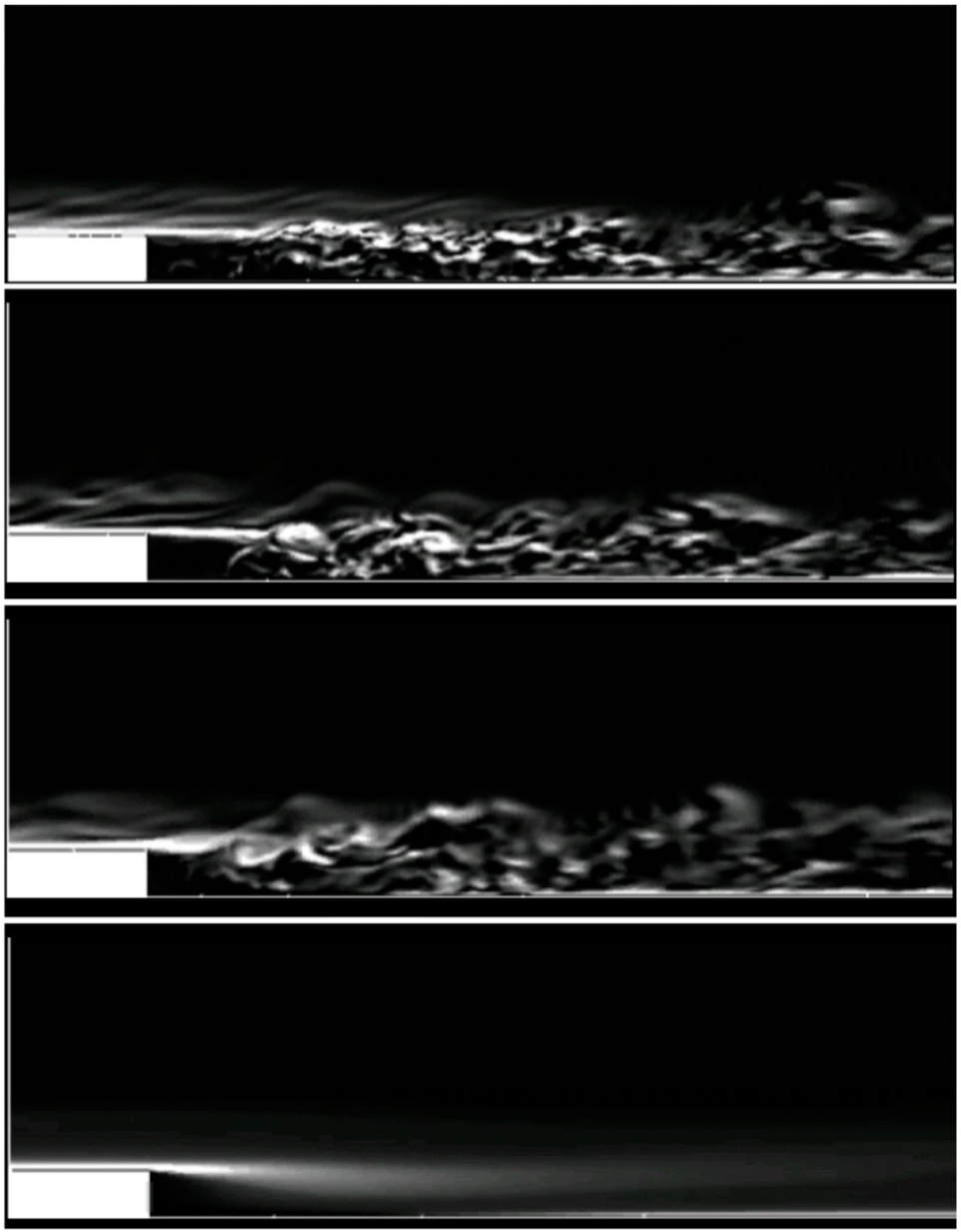


- Large Eddy Simulation (LES)
  - Resolve large flow scales
  - Model small scales only
  - Moderate cost



- Reynolds Averaged Navier-Stokes (RANS)
  - Solve for mean flow
  - Model all fluctuations
  - Low cost

Numerical frameworks to simulate turbulence



The issue of LES for turbulent combustion

- In LES, the Navier-Stokes equations are filtered: only the larger scales of the flow are resolved on the mesh
  - Works great for non-reactive turbulence because in many cases, what happens at the small scales is universal
  - But combustion usually happens at the small scales, and it is definitely not universal (e.g. premixed vs non-premixed)

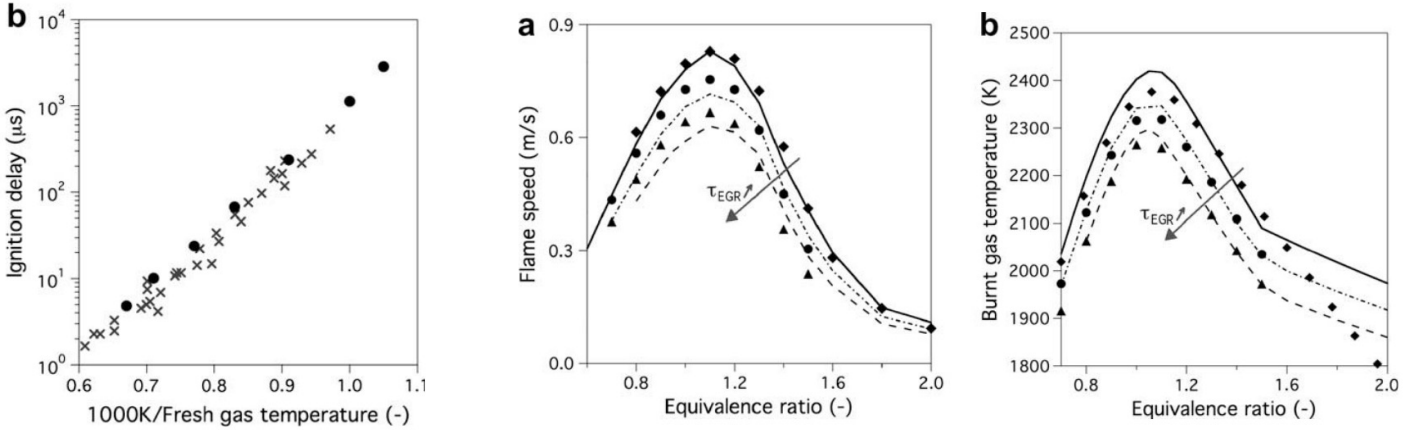
- Very large body of work to develop models to "close" the governing equations and properly account for the effect of the combustion (small scale) on the filtered quantities (large scale)
  - Strong simplification assumption: e.g. eddy dissipation model
  - Conditional moment closure models:
    - Tabulation-based – e.g. FPV, FGM, FPI
    - Monte-Carlo based
  - Thickened flame models
  - …

Not all simulations need the details of the chemistry!

- In many industrial applications, only a few species are of interest and taking into account a large set of species is usually not needed.
- Example: In gas turbines, a large part of the design process may just need :
  - The chamber efficiency (which requires a correct prediction of fuel reaction rates),
  - The outlet temperature (which requires correct equilibrium computations
  - CO composition at the chamber exit
- 2 or 3 step models are able to do that.
  - Ex: 2S_KERO_BFE 2 steps model
    - Parameters fitted to capture flame speed, burnt gas temperature and ignition delays at relevant conditions
    - Fuel can be changed

$$\mathrm{KERO} + 10O_2 \Rightarrow 10CO + 10H_2O,$$
$$CO + 0.5O_2 \Leftrightarrow CO_2.$$

$$k_{f,1} = A_1 f_1(\phi) \mathrm{e}^{(-E_{a,1}/RT)} [\mathrm{KERO}]^{n_{\mathrm{KERO}}} [O_2]^{n_{O_2,1}},$$
$$k_{f,2} = A_2 f_2(\phi) \mathrm{e}^{(-E_{a,2}/RT)} [CO]^{n_{CO}} [O_2]^{n_{O_2,2}},$$



Franzelli et al. Combustion and Flame 157 (2010) 1364–1373

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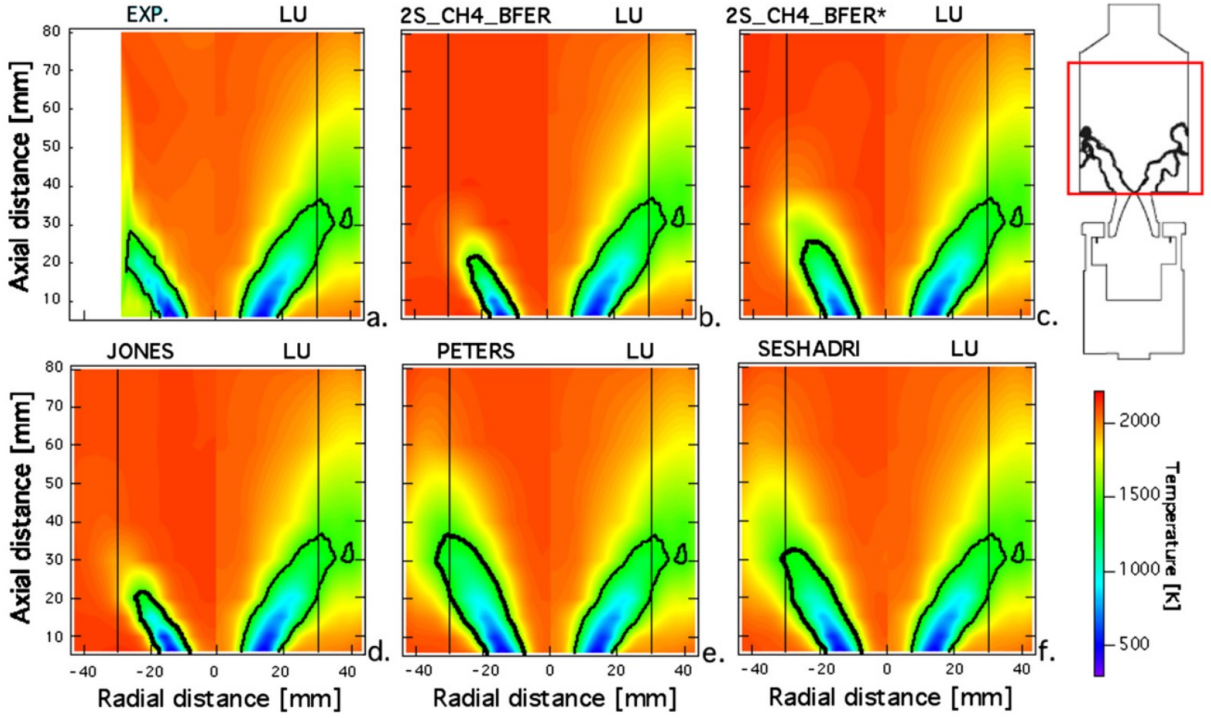

Fig. 5. Mean temperature field in the vertical mid-plane. (a) Comparison between experiments and LU scheme. (b)–(f) Comparison between reduced schemes and reference LU mechanism. The black isoline of progress variable $c = 0.65$ represents the mean flame surface position.

B. Franzelli et al. / C. R. Mecanique 341 (2013) 247–256