
Eliseo Ranzi

Dipartimento di Chimica, Materiali e Ingegneria Chimica “G. Natta”
Politecnico di Milano (Italy)
Detailed Kinetics of Methane Combustion

\[ \text{CH}_4 + 2 \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O} \]

More than the correct rate parameters of specific reaction, it is important to include all the relevant reactions and the proper relative selectivity of parallel reaction paths.
Outlines

Complexity of Pyrolysis and Combustion Systems
- Complexity of Chemical Mechanisms
- Complexity of Liquid Fuels
- Dimension of Detailed Kinetic Mechanisms
- Coupling of Detailed kinetics and Complex Hydrodynamics
- Time Scales in Combustion Processes

Automatic Generation of Reaction Mechanisms Simplifications (QSS) and Lumping Procedures
- Pyrolysis and High Temperature Mechanisms
  - Steam Cracking Process (SPYRO)
  - Extension to Complex Mixtures
- Low Temperature Oxidation Mechanisms

Conclusions
Detailed Oxidation Mechanism of n-pentane


Combustion of large molecules
Complex kinetic mechanisms.
Simplified Scheme of $n$-alkane ($nC_{10}H_{22}$)

Primary Oxidation Reactions

1. Alkyl radicals forms Peroxy radicals
2. Succesive reactions of Peroxy Radicals explain the system reactivity
Detailed Oxidation Mechanism of n-pentane

Pyrolysis Mechanism

Pyrolysis reactions hierarchically precede oxidation reactions.

Combustion of large molecules
Complex kinetic mechanisms.

At High Temperatures, life time of alkyl radicals is lower than $10^{-6}$ to $10^{-8}$ s.

Decomposition and dehydrogenation reactions of alkyl radicals

$$k_{\text{DEC}} = 10^{13.5} \times \exp\left[\frac{-32000}{RT}\right] \quad [\text{s}^{-1}]$$

$$k_{\text{DeHyd}} = 10^{14} \times \exp\left[\frac{-40000}{RT}\right] \quad [\text{s}^{-1}]$$
High Temperature mechanism mainly involves interactions amongst small and stable radicals (H, CH₃, C₂H₃, C₃H₃, ...) and small stable species such as C₂H₄ and C₂H₂ as well as oxigenated species (O₂, O, OH, HO₂, ...).

High Temperature mechanism is not very sensitive to the structure of the hydrocarbon fuel.
Liquid fuels are Complex

Hydrocarbon Mixtures

Typical composition of a kerosene

Liquid fuels are mostly constituted by complex mixtures of large hydrocarbons derived from refinery

GC distribution of alkanes in a liquid fraction

Liquid fuels are complex mixtures of large hydrocarbons derived from the refinery

<table>
<thead>
<tr>
<th>Carbon Number</th>
<th>Boiling Temperature [°C]</th>
<th>Number of Paraffin Isomers</th>
<th>Petroleum Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>126</td>
<td>18</td>
<td>Gasoline and Naphthas</td>
</tr>
<tr>
<td>10</td>
<td>174</td>
<td>75</td>
<td>Kerosene</td>
</tr>
<tr>
<td></td>
<td></td>
<td>355</td>
<td>Jet Fuels</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4347</td>
<td>Diesel Fuels</td>
</tr>
<tr>
<td>20</td>
<td>344</td>
<td>3.66 \times 10^5</td>
<td>Light Gasoil</td>
</tr>
<tr>
<td>25</td>
<td>402</td>
<td>3.67 \times 10^7</td>
<td>Gasoil</td>
</tr>
<tr>
<td>30</td>
<td>449</td>
<td>4.11 \times 10^9</td>
<td>Heavy Gasoil</td>
</tr>
<tr>
<td>35</td>
<td>489</td>
<td>4.93 \times 10^{11}</td>
<td>Atmospheric Residue</td>
</tr>
</tbody>
</table>

The complexity of these mixtures calls for lumping and simplifications

Altgelt and Boduszynski 1994
Size of Detailed Kinetic Mechanisms

Large Methyl esters: Rapeseed and soybean oil
Detailed kinetic mechanism consists 4800 species and ~20,000 reactions

Automatic Generation of kinetic mechanisms easily produces
Large Kinetic Models

Fig. 10. Size of selected detailed and skeletal mechanisms for hydrocarbon fuels, together with the approximate years when the mechanisms were compiled.

T.F. Lu, C.K. Law ‘Toward accommodating realistic fuel chemistry in large-scale computations’
Strong interactions amongst Thermodynamics, Chemistry and Fluidodynamics in Combustion Processes

- **Chemistry**
  Huge Number of Species and Elementary Reactions

- **Fluidodynamics**
  Different description scales

- **Materials**
  Wall and Catalyst reactions

(*) Joseph Grcar ‘Combustion Simulation and Modeling ’ CSET – Scientific Applications Meeting
Argonne National Laboratory   May 3-4, 1999
Time Scales in Combustion Processes

Kinetic post-processor

Slow Processes:
- NOx Formation

Intermediate Processes
- PAH Formation
- Soot Formation

Fast Processes:
- Partial Equilibrium
- Steady State Cond.

Kinetics

100 s

10^{-2} s

10^{-4} s

10^{-6} s

10^{-8} s

Physics

flux, transport, turbulence

Mixed = Burned

→ CFD
Strategy for Mechanism Reduction

**Detailed mechanisms**
- CH$_4$: 30 species
- C$_2$H$_4$: 70 species
- nC$_7$H$_{16}$: 500 species

**Skeletal mechanisms**
- CH$_4$: 13 species
- C$_2$H$_4$: 30 species
- nC$_7$H$_{16}$: 80 species

**Reduced mechanisms**
- CH$_4$: 9 species
- C$_2$H$_4$: 20 species
- nC$_7$H$_{16}$: 60 species

**Reduced mechanism**
- Fewer species/reactions
- Less stiff
- Faster simulation

**Computation cost reduction**

**Diffusion reduction**

**SPDR, DRGASA**
**Isomer Lumping**
**CSP**
**QSSDG**

**Minimal diffusive species**
- C$_2$H$_4$: 9 groups
- nC$_7$H$_{16}$: 20 groups

**Time savings: factors of 10 ~ 100**

**CFD simulations**

- WP Air Force Base
  C$_2$H$_4$, VULCAIN

- Georgia Tech
  C$_2$H$_4$, 3D, LES

- SANDIA
  CH$_4$, 3D, DNS
Outlines

Complexity of Pyrolysis and Combustion Systems
- Complexity of Chemical Mechanisms
- Complexity of Liquid Fuels
- Dimension of Detailed Kinetic Mechanisms
- Coupling of Detailed kinetics and Complex Hydrodynamics
- Time Scales in Combustion Processes

Automatic Generation of Reaction Mechanisms
Simplifications (QSS) and Lumping Procedures
- Pyrolysis and High Temperature Mechanisms
  - Steam Cracking Process (SPYRO)
  - Extension to Complex Mixtures
- Low Temperature Oxidation Mechanisms

Conclusions
Detailed Oxidation Mechanism of \( n\)-C5

Pyrolysis Mechanism

High temperature mechanism is simply constituted by pyrolysis reactions. Only then, oxidation reactions of small olefins and radicals take place.

Pyrolysis reactions hierarchically precede oxidation reactions.
High temperature Reactions of n-pentane

Decomposition and dehydrogenation reactions of alkyl radicals

\[ k_{\text{DEC}} = 10^{13.5} \times \exp\left(-\frac{32000}{RT}\right) \quad [\text{s}^{-1}] \]
\[ k_{\text{DeHyd}} = 10^{14} \times \exp\left(-\frac{40000}{RT}\right) \quad [\text{s}^{-1}] \]

At High Temperatures, life time of alkyl radicals is lower than $10^{-6}$ - $10^{-8}$ s.

High Temperature mechanism requires the analysis of H-abstraction reactions to form alkyl radicals and their successive decomposition paths.
H-Abstraction Reactions on n-dodecane

The Six nC_{12}H_{25} Radicals can isomerize and/or decompose

Pyrolysis mechanism and/or High temperature oxidation mechanism require to define the kinetic parameters of:
- H-abstraction
- Isomerization
- Decomposition Reactions
Isomerization Reactions
(Internal H-abstraction of 2-methyl-pentyl radicals)

(1-5) H transfer

\[
\begin{array}{ccc}
\text{H} & \text{H} & \text{H} \\
\hline
\text{six membered ring intermediate}
\end{array}
\]

\[
\begin{array}{c}
\log A \\
[\text{s}^{-1}] \\
E \\
[\text{kcal/kmol}]
\end{array}
\begin{array}{c}
10.2 \\
14500
\end{array}
\]

(1-4) H transfer

\[
\begin{array}{ccc}
\text{H} & \text{H} & \text{H} \\
\hline
\text{five membered ring intermediate}
\end{array}
\]

\[
\begin{array}{c}
\log A \\
[\text{s}^{-1}] \\
E \\
[\text{kcal/kmol}]
\end{array}
\begin{array}{c}
11.0 \\
19800
\end{array}
\]

Difference in activation energy reflects the strain of the five membered ring.
Difference in frequency factor is due to the \# rotors blocked in the transition phase.
Decomposition and Isomerization Reactions of Large Alkyl Radicals

\[ k_{\text{ISOM}} = 3 \times 10^{10.2} \exp(-14500/RT) \ [1/s] \]

\[ k_{\text{DEC}} = 1 \times 10^{14} \exp(-30000/RT) \ [1/s] \]

At Temperatures higher than 1000 K, decomposition prevails on isomerization reactions.

**Kinetic constants vs T [K]**
Reference Kinetic Parameters

Initial Product Distributions from Pyrolysis of Normal and Branched Paraffins

<table>
<thead>
<tr>
<th>Table XI. Fundamental Kinetic Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-Abstraction Reactions (Primary H-Atoms)</td>
</tr>
<tr>
<td>primary radical</td>
</tr>
<tr>
<td>secondary radical</td>
</tr>
<tr>
<td>tertiary radical</td>
</tr>
<tr>
<td>Isomerization Reactions</td>
</tr>
<tr>
<td>(primary on primary internal H-abstraction)</td>
</tr>
<tr>
<td>1-5 transfer</td>
</tr>
<tr>
<td>1-4 transfer</td>
</tr>
<tr>
<td>ratio between secondary and primary H-abstraction</td>
</tr>
<tr>
<td>ratio between tertiary and primary H-abstraction</td>
</tr>
<tr>
<td>Decomposition Reactions to Form Primary Radicals</td>
</tr>
<tr>
<td>primary radical</td>
</tr>
<tr>
<td>secondary radical</td>
</tr>
<tr>
<td>tertiary radical</td>
</tr>
</tbody>
</table>

Correction in Activation Energy:
(Related to Primary Radical)

| secondary radical | 2.0 kcal/mol |
| tertiary radical | 4.0 kcal/mol |
| methyl radical | $-1.5$ kcal/mol |

Reference Kinetic Parameters mainly depends on:
- the type of radicals
- the type of H

Reference Kinetic Parameters are known since several years.

Outlines

Complexity of Pyrolysis and Combustion Systems

- Complexity of Chemical Mechanisms
- Complexity of Liquid Fuels
- Coupling of Detailed kinetics and Complex Hydrodynamics
- Time Scales in Combustion Processes
- Dimension of Detailed Kinetic Mechanisms

Automatic Generation of Reaction Mechanisms

Simplifications (QSS) and Lumping Procedures

- Pyrolysis and High Temperature Mechanisms
  - Steam Cracking Process (SPYRO)
  - Extension to Complex Mixtures
- Low Temperature Oxidation Mechanisms

Conclusions
Automatic generation of Kinetic Scheme

Classes of reactions

1. H abstraction Reactions
2. Isomerization Reactions $R \leftrightarrow R'$
3. Decomposition of alkyl radicals $R \rightarrow C_nH_{2n}+R'$

Reference kinetic parameters

- **H-Abstraction Reactions** (Primary H-Atoms)
  - Primary radical $\log A = 8.3$, $E = 13500$
  - Secondary radical $\log A = 8.3$, $E = 14500$
  - Tertiary radical $\log A = 8.3$, $E = 15000$

- **Isomerization Reactions** (Primary on primary internal H-abstraction)
  - (1-5) H Transfer $\log A = 10.2$, $E = 14500$
  - (1-4) H Transfer $\log A = 11.0$, $E = 19800$

- **Decomposition Reactions** (to form Primary Radicals)
  - Primary radical $\log A = 14$, $E = 30000$
  - Secondary radical $\log A = 14$, $E = 31000$
  - Tertiary radical $\log A = 14$, $E = 32000$
Automatic Generation of Detailed Reaction Schemes

Primary propagation reactions of n-dodecane pyrolysis
(Units are: m kmol s kcal.)

H-abstraction reactions

\[
\begin{align*}
\text{R}^+ + \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} & \rightarrow \text{C}^*\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} + \text{H atoms} \\
\text{R}^+ + \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} & \rightarrow \text{C}^*\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} + \text{H atoms} \\
\text{R}^+ + \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} & \rightarrow \text{C}^*\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} + \text{H atoms} \\
\text{R}^+ + \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} & \rightarrow \text{C}^*\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} + \text{H atoms} \\
\text{R}^+ + \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} & \rightarrow \text{C}^*\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} + \text{H atoms}
\end{align*}
\]

β-decomposition reactions

\[
\begin{align*}
\text{C}^*\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} & \rightarrow \text{C}=\text{C} + \text{C}^*\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} + \text{H atoms} \\
\text{C}^*\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} & \rightarrow \text{C}=\text{C} + \text{C}^*\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} + \text{H atoms} \\
\text{C}^*\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} & \rightarrow \text{C}=\text{C} + \text{C}^*\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} + \text{H atoms} \\
\text{C}^*\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} & \rightarrow \text{C}=\text{C} + \text{C}^*\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} + \text{H atoms} \\
\text{C}^*\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} & \rightarrow \text{C}=\text{C} + \text{C}^*\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} + \text{H atoms} \\
\text{C}^*\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} & \rightarrow \text{C}=\text{C} + \text{C}^*\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} + \text{H atoms}
\end{align*}
\]

Automatic Generation of Detailed Reaction Schemes

Primary propagation reactions of n-dodecane pyrolysis
(Units are: m kmol s kcal.)

Isomerization (H-transfer) reactions

\[
\begin{align*}
&\text{A} & & \text{E} \\
&1.89E+11 & & 18300 \\
&3.00E+10 & & 12200 \\
&1.20E+10 & & 12200 \\
&1.89E+11 & & 19300 \\
&3.00E+10 & & 13200 \\
&1.20E+10 & & 13200 \\
&1.89E+11 & & 19300 \\
&3.00E+10 & & 13200 \\
&1.20E+10 & & 13200 \\
&2.84E+11 & & 21600 \\
&1.89E+11 & & 19300 \\
&3.00E+10 & & 13200 \\
&4.30E+10 & & 13300 \\
&3.00E+10 & & 13200 \\
&1.20E+10 & & 13200 \\
&1.89E+11 & & 19300 \\
&3.00E+10 & & 13200 \\
\end{align*}
\]

Dimension of these detailed kinetic schemes calls for simplifications.

It is not of interest to generate detailed mechanisms with thousands of species and reactions.

A compromise has to be found between computation efforts and prediction accuracy.
Outlines

Complexity of Pyrolysis and Combustion Systems
- Complexity of Chemical Mechanisms
- Complexity of Liquid Fuels
- Coupling of Detailed kinetics and Complex Hydrodynamics
- Time Scales in Combustion Processes
- Dimension of Detailed Kinetic Mechanisms

Automatic Generation of Reaction Mechanisms

Simplifications (QSS) and Lumping Procedures
- Pyrolysis and High Temperature Mechanisms
  - Steam Cracking Process (SPYRO)
  - Extension to Complex Mixtures
- Low Temperature Oxidation Mechanisms

Conclusions
Automatic generation of Lumped Reactions

Classes of reactions

1. H abstraction Reactions
2. isomerization Reactions \( R \leftrightarrow R' \)
3. Decomposition of alkyl radicals
   \[ R \rightarrow C_nH_{2n} + R' \]

Reference kinetic parameters

- **H-Abstraction Reactions** (Primary H-Atoms)
  - Primary radical: \( \log A = 8.3, E = 13500 \)
  - Secondary radical: \( \log A = 8.3, E = 14500 \)
  - Tertiary radical: \( \log A = 8.3, E = 15000 \)

- **Isomerization Reactions** (Primary on primary internal H-abstraction)
  - (1-5) H Transfer: \( \log A = 10.2, E = 14500 \)
  - (1-4) H Transfer: \( \log A = 11.0, E = 19800 \)

- **Decomposition Reactions** (to form Primary Radicals)
  - Primary radical: \( \log A = 14, E = 30000 \)
  - Secondary radical: \( \log A = 14, E = 31000 \)
  - Tertiary radical: \( \log A = 14, E = 32000 \)

MAMA Program

1-Generation of Primary Reactions
2- QSS Assumption for Large Alkyl Radicals
3- Generation of Lumped Reactions

It is convenient to directly link a post-processor to the kinetic generator with the purpose of lumping intermediate and final products into a limited number of lumped components.
MAMA PROGRAM generates ‘lumped reactions’ (at 1040K)

H-abstractions on large molecules are lumped into a single equivalent reaction. Intermediate radicals larger than C4 are linearly transformed (QSSA -isomerized and decomposed) into their final products.

Interactions of alkyl radicals with the reacting mixture (Additions and H-Abstractions) are negligible

Large Alkyl Radicals \( (R_j) \), initially formed at rate \( P_j \), are involved in \textbf{Decomposition} \( (k^D) \) and \textbf{Isomerization} \( (k^I) \) Reactions.

Continuity equations of isomer radicals give rise to a system of linear equations:

\[
R_j \left( \sum_{i \in I_j} k^I_{j,i} + \sum_{i \in D_j} k^D_{j,i} \right) = \sum_{i \in I_j} k^I_{i,j} \cdot R_i + \dot{P}_j
\]
H-Abstraction Reactions on n-dodecane

The linear system of continuity equations (SSA) of the six nC_{12}H_{25} radicals gives the first decomposition path.

\[
R_j \left( \sum_{i \in I_j} k^I_{j,i} + \sum_{i \in D_j} k^D_{j,i} \right) = \sum_{i \in I_j} k^I_{i,j} \cdot R_i + \dot{P}_j
\]

\[ (j = 1, 6) \]
Chain radical propagation reactions of n-decane

Primary H-abstraction reactions on n-decane produce 5 n-decyl radicals. Again, successive reactions include isomerization and β-decomposition reactions.
Lumped Pyrolysis Mechanism of n-decane

Intermediate radicals (larger than C4) are transformed into their final products (QSSA).
Lumped Reactions of n-decane

On the basis of detailed kinetics and SSA of large Alkyl Radicals, it is possible to generate the ‘lumped reactions’

\[ \text{R}^\bullet + n\text{C}_{10}\text{H}_{22} \rightarrow \text{RH} + \{\text{mixC}_{10}\text{H}_{21}\} \]

\[ \{\text{mixC}_{10}\text{H}_{21}\} \rightarrow 0.0205 \text{H}^\bullet + 0.0803 \text{CH}_3^\bullet + 0.2593 \text{C}_2\text{H}_5^\bullet + 0.4061 n\text{C}_3\text{H}_7^\bullet + 0.2339 \text{1C}_4\text{H}_9^\bullet \]

\[ + 0.3785 \text{C}_2\text{H}_4 + 0.3127 \text{C}_3\text{H}_6 + 0.2114 \text{1-C}_4\text{H}_8 + 0.1870 \text{1-C}_5\text{H}_{10} + 0.1815 \text{1-C}_6\text{H}_{12} \]

\[ + 0.1461 \text{1-C}_7\text{H}_{14} + 0.1284 \text{1-C}_8\text{H}_{16} + 0.0540 \text{1-C}_9\text{H}_{18} + 0.0025 \text{1-C}_{10}\text{H}_{20} \]

\[ + 0.0006 \text{2-C}_5\text{H}_{10} + 0.0012 \text{C}_6\text{H}_{12}^\bullet + 0.0013 \text{C}_7\text{H}_{14}^\bullet + 0.0005 \text{C}_8\text{H}_{16}^\bullet + 0.0100 \text{C}_{10}\text{H}_{20}^\bullet \]

Together with a similar ‘lumped’ initiation reaction, these are the ‘new’ reactions needed to extend the overall kinetic scheme.

These stoichiometries, i.e. the slate of products of the decomposition of large radicals, are evaluated at a given temperature (T=1040 K).

At low temperatures (T<900 K), alkyl radicals also add on oxygen to form peroxyl radicals, before decomposition. Other reactions need to be included.
‘Lumped Reactions’
are generated at a fixed Temperature (@ 1040K)

Intermediate radicals larger than C4 are transformed
(QSSA - isomerized and decomposed) into their final products.

Lumped H-abstraction Reactions on large molecules become:

\[ R + nC12H26 \rightarrow RH + [\text{mix C12H25}] \]

\[ [\text{mixC12H25}] \rightarrow .0226 \ H + .0735 \ \text{CH3} + .2518 \ \text{C2H5} + .4283 \ \text{1C3H7} + .2238 \ \text{1C4H9} \]
\[ \quad + .4529 \ \text{C2H4} + .2936 \ \text{C3H6} + .1935 \ \text{1C4H8} + .1857 \ \text{1C5H10} + .00054 \ 2C5H10 \]
\[ \quad + .2056 \ \text{1C6H12} + .00091 \ 2C6H12 + .00023 \ 3C6H12 + .1352 \ \text{1C7H14} + .00121 \ C7H14s \]
\[ \quad + .1179 \ \text{1C8H16} + .00088 \ C8H16s + .1057 \ \text{1C9H18} + .00081 \ C9H18s + .1002 \ \text{1C10H20} \]
\[ \quad + .00042 \ C10H20s + .04506 \ \text{1C11H22} + .00194 \ \text{1C12H24} + .01005 \ C12H24s \]

Similarly, in pyrolysis conditions or at high temperatures, decyl radicals decomposes:

\[ [\text{mixC10H21}] \rightarrow .0205 \ H\bullet + .0803 \ \text{CH3\bullet} + .2593 \ \text{C2H5\bullet} + .4061 \ nC3H7\bullet + .2339 \ 1C4H9\bullet \]
\[ \quad + .3475 \ C2H4 + .3127 \ C3H6 + .2114 \ 1- C4H8 + .1870 \ 1-C5H10 \]
\[ \quad + .1815 \ 1-C6H12 + .1461 \ 1-C7H14 + .1284 \ 1-C8H16 + .0540 \ 1-C9H18 + .0025 \ 1-C10H20 \]
\[ \quad + .0006 \ 2-C5H10 + .0012 \ C6H12s + .0013 \ C7H14s + .0005 \ C8H16s + 0100 \ C10H20s \]

Significant reduction of both species and reactions, but ...

\\[\text{weak temperature dependence}\]
**Temperature effect:**

At different T, different ‘lumped reactions’ of n-heptane are obtained:

At 1040 K: \( \{\text{mixC}_7\text{H}_{15}\bullet\} = 0.0211 \text{ H} + 0.0806 \text{ CH}_3 + 0.2297 \text{ C}_2\text{H}_4 + 0.3629 1\text{-C}_3\text{H}_7 + 0.3057 1\text{-C}_4\text{H}_9 + 0.2277 \text{ C}_2\text{H}_4 + 0.3463 \text{ C}_3\text{H}_6 + 0.2705 \text{ C}_4\text{H}_8 + 0.1912 \text{ C}_5\text{H}_{10} + 0.0806 \text{ C}_6\text{H}_{12} + 0.0189 \text{ C}_7\text{H}_{14} \)

At 1500 K: \( \{\text{MixC}_7\text{H}_{15}\bullet\} = 0.0747 \text{ H} + 0.0920 \text{ CH}_3 + 0.1722 \text{ C}_2\text{H}_4 + 0.3819 1\text{-C}_3\text{H}_7 + 0.2792 1\text{-C}_4\text{H}_9 + 0.3623 \text{ C}_2\text{H}_4 + 0.2939 \text{ C}_3\text{H}_6 + 0.2129 \text{ C}_4\text{H}_8 + 0.1671 \text{ C}_5\text{H}_{10} + 0.0920 \text{ C}_6\text{H}_{12} + 0.0651 \text{ C}_7\text{H}_{14} \)

Despite of the large difference in the temperatures (1040 vs 1500 K), fuel decomposition, intermediate products, and radicals formations are very similar in both the conditions.

**Pyrolysis of n-heptane at 1300 K**

Predicted mole fractions of relevant species.

Lumped kinetics at 1040 K (lines) and 1500 K (dashed lines)
Reliability of QSSA and lumped reactions.

‘Methyl concentration time-histories during iso-octane and n-heptane oxidation and pyrolysis’

Model predictions (lines) vs experimental measurements (points).
Reliability of QSSA and lumped reactions.

Species time-histories for ndodecane, OH and C2H4.
Points: experiments. Lines: simulations.

Initial reflected shock conditions:
1410 K, 2.37 atm, 457 ppm nC12, 7577 ppm O2/Ar
Outlines

Complexity of Pyrolysis and Combustion Systems
- Complexity of Chemical Mechanisms
- Complexity of Liquid Fuels
- Coupling of Detailed kinetics and Complex Hydrodynamics
- Time Scales in Combustion Processes
- Dimension of Detailed Kinetic Mechanisms

Automatic Generation of Reaction Mechanisms Simplifications (QSS) and Lumping Procedures
- Pyrolysis and High Temperature Mechanisms
  - Steam Cracking Process (SPYRO)
  - Extension to Complex Mixtures
- Low Temperature Oxidation Mechanisms

Conclusions
STEAM CRACKING OF HYDROCARBONS

Operating Conditions

- Temperature 900-1150 K
- Pressure: 1.5-2.5 bar
- Contact time: 100-400 ms

The proper knowledge of ethylene selectivity first requires the correct knowledge of the feed → Complexity of the Liquid Mixtures

Feeds

- Ethane and gases E/P
- Naphthas (C4-C10)
- Gasoils

## Complexity of the Liquid Feedstocks: Naphthas, Kerosene, and Gasoils

<table>
<thead>
<tr>
<th>Carbon Number</th>
<th>Boiling Temperature [°C]</th>
<th>Number of Paraffin Isomers</th>
<th>Petroleum Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>126</td>
<td>18</td>
<td>Gasoline and Naphthas</td>
</tr>
<tr>
<td>10</td>
<td>174</td>
<td>75</td>
<td>Kerosene</td>
</tr>
<tr>
<td>12</td>
<td>216</td>
<td>355</td>
<td>Jet Fuels</td>
</tr>
<tr>
<td>15</td>
<td>271</td>
<td>4347</td>
<td>Diesel Fuels</td>
</tr>
<tr>
<td>20</td>
<td>344</td>
<td>3.66 \times 10^5</td>
<td>Light Gasoil</td>
</tr>
<tr>
<td>25</td>
<td>402</td>
<td>3.67 \times 10^7</td>
<td>Gasoil</td>
</tr>
<tr>
<td>30</td>
<td>449</td>
<td>4.11 \times 10^9</td>
<td>Heavy Gasoil</td>
</tr>
<tr>
<td>35</td>
<td>489</td>
<td>4.93 \times 10^{11}</td>
<td>Atmospheric Residue</td>
</tr>
</tbody>
</table>

Altgelt and Boduszynski 1994
Naphtha Fractions

17 Isomers of branched paraffines $C_8H_{18}$

- 2MEC7
- 3MEC7
- 4MEC7
- 23DMEC6
- 24DMEC6
- 25DMEC6
- 34DMEC6
- 3ETC6
- 22DMEC6
- 33DMEC6
- 2ME3ETC5
- 234MEC5
- 223MEC5
- 224MEC5
- 233MEC5
- 3ME3ETC5
- 2233MEC4
Pyrolysis of Different C8 Isomers.

Equivalent stoichiometries evaluated by MAMA Program @ 1040 K

\[ R\cdot + 2\text{MEC7} = RH + 0.152 \text{CH3} + 0.111 \text{C2H5} + 0.159 \text{nC3H7} + 0.258 \text{iC3H7} + 0.196 \text{1C4H9} + 0.122 \text{1iC4H9} + 0.211 \text{C2H4} + 0.272 \text{C3H6} + 0.116 \text{1C4H8} + 0.208 \text{iC4H8} + 0.148 \text{1C5H10} + 0.101 \text{3me1C4H8} + 0.053 \text{me1C5H10} + 0.030 \text{1C7H14} + 0.114 \text{oleC7} \]

\[ R\cdot + 3\text{MEC7} = RH + 0.172 \text{CH3} + 0.251 \text{C2H5} + 0.211 \text{nC3H7} + 0.147 \text{1C4H9} + 0.201 \text{2C4H9} + 0.175 \text{C2H4} + 0.219 \text{C3H6} + 0.235 \text{1C4H8} + 0.106 \text{2C4H8} + 0.002 \text{1C5H10} + 0.002 \text{2C5H10} + 0.164 \text{2me1C4H8} + 0.035 \text{1C6H12} + 0.068 \text{noleC6} + 0.068 \text{me1C5H10} + 0.144 \text{oleC7} \]

\[ R\cdot + 4\text{MEC7} = RH + 0.131 \text{CH3} + 0.533 \text{C2H5} + 0.309 \text{nC3H7} + 0.008 \text{1iC4H9} + 0.135 \text{C2H4} + 0.677 \text{C3H6} + 0.007 \text{iC4H8} + 0.073 \text{1C5H10} + 0.164 \text{2C5H10} + 0.238 \text{me1C4H8} + 0.212 \text{C3H6} + 0.002 \text{2C4H8} + 0.002 \text{1C5H10} + 0.123 \text{2C5H10} + 0.007 \text{3me1C4H8} + 0.140 \text{2me2C4H8} + 0.133 \text{me2C5H10} + 0.197 \text{oleC7} \]

\[ R\cdot + 2\text{3DC6} = RH + 0.370 \text{CH3} + 0.233 \text{C2H5} + 0.180 \text{nC3H7} + 0.217 \text{iC3H7} + 0.056 \text{C2H4} + 0.421 \text{C3H6} + 0.168 \text{2C4H8} + 0.06 \text{1C5H10} + 0.123 \text{2C5H10} + 0.026 \text{3me1C4H8} + 0.140 \text{2me2C4H8} + 0.133 \text{me2C5H10} + 0.197 \text{oleC7} \]

\[ R\cdot + 3\text{ETC6} = RH + 0.315 \text{CH3} + 0.507 \text{C2H5} + 0.159 \text{nC3H7} + 0.009 \text{1C4H9} + 0.011 \text{2C4H9} + 0.187 \text{C2H4} + 0.179 \text{C3H6} + 0.271 \text{1C4H8} + 0.002 \text{2C4H8} + 0.03 \text{1C5H10} + 0.148 \text{2C5H10} + 0.271 \text{noleC6} + 0.130 \text{me1C5H10} + 0.117 \text{oleC7} \]

\[ R\cdot + \text{TRMC5} = RH + 0.525 \text{CH3} + 0.475 \text{iC3H7} + 0.212 \text{C3H6} + 0.212 \text{2C4H8} + 0.071 \text{3me1C4H8} + 0.405 \text{2me2C4H8} + 0.313 \text{oleC7} \]
## Pyrolysis of Different C8 Isomers.
Yields predictions (wt. %) @ Reference Cracking Conditions

<table>
<thead>
<tr>
<th></th>
<th>2MEC7</th>
<th>3MEC7</th>
<th>4MEC7</th>
<th>23DIME C6</th>
<th>234-TRIME C5</th>
<th>3ETC6</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2</td>
<td>0.79</td>
<td>0.75</td>
<td>0.81</td>
<td>0.78</td>
<td>0.82</td>
<td>0.86</td>
</tr>
<tr>
<td>CH4</td>
<td>12.73</td>
<td>14.45</td>
<td>13.00</td>
<td>16.45</td>
<td>18.48</td>
<td>14.83</td>
</tr>
<tr>
<td>C2H4</td>
<td>30.84</td>
<td>30.44</td>
<td>32.16</td>
<td>22.28</td>
<td>14.95</td>
<td>31.71</td>
</tr>
<tr>
<td>BTD</td>
<td>4.54</td>
<td>5.58</td>
<td>5.28</td>
<td>6.69</td>
<td>7.12</td>
<td>7.16</td>
</tr>
<tr>
<td>1C4H8</td>
<td>2.38</td>
<td>2.81</td>
<td>2.01</td>
<td>2.18</td>
<td>2.15</td>
<td>2.92</td>
</tr>
<tr>
<td>2C4H8</td>
<td>0.76</td>
<td>1.45</td>
<td>0.57</td>
<td>2.41</td>
<td>3.83</td>
<td>0.88</td>
</tr>
<tr>
<td>iC4H8</td>
<td>5.56</td>
<td>2.20</td>
<td>1.88</td>
<td>2.04</td>
<td>3.63</td>
<td>1.31</td>
</tr>
<tr>
<td>C5-</td>
<td>84.75</td>
<td>82.46</td>
<td>83.97</td>
<td>79.09</td>
<td>76.00</td>
<td>81.69</td>
</tr>
<tr>
<td>ISOPR</td>
<td>0.63</td>
<td>1.19</td>
<td>0.72</td>
<td>1.45</td>
<td>2.03</td>
<td>0.50</td>
</tr>
</tbody>
</table>
## Relative Amount of Branched Isomers in $\text{iso-C}_8\text{H}_{18}$ fraction of Virgin Feeds

A relative regularity is observed in the virgin feedstocks. A single ‘lumped’ or equivalent component can substitute the mixture.

<table>
<thead>
<tr>
<th>Isomers (wt%)</th>
<th>Ponca</th>
<th>Occidental</th>
<th>Texas</th>
<th>Default</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-methylheptane</td>
<td>46.3</td>
<td>36.9</td>
<td>42.1</td>
<td>45.8</td>
</tr>
<tr>
<td>3-methylheptane</td>
<td>15.4</td>
<td>28.5</td>
<td>23.4</td>
<td>22.9</td>
</tr>
<tr>
<td>4-methylheptane</td>
<td>10.3</td>
<td>10.2</td>
<td>9.3</td>
<td></td>
</tr>
<tr>
<td>2,3-dimethylhexane</td>
<td>3.6</td>
<td>5.4</td>
<td>6.3</td>
<td></td>
</tr>
<tr>
<td>2,4-dimethylhexane</td>
<td>3.1</td>
<td>5.5</td>
<td>4.2</td>
<td></td>
</tr>
<tr>
<td>2,5-dimethylhexane</td>
<td>3.1</td>
<td>5.7</td>
<td>4.0</td>
<td>3.4</td>
</tr>
<tr>
<td>3,4-dimethylhexane</td>
<td>6.7</td>
<td>2.6</td>
<td>3.7</td>
<td>3.4</td>
</tr>
<tr>
<td>2,2-dimethylhexane</td>
<td>0.5</td>
<td>-</td>
<td>0.3</td>
<td>-</td>
</tr>
<tr>
<td>3,3-dimethylhexane</td>
<td>1.5</td>
<td>1.7</td>
<td>0.4</td>
<td>-</td>
</tr>
<tr>
<td>2,3,4-trimethylpentane</td>
<td>0.3</td>
<td>-</td>
<td>1.1</td>
<td>1.2</td>
</tr>
<tr>
<td>2,2,3-trimethylpentane</td>
<td>0.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2,3,3-trimethylpentane</td>
<td>0.3</td>
<td>-</td>
<td>0.6</td>
<td>-</td>
</tr>
<tr>
<td>3-ethylhexane</td>
<td>4.6</td>
<td>3.5</td>
<td>3.1</td>
<td>3.8</td>
</tr>
<tr>
<td>2-methyl-3-ethylpentane</td>
<td>3.1</td>
<td>-</td>
<td>1.5</td>
<td>1.2</td>
</tr>
<tr>
<td>3-methyl-3-ethylpentane</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

**Notes:**
- 2-methyl heptane is more abundant than other methyl-heptanes.
- 3-ethylhexane is the most abundant ethyl-substituted isomer.
- Mono-methyl > di-methyl > quaternary;
- C atoms are negligible; methyl > ethyl-substitutions.
Relative Amount of Branched Isomers in $iso-C_8H_{18}$ fraction of Virgin Feeds

<table>
<thead>
<tr>
<th>Isomers (wt%)</th>
<th>Ponca</th>
<th>Occidental</th>
<th>Texas</th>
<th>Default</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-methylheptane</td>
<td>46.3</td>
<td>36.9</td>
<td>42.1</td>
<td>45.8</td>
</tr>
<tr>
<td>3-methylheptane</td>
<td>15.4</td>
<td>28.5</td>
<td>23.4</td>
<td>22.9</td>
</tr>
<tr>
<td>4-methylheptane</td>
<td>10.3</td>
<td>10.2</td>
<td>9.3</td>
<td>11.5</td>
</tr>
<tr>
<td>2,3-dimethylhexane</td>
<td>3.6</td>
<td>5.4</td>
<td>6.3</td>
<td>3.4</td>
</tr>
<tr>
<td>2,4-dimethylhexane</td>
<td>3.1</td>
<td>5.5</td>
<td>4.2</td>
<td>3.4</td>
</tr>
<tr>
<td>2,5-dimethylhexane</td>
<td>3.1</td>
<td>5.7</td>
<td>4.0</td>
<td>3.4</td>
</tr>
<tr>
<td>3,4-dimethylhexane</td>
<td>6.7</td>
<td>2.6</td>
<td>3.7</td>
<td>3.4</td>
</tr>
<tr>
<td>2,2-diethylhexane</td>
<td>0.5</td>
<td>-</td>
<td>0.3</td>
<td>-</td>
</tr>
<tr>
<td>3,3-diethylhexane</td>
<td>1.5</td>
<td>1.7</td>
<td>0.4</td>
<td>-</td>
</tr>
<tr>
<td>2,3,4-trimethylpentane</td>
<td>0.3</td>
<td>-</td>
<td>1.1</td>
<td>1.2</td>
</tr>
<tr>
<td>2,2,3-trimethylpentane</td>
<td>0.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2,3,3-trimethylpentane</td>
<td>0.3</td>
<td>-</td>
<td>0.6</td>
<td>-</td>
</tr>
<tr>
<td>3-ethylhexane</td>
<td>4.6</td>
<td>3.5</td>
<td>3.1</td>
<td>3.8</td>
</tr>
<tr>
<td>2-methyl-3-ethylpentane</td>
<td>3.1</td>
<td>-</td>
<td>1.5</td>
<td>1.2</td>
</tr>
<tr>
<td>3-methyl-3-ethylpentane</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

A relative regularity is observed in the virgin feedstocks. A single ‘lumped’ or equivalent component can substitute the mixture.
## Pyrolysis of Different C8 Isomers.

A single ‘lumped’ or equivalent component MIXC8 substitutes the mixture

\[
\begin{align*}
R^* + C8\text{ISO} &= RH + 0.180 \text{CH3}^* + 0.218 \text{C2H5}^* + 0.169 \text{nC3H7}^* + 0.166 \text{iC3H7}^* + 0.124 \text{1iC4H9}^* \\
&+ 0.074 \text{1C4H9}^* + 0.069 \text{2C4H9}^* + 0.175 \text{C2H4} + 0.290 \text{C3H6} + 0.124 \text{1C4H8} \\
&+ 0.047 \text{2C4H8} + 0.118 \text{iC4H8} + 0.080 \text{1C5H10} + 0.034 \text{2C5H10} + 0.045 \text{2me1C4H8} \\
&+ 0.058 \text{3me1C4H8} + 0.010 \text{2me2C4H8} + 0.008 \text{1C6H12} + 0.026 \text{noleC6} \\
&+ 0.074 \text{me1C5H10} + 0.019 \text{me2C5H10} + 0.014 \text{1C7H14} + 0.135 \text{oleC7}
\end{align*}
\]

<table>
<thead>
<tr>
<th>MIX C8</th>
<th>2MEC7</th>
<th>3MEC7</th>
<th>4MEC7</th>
<th>23DIMEC6</th>
<th>234,TRIMC5</th>
<th>3ETC6</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2</td>
<td>0.79</td>
<td>0.79</td>
<td>0.75</td>
<td>0.81</td>
<td>0.78</td>
<td>0.82</td>
</tr>
<tr>
<td>CH4</td>
<td>13.87</td>
<td>12.73</td>
<td>14.45</td>
<td>13.00</td>
<td>16.45</td>
<td>18.48</td>
</tr>
<tr>
<td>C2H4</td>
<td>29.09</td>
<td>30.84</td>
<td>30.44</td>
<td>32.16</td>
<td>22.28</td>
<td>14.95</td>
</tr>
<tr>
<td>C3H6</td>
<td>20.54</td>
<td>21.44</td>
<td>18.88</td>
<td>21.61</td>
<td>21.22</td>
<td>20.98</td>
</tr>
<tr>
<td>BTD</td>
<td>5.29</td>
<td>4.54</td>
<td>5.58</td>
<td>5.28</td>
<td>6.69</td>
<td>7.12</td>
</tr>
<tr>
<td>1C4H8</td>
<td>2.43</td>
<td>2.38</td>
<td>2.81</td>
<td>2.01</td>
<td>2.18</td>
<td>2.15</td>
</tr>
<tr>
<td>2C4H8</td>
<td>1.10</td>
<td>0.76</td>
<td>1.45</td>
<td>0.57</td>
<td>2.41</td>
<td>3.83</td>
</tr>
<tr>
<td>iC4H8</td>
<td>4.04</td>
<td>5.56</td>
<td>2.20</td>
<td>1.88</td>
<td>2.04</td>
<td>3.63</td>
</tr>
<tr>
<td>C5-</td>
<td>82.84</td>
<td>84.75</td>
<td>82.46</td>
<td>83.97</td>
<td>79.09</td>
<td>76.00</td>
</tr>
<tr>
<td>ISOPR</td>
<td>0.91</td>
<td>0.63</td>
<td>1.19</td>
<td>0.72</td>
<td>1.45</td>
<td>2.03</td>
</tr>
</tbody>
</table>

The ‘lumped’ component with a ‘default’ composition represents the overall mixture of isomers C8.
Distribution of pseudocomponents $C_nH_{2n-z}$

Number of C atoms vs. Z (dehydrogenation degree)

**SPYRO 2000**

Horizontal and Vertical Lumping allows to reduce the total number of species

Only 240 molecular and radical species characterize the pyrolysis system.
## Wide Range Naphtha - Pyrolysis Yields (wt)

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>H2</strong></td>
<td>0.48</td>
<td>0.54</td>
<td>0.61</td>
<td>0.67</td>
<td>0.77</td>
<td>0.83</td>
<td>0.89</td>
<td>0.98</td>
<td>1.01</td>
<td>1.10</td>
</tr>
<tr>
<td><strong>CH4</strong></td>
<td>8.45</td>
<td>8.64</td>
<td>10.54</td>
<td>10.65</td>
<td>12.88</td>
<td>12.97</td>
<td>14.86</td>
<td>14.93</td>
<td>16.55</td>
<td>16.58</td>
</tr>
<tr>
<td><strong>C2H2</strong></td>
<td>0.09</td>
<td>0.09</td>
<td>0.17</td>
<td>0.18</td>
<td>0.27</td>
<td>0.31</td>
<td>0.45</td>
<td>0.51</td>
<td>0.68</td>
<td>0.79</td>
</tr>
<tr>
<td><strong>C2H4</strong></td>
<td>19.57</td>
<td>19.74</td>
<td>23.76</td>
<td>23.64</td>
<td>27.49</td>
<td>27.46</td>
<td>29.97</td>
<td>30.25</td>
<td>31.75</td>
<td>31.97</td>
</tr>
<tr>
<td><strong>C2H6</strong></td>
<td>3.33</td>
<td>3.34</td>
<td>3.57</td>
<td>3.44</td>
<td>3.67</td>
<td>3.38</td>
<td>3.41</td>
<td>3.22</td>
<td>3.08</td>
<td>2.97</td>
</tr>
<tr>
<td><strong>Allene</strong></td>
<td>0.12</td>
<td>0.09</td>
<td>0.19</td>
<td>0.15</td>
<td>0.27</td>
<td>0.21</td>
<td>0.32</td>
<td>0.27</td>
<td>0.33</td>
<td>0.31</td>
</tr>
<tr>
<td><strong>Propyne</strong></td>
<td>0.22</td>
<td>0.12</td>
<td>0.31</td>
<td>0.20</td>
<td>0.00</td>
<td>0.30</td>
<td>0.00</td>
<td>0.39</td>
<td>0.60</td>
<td>0.46</td>
</tr>
<tr>
<td><strong>C3H6</strong></td>
<td>15.50</td>
<td>15.71</td>
<td>16.62</td>
<td>16.73</td>
<td>16.21</td>
<td>16.16</td>
<td>13.88</td>
<td>14.12</td>
<td>11.24</td>
<td>11.46</td>
</tr>
<tr>
<td><strong>C3H8</strong></td>
<td>0.62</td>
<td>0.58</td>
<td>0.65</td>
<td>0.57</td>
<td>0.60</td>
<td>0.51</td>
<td>0.48</td>
<td>0.43</td>
<td>0.35</td>
<td>0.33</td>
</tr>
<tr>
<td><strong>nC4H10</strong></td>
<td>1.73</td>
<td>1.92</td>
<td>1.31</td>
<td>1.44</td>
<td>0.82</td>
<td>0.90</td>
<td>0.42</td>
<td>0.49</td>
<td>0.17</td>
<td>0.22</td>
</tr>
<tr>
<td><strong>iC4H10</strong></td>
<td>0.28</td>
<td>0.30</td>
<td>0.23</td>
<td>0.23</td>
<td>0.15</td>
<td>0.15</td>
<td>0.08</td>
<td>0.08</td>
<td>0.03</td>
<td>0.04</td>
</tr>
<tr>
<td><strong>iC4H8</strong></td>
<td>3.19</td>
<td>3.02</td>
<td>3.17</td>
<td>2.94</td>
<td>2.73</td>
<td>2.49</td>
<td>1.92</td>
<td>1.85</td>
<td>1.21</td>
<td>1.24</td>
</tr>
<tr>
<td><strong>1C4H8</strong></td>
<td>3.63</td>
<td>3.34</td>
<td>3.09</td>
<td>2.84</td>
<td>1.98</td>
<td>1.93</td>
<td>0.98</td>
<td>1.13</td>
<td>0.44</td>
<td>0.65</td>
</tr>
<tr>
<td><strong>trans-2C4H8</strong></td>
<td>0.79</td>
<td>0.78</td>
<td>0.72</td>
<td>0.71</td>
<td>0.57</td>
<td>0.55</td>
<td>0.36</td>
<td>0.37</td>
<td>0.23</td>
<td>0.23</td>
</tr>
<tr>
<td><strong>cis-2C4H8</strong></td>
<td>0.62</td>
<td>0.57</td>
<td>0.59</td>
<td>0.52</td>
<td>0.47</td>
<td>0.40</td>
<td>0.30</td>
<td>0.27</td>
<td>0.18</td>
<td>0.17</td>
</tr>
<tr>
<td><strong>1,3-butadiene</strong></td>
<td>4.06</td>
<td>3.93</td>
<td>4.91</td>
<td>4.59</td>
<td>5.25</td>
<td>4.85</td>
<td>5.00</td>
<td>4.68</td>
<td>4.51</td>
<td>4.28</td>
</tr>
<tr>
<td><strong>nC5H12</strong></td>
<td>2.57</td>
<td>2.73</td>
<td>1.71</td>
<td>1.79</td>
<td>0.85</td>
<td>0.90</td>
<td>0.32</td>
<td>0.35</td>
<td>0.08</td>
<td>0.10</td>
</tr>
<tr>
<td><strong>C5ISO</strong></td>
<td>2.03</td>
<td>2.16</td>
<td>1.33</td>
<td>1.42</td>
<td>1.03</td>
<td>0.70</td>
<td>0.72</td>
<td>0.26</td>
<td>0.00</td>
<td>0.06</td>
</tr>
<tr>
<td><strong>CycloC5H10</strong></td>
<td>0.00</td>
<td>0.07</td>
<td>0.00</td>
<td>0.05</td>
<td>0.00</td>
<td>0.02</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.00</td>
</tr>
<tr>
<td><strong>1C5H10</strong></td>
<td>0.74</td>
<td>0.75</td>
<td>0.40</td>
<td>0.41</td>
<td>0.18</td>
<td>0.16</td>
<td>0.07</td>
<td>0.06</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td><strong>2C5H10</strong></td>
<td>0.61</td>
<td>0.40</td>
<td>0.44</td>
<td>0.29</td>
<td>0.19</td>
<td>0.14</td>
<td>0.08</td>
<td>0.05</td>
<td>0.03</td>
<td>0.02</td>
</tr>
<tr>
<td><strong>2me-1butene</strong></td>
<td>0.68</td>
<td>0.57</td>
<td>0.53</td>
<td>0.45</td>
<td>0.28</td>
<td>0.26</td>
<td>0.11</td>
<td>0.12</td>
<td>0.04</td>
<td>0.05</td>
</tr>
<tr>
<td><strong>3me-1butene</strong></td>
<td>0.19</td>
<td>0.19</td>
<td>0.10</td>
<td>0.12</td>
<td>0.04</td>
<td>0.05</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.00</td>
</tr>
<tr>
<td><strong>2me-2butene</strong></td>
<td>0.22</td>
<td>0.16</td>
<td>0.18</td>
<td>0.10</td>
<td>0.12</td>
<td>0.04</td>
<td>0.06</td>
<td>0.01</td>
<td>0.03</td>
<td>0.00</td>
</tr>
<tr>
<td><strong>1,3-pentadiene</strong></td>
<td>0.81</td>
<td>0.71</td>
<td>0.75</td>
<td>0.65</td>
<td>0.62</td>
<td>0.51</td>
<td>0.48</td>
<td>0.39</td>
<td>0.34</td>
<td>0.30</td>
</tr>
<tr>
<td><strong>isoprene +</strong></td>
<td>1.84</td>
<td>0.95</td>
<td>2.09</td>
<td>0.89</td>
<td>2.19</td>
<td>0.67</td>
<td>2.00</td>
<td>0.42</td>
<td>1.81</td>
<td>0.24</td>
</tr>
<tr>
<td><strong>(cyclopentadiene)</strong></td>
<td>1.23</td>
<td>1.55</td>
<td>1.61</td>
<td>1.33</td>
<td>0.61</td>
<td>0.94</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Despite of all the simplifications, also minor species are well predicted by the model.
Size of SPYRO Mechanism for the simulation of Steam Cracking Process

T.F. Lu, C.K. Law ‘Toward accommodating realistic fuel chemistry in large-scale computations’
Outlines

Complexity of Pyrolysis and Combustion Systems
- Complexity of Chemical Mechanisms
- Complexity of Liquid Fuels
- Coupling of Detailed kinetics and Complex Hydrodynamics
- Time Scales in Combustion Processes
- Dimension of Detailed Kinetic Mechanisms

Automatic Generation of Reaction Mechanisms Simplifications (QSS) and Lumping Procedures
- Pyrolysis and High Temperature Mechanisms
  - Steam Cracking Process (SPYRO)
  - Extension to Complex Mixtures
- Low Temperature Oxidation Mechanisms

Conclusions
High Temperature Oxidation Mechanism
Decomposition of Large Molecules

High Temperature mechanism mainly involves interactions amongst small and stable radicals (H, CH₃, C₂H₃, C₃H₃, ...) and small stable species such as C₂H₄ and C₂H₂ as well as oxigenated species (O₂, O, OH, HO₂, ...). High Temperature mechanism is not very sensitive to the structure of the hydrocarbon fuel.
Low Temperature Oxidation Mechanism

Low Temperature oxidation mechanism requires to define new reaction classes
Simplified Scheme of $n$-alkane ($nC_{10}H_{22}$) Primary Oxidation Reactions

Alkyl radicals forms Peroxy radicals

Peroxy radicals isomerize to form Alkyl-hydroperoxy radicals

Succeessive reactions of these radicals explain the system reactivity
Reaction Classes

**High temperature mechanism**

Reaction class 1: Unimolecular fuel decomposition
Reaction class 2: H-atom abstractions
Reaction class 3: Alkyl radical decomposition
Reaction class 4: Alkyl radical+O2=olefin+HO2
Reaction class 5: Alkyl radical isomerization
Reaction class 6: H atom abstraction from olefins
Reaction class 7: Addition of radical species to olefins
Reaction class 8: Alkenyl radical decomposition
Reaction class 9: Olefin decomposition

**Low temperature (high pressure) mechanism**

Reaction class 10: Alkyl radical addition to O2
Reaction class 11: R+R'O2=RO+R'O
Reaction class 12: Alkylperoxy radical isomerization
Reaction class 13: RO2+HO2=ROOH+O2
Reaction class 14: RO2+H2O2=ROOH+HO2
Reaction class 15: RO2+CH3O2=RO+CH3O+O2
Reaction class 16: RO2+R'O2=RO+R'O+O2
Reaction class 17: RO2H=RO+OH
Reaction class 18: Alkoxy radical decomposition
Reaction class 19: QOOH decomposition and production of cyclic ethers
Reaction class 20: QOOH beta decomposition to produce olefin+HO2
Reaction class 21: QOOH decomposition to small olefin, aldehyde and OH
Reaction class 22: Addition of QOOH to molecular oxygen O2
Reaction class 23: O2QOOH isomerization to carbonylhydroperoxide + OH
Reaction class 24: Carbonylhydroperoxide decomposition
Reaction class 25: Reactions of cyclic ethers with OH and HO2

### Automatic generation

#### Classes of reactions

1. Decomposition of alkyl radicals $R \rightarrow C_nH_{2n}+R'$
2. $O_2$ addition to alkyl radicals $R+O_2 \rightleftharpoons ROO$
3. Internal isomerization $ROO \rightleftharpoons QOOH$
4. $O_2$ addition to hydroperoxyalkyl radicals $QOOH+O_2 \rightleftharpoons OOQOOH$
5. Decomposition of hydroperoxyalkyl peroxy radicals $OOQOOH \rightleftharpoons OOQOOH+OH$

#### Reference kinetic parameters

<table>
<thead>
<tr>
<th>H-Abstraction Reactions</th>
<th>Primary H atom</th>
<th>Secondary H atom</th>
<th>Tertiary H atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary radical</td>
<td>$10^{8.0} \exp (-13.5/RT)$</td>
<td>$10^{8.0} \exp (-11.2/RT)$</td>
<td>$10^{8.0} \exp (-9/RT)$</td>
</tr>
<tr>
<td>Secondary radical</td>
<td>$10^{8.0} \exp (-14.5/RT)$</td>
<td>$10^{8.0} \exp (-12.2/RT)$</td>
<td>$10^{8.0} \exp (-10/RT)$</td>
</tr>
<tr>
<td>Tertiary radical</td>
<td>$10^{8.0} \exp (-15/RT)$</td>
<td>$10^{8.0} \exp (-12.7/RT)$</td>
<td>$10^{8.0} \exp (-10.5/RT)$</td>
</tr>
<tr>
<td>Peroxyl radical</td>
<td>$10^{8.7} \exp (-21.5/RT)$</td>
<td>$10^{8.7} \exp (-18.8/RT)$</td>
<td>$10^{8.7} \exp (-16.5/RT)$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Isomerization Reactions</th>
<th>(Transfer of a Primary H-atom)</th>
<th>1-4 H Transfer</th>
<th>1-5 H Transfer</th>
<th>1-6 H Transfer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary radical</td>
<td>$10^{11.0} \exp (-20.6/RT)$</td>
<td>$10^{10.2} \exp (-14.5/RT)$</td>
<td>$10^{9.7} \exp (-14.5/RT)$</td>
<td></td>
</tr>
<tr>
<td>Peroxyl radical</td>
<td>$10^{11.8} \exp (-29.1/RT)$</td>
<td>$10^{11.0} \exp (-23.0/RT)$</td>
<td>$10^{10.6} \exp (-23.0/RT)$</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Alkyl Radical Decomposition Reactions to form Primary Radicals</th>
<th>Primary radical</th>
<th>Secondary radical</th>
<th>Tertiary radical</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$10^{14.0} \exp (-30/RT)$</td>
<td>$10^{14.0} \exp (-31/RT)$</td>
<td>$10^{14.0} \exp (-31.5/RT)$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Hydperoxy-Alkyl Radical Decomposition Reactions to form</th>
<th>HO2$^+$ and Conjugate Olefins</th>
<th>Smaller Olefins</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$10^{14.0} \exp (-23/RT)$</td>
<td>$10^{13.2} \exp (-22.5/RT)$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Corrections in Activation Energy to form:</th>
<th>Methyl radical</th>
<th>Secondary radical</th>
<th>Tertiary radical</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$+2.$</td>
<td>$-2.$</td>
<td>$-3.$</td>
</tr>
</tbody>
</table>

Combustion Reactions

Automatic Generation of Detailed Reaction Schemes

Primary propagation reactions of n-dodecane pyrolysis

(Units are: m kmol s kcal).

R5a - Isomerization of ROO• to •QOOH radicals

<table>
<thead>
<tr>
<th>Reaction</th>
<th>A</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>COO*-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C</td>
<td>1.26E+12</td>
<td>26800</td>
</tr>
<tr>
<td>COO*-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C</td>
<td>2.00E+11</td>
<td>20700</td>
</tr>
<tr>
<td>COO*-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C</td>
<td>8.00E+10</td>
<td>20700</td>
</tr>
<tr>
<td>C-COO*-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C</td>
<td>2.00E+12</td>
<td>29100</td>
</tr>
<tr>
<td>C-COO*-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C</td>
<td>1.26E+12</td>
<td>26800</td>
</tr>
<tr>
<td>C-COO*-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C</td>
<td>2.00E+11</td>
<td>20700</td>
</tr>
<tr>
<td>C-COO*-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C</td>
<td>8.00E+10</td>
<td>20700</td>
</tr>
<tr>
<td>C-COO*-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C</td>
<td>1.26E+12</td>
<td>26800</td>
</tr>
<tr>
<td>C-COO*-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C</td>
<td>1.26E+12</td>
<td>26800</td>
</tr>
<tr>
<td>C-C-COO*-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C</td>
<td>3.00E+11</td>
<td>23000</td>
</tr>
<tr>
<td>C-C-COO*-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C</td>
<td>2.00E+11</td>
<td>20700</td>
</tr>
<tr>
<td>C-C-COO*-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C</td>
<td>8.00E+10</td>
<td>20700</td>
</tr>
<tr>
<td>C-C-C-COO*-C-C-C-C-C-C-C-C-C-C-C-C-C-C</td>
<td>1.26E+12</td>
<td>26800</td>
</tr>
<tr>
<td>C-C-C-COO*-C-C-C-C-C-C-C-C-C-C-C-C-C-C</td>
<td>1.26E+12</td>
<td>26800</td>
</tr>
<tr>
<td>C-C-C-C-COO*-C-C-C-C-C-C-C-C-C-C-C-C-C</td>
<td>2.00E+11</td>
<td>20700</td>
</tr>
<tr>
<td>C-C-C-C-COO*-C-C-C-C-C-C-C-C-C-C-C-C-C</td>
<td>2.00E+11</td>
<td>20700</td>
</tr>
</tbody>
</table>
Combustion Reactions

Automatic Generation of Detailed Reaction Schemes
Primary propagation reactions of n-dodecane pyrolysis

(Units are: m kmol s kcal).

R5b  -Isomerization of •QOOH to ROO• radicals

<table>
<thead>
<tr>
<th>Reaction</th>
<th>A</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>COOH-•C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C</td>
<td>9.45E+10</td>
<td>19100</td>
</tr>
<tr>
<td>COOH-•C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C</td>
<td>1.50E+10</td>
<td>13000</td>
</tr>
<tr>
<td>COOH-•C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C</td>
<td>6.00E+09</td>
<td>13000</td>
</tr>
<tr>
<td>COOH-•C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C</td>
<td>9.45E+10</td>
<td>18100</td>
</tr>
<tr>
<td>C-COOH-•C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C</td>
<td>9.45E+10</td>
<td>19100</td>
</tr>
<tr>
<td>C-COOH-•C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C</td>
<td>1.50E+10</td>
<td>13000</td>
</tr>
<tr>
<td>C-COOH-•C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C</td>
<td>6.00E+09</td>
<td>13000</td>
</tr>
<tr>
<td>C-COOH-•C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C</td>
<td>1.50E+10</td>
<td>12000</td>
</tr>
<tr>
<td>C-COOH-•C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C</td>
<td>9.45E+10</td>
<td>19100</td>
</tr>
<tr>
<td>C-COOH-•C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C</td>
<td>9.45E+10</td>
<td>19100</td>
</tr>
<tr>
<td>C-COOH-•C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C</td>
<td>1.50E+10</td>
<td>13000</td>
</tr>
<tr>
<td>C-COOH-•C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C</td>
<td>6.00E+09</td>
<td>13000</td>
</tr>
<tr>
<td>C-COOH-•C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C</td>
<td>1.50E+10</td>
<td>13000</td>
</tr>
<tr>
<td>C-COOH-•C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C</td>
<td>6.00E+09</td>
<td>12000</td>
</tr>
<tr>
<td>C-COOH-•C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C</td>
<td>1.50E+10</td>
<td>13000</td>
</tr>
<tr>
<td>C-COOH-•C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C</td>
<td>9.45E+10</td>
<td>19100</td>
</tr>
<tr>
<td>C-C-COOH-•C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C</td>
<td>9.45E+10</td>
<td>19100</td>
</tr>
<tr>
<td>C-C-COOH-•C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C</td>
<td>1.50E+10</td>
<td>13000</td>
</tr>
<tr>
<td>C-C-COOH-•C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C</td>
<td>6.00E+09</td>
<td>13000</td>
</tr>
<tr>
<td>C-C-COOH-•C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C</td>
<td>1.50E+10</td>
<td>13000</td>
</tr>
<tr>
<td>C-C-C-COOH-•C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C</td>
<td>6.00E+09</td>
<td>12000</td>
</tr>
<tr>
<td>C-C-C-C-COOH-•C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C</td>
<td>1.50E+10</td>
<td>13000</td>
</tr>
<tr>
<td>C-C-C-C-C-COOH-•C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C</td>
<td>9.45E+10</td>
<td>19100</td>
</tr>
</tbody>
</table>
Detailed Mechanisms of n-Alkane Oxidation

Table 1. Detailed Mechanism of n-Alkane Oxidation; Number of Primary Propagation Reactions

<table>
<thead>
<tr>
<th>reaction classes</th>
<th>C_7H_{16}</th>
<th>C_{10}H_{22}</th>
<th>C_{12}H_{26}</th>
<th>C_{14}H_{30}</th>
<th>C_{16}H_{34}</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>10</td>
<td>18</td>
<td>24</td>
<td>30</td>
<td>36</td>
</tr>
<tr>
<td>R2</td>
<td>6</td>
<td>8</td>
<td>10</td>
<td>12</td>
<td>14</td>
</tr>
<tr>
<td>R3</td>
<td>7</td>
<td>9</td>
<td>11</td>
<td>13</td>
<td>15</td>
</tr>
<tr>
<td>R4</td>
<td>8</td>
<td>10</td>
<td>12</td>
<td>14</td>
<td>16</td>
</tr>
<tr>
<td>R5</td>
<td>33</td>
<td>48</td>
<td>60</td>
<td>72</td>
<td>84</td>
</tr>
<tr>
<td>R6</td>
<td>5</td>
<td>8</td>
<td>10</td>
<td>12</td>
<td>14</td>
</tr>
<tr>
<td>R7</td>
<td>6</td>
<td>9</td>
<td>11</td>
<td>13</td>
<td>15</td>
</tr>
<tr>
<td>R8</td>
<td>15</td>
<td>24</td>
<td>30</td>
<td>36</td>
<td>42</td>
</tr>
<tr>
<td>R9</td>
<td>30</td>
<td>48</td>
<td>60</td>
<td>72</td>
<td>84</td>
</tr>
<tr>
<td>R10</td>
<td>15</td>
<td>24</td>
<td>30</td>
<td>36</td>
<td>42</td>
</tr>
<tr>
<td>total</td>
<td>135</td>
<td>206</td>
<td>258</td>
<td>310</td>
<td>362</td>
</tr>
</tbody>
</table>

Table 2. Detailed Mechanism of n-Alkane Oxidation

<table>
<thead>
<tr>
<th>primary propagating radicals</th>
<th>fuel</th>
<th>alkyl R^*</th>
<th>peroxy ROO^*</th>
<th>hydroperoxy-alkyl QOOOH</th>
<th>hydroperoxy-alkylperoxy OOQOOOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-C_7H_{16}</td>
<td>4</td>
<td>4</td>
<td>15</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>n-C_{10}H_{22}</td>
<td>5</td>
<td>5</td>
<td>24</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>n-C_{12}H_{26}</td>
<td>6</td>
<td>6</td>
<td>30</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>n-C_{14}H_{30}</td>
<td>7</td>
<td>7</td>
<td>36</td>
<td>36</td>
<td></td>
</tr>
<tr>
<td>n-C_{16}H_{34}</td>
<td>8</td>
<td>8</td>
<td>42</td>
<td>42</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>primary products</th>
<th>fuel</th>
<th>conjugate alkenes</th>
<th>O-heterocycles</th>
<th>hydroperoxides</th>
<th>carbonyl-hydroperoxides</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-C_7H_{16}</td>
<td>3</td>
<td>8</td>
<td>4</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>n-C_{10}H_{22}</td>
<td>5</td>
<td>13</td>
<td>5</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>n-C_{12}H_{26}</td>
<td>6</td>
<td>16</td>
<td>6</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>n-C_{14}H_{30}</td>
<td>7</td>
<td>19</td>
<td>7</td>
<td>36</td>
<td></td>
</tr>
<tr>
<td>n-C_{16}H_{34}</td>
<td>8</td>
<td>22</td>
<td>8</td>
<td>42</td>
<td></td>
</tr>
</tbody>
</table>


Colloquia on Reaction Engineering January 24th, 2014
$n$-dodecane Primary Oxidation Reactions

**Detailed Scheme**

- **258** Primary reactions
- **72** Intermediate radicals
- **58** Primary products  
  (retaining nC12 structure)
  - 6 n-dodecenes
  - 16 O-cyclic-ethers
  - 6 hydroperoxides
  - 30 keto-hydroperoxides

Low and High Temperature oxidation mechanisms are conveniently simplified by grouping intermediate Species and Reactions.
Lumping of Alkenes, Cyclic ethers, Peroxides and Ketohydroperoxides

Lumping of Alkyl, Peroxy, Alkyl-hydroperoxy and Peroxy-alkyl-hydroperoxy
Lumped Scheme of $n$-alkane Primary Oxidation Reactions

Lumped oxidation mechanism of $n$-decane.

Lumping of Alkyl, Peroxy, Alkyl-hydroperoxy and Peroxy-alkyl-hydroperoxy

Lumping of Alkenes, Cyclic ethers, Peroxides and Ketohydroperoxides
Detailed Scheme

258 Primary reactions

72 Intermediate radicals

58 Primary products
  (retaining nC12 structure)

  6  n-dodecenes
  16  O-cyclic-ethers
  6  hydroperoxides
  30  keto-hydroperoxides

Lumped Scheme

15 Primary lumped reactions

4 Intermediate radicals

4 Primary lumped products

  1 lumped  n-dodecenes
  1 lumped  O-cyclic-ethers
  1 lumped  hydroperoxides
  1 lumped  keto-hydroperoxides

Kinetic Models always require a reasonable and well balanced presence of ‘primary’ and ‘secondary’ reactions.

Lumped Mechanisms of Heavy n-Alkane Oxidation

Table 3. Kinetic Parameters of the Lumped Oxidation Reactions of n-Alkanes (Units Are kmol, m, s, K)

<table>
<thead>
<tr>
<th>lumped reactions</th>
<th>$nC_7H_{16}$</th>
<th>$nC_{10}H_{22}$</th>
<th>$nC_{12}H_{26}$</th>
<th>$nC_{16}H_{34}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>initiation</td>
<td>$2 \times 10^{17}$</td>
<td>40 750</td>
<td>$3.5 \times 10^{17}$</td>
<td>40 750</td>
</tr>
<tr>
<td>H abstractions$^a$</td>
<td>$10 \text{ Hs} + 6 \text{ Hp}$</td>
<td>$16 \text{ Hs} + 6 \text{ Hp}$</td>
<td>$20 \text{ Hs} + 6 \text{ Hp}$</td>
<td>$28 \text{ Hs} + 6 \text{ Hp}$</td>
</tr>
<tr>
<td>$\text{O}_2 + R^* \rightarrow \text{HO}_2 + \text{alkene}$</td>
<td>$5 \times 10^{8}$</td>
<td>1 750</td>
<td>$5 \times 10^{8}$</td>
<td>1 750</td>
</tr>
<tr>
<td>$R^* \rightarrow \beta$ decomposition</td>
<td>$3.3 \times 10^{13}$</td>
<td>15 100</td>
<td>$3.3 \times 10^{13}$</td>
<td>15 100</td>
</tr>
<tr>
<td>$O_2 + R^* \rightarrow \text{ROO}^*$</td>
<td>$2 \times 10^9$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>ROOH$^<em>$ $\rightarrow$ R$^</em> +$ O$_2$</td>
<td>$5 \times 10^{13}$</td>
<td>15 600</td>
<td>$5 \times 10^{13}$</td>
<td>15 600</td>
</tr>
<tr>
<td>ROOH$^<em>$ $\rightarrow$ QOOH$^</em>$</td>
<td>$3 \times 10^{12}$</td>
<td>12 100</td>
<td>$3 \times 10^{12}$</td>
<td>12 100</td>
</tr>
<tr>
<td>QOOH$^<em>$ $\rightarrow$ ROO$^</em>$</td>
<td>$2 \times 10^{10}$</td>
<td>8 100</td>
<td>$2 \times 10^{10}$</td>
<td>8 100</td>
</tr>
<tr>
<td>QOOH$^<em>$ $\rightarrow$ HO$_2^</em>$ $+$ alkene</td>
<td>$8 \times 10^{12}$</td>
<td>12 100</td>
<td>$4.5 \times 10^{12}$</td>
<td>12 100</td>
</tr>
<tr>
<td>QOOH$^<em>$ $\rightarrow$ OH$^</em> +$ ethers</td>
<td>$1 \times 10^{10}$</td>
<td>7 100</td>
<td>$1.5 \times 10^{10}$</td>
<td>7 100</td>
</tr>
<tr>
<td>QOOH$^<em>$ $\rightarrow$ OH$^</em> +$ R$^* +$ RCHO</td>
<td>$2 \times 10^{12}$</td>
<td>11 300</td>
<td>$2 \times 10^{12}$</td>
<td>11 300</td>
</tr>
<tr>
<td>QOOH$^<em>$ $\rightarrow$ O$_2$ $\rightarrow$ QOOH$^</em>$</td>
<td>$2 \times 10^9$</td>
<td>0</td>
<td>$2 \times 10^9$</td>
<td>0</td>
</tr>
<tr>
<td>QOOOH$^<em>$ $\rightarrow$ QOOH$^</em>$ $+$ O$_2$</td>
<td>$2 \times 10^{14}$</td>
<td>14 600</td>
<td>$2 \times 10^{14}$</td>
<td>14 600</td>
</tr>
<tr>
<td>QOOOH$^<em>$ $\rightarrow$ QOOH$^</em>$ $+$ OH$^*$</td>
<td>$1 \times 10^{12}$</td>
<td>12 350</td>
<td>$1 \times 10^{12}$</td>
<td>11 600</td>
</tr>
<tr>
<td>QOOOH$^<em>$ $\rightarrow$ OH$^</em> +$ R$^* +$ P</td>
<td>$1 \times 10^{15}$</td>
<td>20 100</td>
<td>$1 \times 10^{15}$</td>
<td>20 300</td>
</tr>
</tbody>
</table>

$^a$ Hp and Hs stand for primary and secondary H atoms, respectively.

Low and High temperature primary mechanism
of different n-alkanes heavier than n-heptane are always described with

4 lumped radicals (R, ROO, QOOH, and OOQOOH) and

15 similar reactions, with the same lumped kinetic parameters

Overall Oxidation Mechanism

• GRI scheme for Gases

• PRF (nC7-iC8) and additives for Gasolines

• Alcohols

• Diesel and Jet Fuels

• Biofuels – FAME – FAEE

Hierarchy and Modularity are the main features of Detailed Kinetic Schemes

N-Heptane Oxidation
Low and High Temperature Ignitions

Pressure effect on the NTC region

Combust. Flame 103: 91-106
Gasoline and Primary Reference Fuels
Mixtures n-heptane / iso-octane (1,2,3)

Lille RCM
Total ignition time [ms]

Princeton PFR
Released Heat [T(i) – T]


Lumped kinetic models allow an easier and more effective successive reduction, for CFD applications.

T.F. Lu, C.K. Law ‘Toward accommodating realistic fuel chemistry in large-scale computations’
Reduction of Detailed Kinetics

Lumped kinetic models allow a easier and more effective successive reduction.

A skeletal kinetic mechanism of n-dodecane oxidation derived from a lumped scheme involves ~120 species, while the one obtained via a detailed scheme involves ~ 300 species.

Detailed Kinetics always require a successive lumping phase in order to significantly reduce the number of species.
Reduction of Detailed Kinetics
Skeletal Mechanisms of n-dodecane and Bio-Diesel Fuels


Colloquia on Reaction Engineering | January 24th, 2014
POLITECNICO DI MILANO
Reduction of Detailed Kinetics

Species involved in the different mechanisms of fuel surrogates
Importance of the $C_0$-$C_4$ sub-mechanism.
Thanks for the attention

CRECK Modeling Group at Politecnico di Milano
Abstract

Chemical lumping procedures are applied to the development of detailed kinetic schemes of pyrolysis and combustion of complex hydrocarbon mixtures, such as naphtha, gasoline, gasoil and diesel fuels.

The automatic generation of detailed kinetic schemes of pyrolysis and combustion of primary reference fuels (n-heptane and iso-octane) is discussed, advantages and limitations of chemical lumping are analysed. The extension of the lumping approach towards heavier and more complex mixtures in case of steam cracking process is also addressed.

It is not of interest to automatically generate detailed mechanisms with several thousands of species and elementary reactions. A compromise has to be found between computation efforts and prediction accuracy.

From a modeling point of view, it is more convenient to directly link a post-processor to the kinetic generator with the purpose of lumping intermediate and final products into a limited number of lumped components.

A further advantage of semi-detailed kinetic models, reduced with a chemical lumping, is that it is easier and more effective to apply further reduction techniques.
Time Scales in Combustion Processes

Inlet mixture: $C_3H_8 + \text{Air}$
Temperature: 1800 K

A wide range of time scales are involved in Combustion Chemistry
H-abstraction reaction on n-decane

Temperature effect on primary product distribution from β-decomposition reaction of n-decyl radical

<table>
<thead>
<tr>
<th></th>
<th>800 K</th>
<th>1000 K</th>
<th>1200 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₈H₁₈ + CH₃•</td>
<td>0.0424</td>
<td>0.0516</td>
<td>0.0588</td>
</tr>
<tr>
<td>C₆H₁₆ + C₂H₅•</td>
<td>0.1478</td>
<td>0.1332</td>
<td>0.1193</td>
</tr>
<tr>
<td>C₇H₁₄ + C₃H₇•</td>
<td>0.1519</td>
<td>0.1475</td>
<td>0.1346</td>
</tr>
<tr>
<td>C₆H₁₂ + C₄H₉•</td>
<td>0.1519</td>
<td>0.1475</td>
<td>0.1346</td>
</tr>
<tr>
<td>C₅H₁₀ + C₅H₁₁•</td>
<td>0.1479</td>
<td>0.1332</td>
<td>0.1193</td>
</tr>
<tr>
<td>C₄H₈ + C₆H₁₃•</td>
<td>0.1492</td>
<td>0.1412</td>
<td>0.1359</td>
</tr>
<tr>
<td>C₅H₆ + C₇H₁₅•</td>
<td>0.1526</td>
<td>0.1569</td>
<td>0.1677</td>
</tr>
<tr>
<td>C₆H₄ + C₈H₁₇•</td>
<td>0.0563</td>
<td>0.0889</td>
<td>0.1300</td>
</tr>
</tbody>
</table>

The product distribution and corresponding ‘lumped’ stoichiometry shows a weak T dependence.
**Detailed Scheme**

- 258 Primary reactions
- 72 Intermediate radicals

**Lumped Scheme**

- 15 Primary lumped reactions
- 4 Intermediate radicals

Low and High temperature *primary mechanism* of n-alkanes heavier than n-heptane are described with

- 4 lumped radicals (R, ROO, QOOH, and OOQOOH) and
- 15 similar reactions, with the same lumped kinetic parameters

---

Knocking Propensity of Primary Reference Fuels

\[ n\text{-heptane } ON=0 \]

\[
\begin{align*}
\text{Peroxy radicals} & \quad \text{Isomerization reactions of peroxy radicals explain the different ignition times of the two PRF} \\
\text{4 secondary} & \quad \text{(1-5) H-abstractions} \\
\text{k=4 } 10^{11.0} & \text{exp(-20000/RT)} \\
\text{k(700)} & = 10^{5.4} \text{ [s}^{-1}\text{]} \\
\text{Alkyl-hydroperoxy-radicals} & \quad \text{(1-4) H-abstractions} \\
\text{k= 2 } 10^{11.8} & \text{exp (-26000/RT)} \\
\text{k(700)} & = 10^{4.0} \text{ [s}^{-1}\text{]} \\
\end{align*}
\]

\[ iso\text{-octane } ON=100 \]