Title: Reduced syngas-based chemical kinetics mechanisms for dual fuel engine combustion applications

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Date: 19/11/2018
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- Conclusions
Introduction

- Shortage of petroleum resources
- Global warming

\[ \text{Alternative fuel consumption \%} \]

\[ \text{Years} \]

- Higher thermal efficiency
- Reduction of CO$_2$

Advantages of gaseous fuel

- Variety in composition
- Clean exhaust $\rightarrow$ ultra low SO$_x$, PM and CO$_2$
- High ignition temperature $\rightarrow$ improved knock resistance

Different engine combustion technologies

- Homogeneous Charge Compression Ignition (HCCI)
- Diesel (CI) combustion
- Spark ignition (SI) combustion

Adiabatic flame temperature in air (21% O₂)
CO to CO₂ conversion diminishes
Adiabatic flame temperature 10% O₂

DCDC

Homogeneous Charge Compression Ignition (HCCI)
Different engine combustion technologies

- Diesel (CI) combustion
  - Controlled heat release (mixing)
  - Controlled combustion timing
  - Wide load range
  - High efficiency (relative to SI)
  - NOx and PM emissions

- Spark ignition (SI) combustion
  - Controlled heat release (flame propagation)
  - Controlled combustion timing
  - Wide load range
  - Three-way catalyst
  - Low efficiency (relative to diesel)

Homogeneous Charge Compression Ignition (HCCI)

- Load range?
- Combustion timing?
- Heat release rate?
- Transient control?
- Fuel?
Ignition systems

Spark plug

Gaseous fuel

Air

Glow plug

Gaseous fuel

HCCI / CAI

Heater

Dual fuel

Gaseous fuel

Gaseous fuel

Diesel fuel
Dual-fuel engine combustion

Diesel fuel 10 mg + Syngas

Diesel fuel 2 mg + Syngas

Conventional diesel injection [188]

High soot and NOx emissions

Micro-pilot diesel injection [188]

Ultra-low soot and NOx emissions

Diesel fuel 10 mg + Syngas
Diesel fuel 2 mg + Syngas
Numerical analysis of the combustion process

• Chemical kinetics mechanisms that were developed during the past years were mainly focused on simulating the combustion of pure H\textsubscript{2} or H\textsubscript{2}/CO syngas mixtures.

• However, simple H\textsubscript{2}/CO mixtures are not fully adequate to represent real syngas fuels, since CH\textsubscript{4} has a significant influence on the combustion process.

• Moreover, chemical kinetics mechanisms that have been developed for the simulation of n-heptane oxidation consist of a huge number of species of reactions and cannot be implemented in multidimensional CFD simulations.

There is a need for a robust, reduced and computational efficient chemical kinetics mechanism for the simulation of multicomponent syngas combustion, syngas/n-heptane co-oxidation and NO\textsubscript{x} formation.
Development of a reduced chemical kinetics mechanism for n-heptane/syngas co-oxidation, syngas combustion and NOx formation.

**Mechanism development steps**

- Selection of the n-heptane mechanism
- N-heptane mechanism reduction
- Coupling between the syngas/NOx mechanism and the reduced n-heptane mechanism
- Validation of the coupled mechanism against exp. data and simulated results using other mechanisms
- Multidimensional CFD simulation

**N-heptane mechanism selection**

- **LLNL Detail mechanism** [22]
- **Creck Reduced mechanism** [262]
- **Lu et al Skeletal mechanism** [263,264]
- **Wiscosin Reduced mechanism** [265]
- **Experiment Ciezki et al** [177]

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The reduced Creck mechanism [5] was used for the reduction and coupling with the syngas/NOx mechanism developed in Part 2.

The reduction of the n-heptane mechanism was performed by using the necessity analysis method.

Necessity analysis is a hybrid reduction tool as it combines both flow analysis and sensitivity analysis reduction methods in order to find the reactions and species that are the most necessary for the consumption or the formation of specific targets.

Once necessity analysis is complete, a necessity factor is calculated for each individual species in the mechanism (0<nf≤1). The closest to 1 is the most important species, while the closest to zero is the lowest important species and therefore can be eliminated from the mechanism.

The higher the necessity factor the lower is the number of reactions in the skeletal mechanism.

Two loop stopping criteria were used: a) deviation between the skeletal mechanism and the original to be lower than 0.5% and the reactions number to be close to 300.

Overall mean error and number of reactions of each skeletal mechanism

<table>
<thead>
<tr>
<th>Skeletal Mechanism</th>
<th>Overall mean error, $\bar{\epsilon}$ (%)</th>
<th>Number of Reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N-heptane</td>
<td>Syngas</td>
</tr>
<tr>
<td>Generation 0 /Original Mech.[5]</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Generation 10</td>
<td>0.092</td>
<td>0.034</td>
</tr>
<tr>
<td>Generation 15</td>
<td>0.146</td>
<td>0.091</td>
</tr>
<tr>
<td><strong>Generation 22</strong></td>
<td><strong>0.290</strong></td>
<td><strong>0.154</strong></td>
</tr>
<tr>
<td>Generation 24</td>
<td>2.31</td>
<td>0.585</td>
</tr>
</tbody>
</table>

Generation 22 was chosen because the number of reactions lies inside the pre-set criterion (≤ 300 reactions), and, additionally, the calculated error is inside the pre-set error limit (≤ 0.5%).

Mechanisms coupling

- For syngas combustion and NOx formation, the reduced mechanism for syngas/NOx constructed in Part 2 was selected for the coupling with the 22nd Generation n-heptane skeletal mechanism.

- N-heptane skeletal mechanism includes full CH₄, H₂ and CO chemistry and therefore, no additional reactions were incorporated during the coupling. Only the rate constants were adopted from syngas/NOx mechanism. The new mechanism is called University of Northumbria at Newcastle (UNN-1) mechanism.

- According to the comparison UNN-1, is lower at NTC region for n-heptane while under-predicts the original mechanism at low temperatures for syngas.

- In order to reduce the uncertainty the rate constants of important n-heptane reactions were adjusted.

- The new final mechanism has been designed and called UNN-2

| Modified n-heptane based reactions (A units cal-cm-sec-K, E units cal/mol) |
|-----------------------------|-----------------------------|
| Reaction                  | Old rate constant | New rate constant |
|                            | A  | n  | E      | A  | n  | E      |
| NC₇H₁₆+OH=NC₇H₁₅+H₂O    | 4.8E06 | 2.0 | -2259.83 | 1.8E07 | 2.0 | -2259.83 |
| NC₇H₁₆+HO₂=NC₇H₁₅+H₂O₂   | 1.76E05 | 2.5 | 14860.00 | 1.76E04 | 2.5 | 14860.00 |
| NC₇H₁₅+O₂=NC₇H₁₅O₂       | 2.0E11 | 0.0 | 0.0     | 2.0E12 | 0.0 | 0.0     |
# UNN-2 mechanism (A units cal-cm-sec-K, E units cal/mol)

<table>
<thead>
<tr>
<th>Reactions</th>
<th>A</th>
<th>n</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Syngas reactions</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R1</td>
<td>C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;16&lt;/sub&gt;+11O&lt;sub&gt;2&lt;/sub&gt;=7CO&lt;sub&gt;2&lt;/sub&gt;+8H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>R2</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;+O=O+H</td>
<td>5.06E4</td>
<td>2.67</td>
</tr>
<tr>
<td>R3</td>
<td>H+O&lt;sub&gt;2&lt;/sub&gt;=OH+O</td>
<td>3.520E16</td>
<td>-0.7</td>
</tr>
<tr>
<td>R4</td>
<td>H+O&lt;sub&gt;2&lt;/sub&gt;(+M)=HO&lt;sub&gt;2&lt;/sub&gt;(+M)</td>
<td>4.6E12</td>
<td>0.4</td>
</tr>
</tbody>
</table>

/M/AR/0.0/ H<sub>2</sub>/1.3/ H<sub>2</sub>O/10.0/ CO/1.9/ CO<sub>2</sub>/3.8/ 

| R5        | OH+HO<sub>2</sub>=O<sub>2</sub>+H<sub>2</sub>O | 2.89E13 | 0.0 | -496.9 |

<table>
<thead>
<tr>
<th><strong>N-heptane reactions</strong></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>R238</td>
<td>NC&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;16&lt;/sub&gt;+CH&lt;sub&gt;3&lt;/sub&gt;CO=CH&lt;sub&gt;2&lt;/sub&gt;CHO+NC&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;15&lt;/sub&gt;</td>
<td>1.6240E06</td>
<td>2.0</td>
</tr>
<tr>
<td>R239</td>
<td>NC&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;16&lt;/sub&gt;+HCO=CH&lt;sub&gt;2&lt;/sub&gt;O+NC&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;15&lt;/sub&gt;</td>
<td>1.5160E06</td>
<td>2.0</td>
</tr>
<tr>
<td>R240</td>
<td>NC&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;16&lt;/sub&gt;+HCCO=CH&lt;sub&gt;2&lt;/sub&gt;CO+NC&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;15&lt;/sub&gt;</td>
<td>5.1360E05</td>
<td>2.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>NOx reactions</strong></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>R273</td>
<td>HO&lt;sub&gt;2&lt;/sub&gt;+NO=NO&lt;sub&gt;2&lt;/sub&gt;+OH</td>
<td>2.11E12</td>
<td>0.0</td>
</tr>
<tr>
<td>R274</td>
<td>NO+(+M)=NO&lt;sub&gt;2&lt;/sub&gt;(+M)</td>
<td>1.06E20</td>
<td>-1.41</td>
</tr>
</tbody>
</table>

/M/ H<sub>2</sub>/2.0/ H<sub>2</sub>O/6.0/ CH<sub>4</sub>/2.0/ CO/1.5/ CO<sub>2</sub>/2.0/ 

| R275            | NO<sub>2</sub>+O=NO+O<sub>2</sub> | 3.9E12 | 0.0 | -240.0 |
| R276            | NO<sub>2</sub>+H=NO+OH | 1.32E14 | 0.0 | 360.0 |
Validation

N-heptane oxidation


Laminar flame speed (different fuel compositions)

Ingition delay time (different equivalence ratios)

NO concentration (different equivalence ratios)

\[\text{Fuel 8}
\begin{align*}
\text{Type 1} & : 
\begin{array}{l}
\text{H}_2/\text{CO}/\text{CH}_4: \text{47.5\%/47.5\%/5\%} \\
\text{Eq. Ratio} = 0.4 - 2.5
\end{array} \\
\text{UNN-2 mechanism} & : \\
\text{GRI Mech. 3.0} & : \\
\text{Experiment Lapalme et al}[14] & : \\
\end{align*}
\]

\[\text{Fuel 5 Type 2} \\
\begin{align*}
\text{H}_2/\text{CO}/\text{CO}_2 : \text{35\%/35\%/30\%} \\
\text{Eq. Ratio} = 0.3
\end{align*}
\]

\[\text{Fuel 12} \\
\begin{align*}
\text{Eq. ratio} = 0.71 & : \\
\text{Eq. ratio} = 1.03 & : \\
\text{Eq. ratio} = 1.34 & : \\
\text{UNN-2 mechanism} & : \\
\text{GRI Mech. 3.0} & : \\
\text{Experiment Watson et al}[16] & : \\
\end{align*}
\]

\[\text{Fuel 12} \\
\begin{align*}
\text{Eq. ratio} = 0.71 & : \\
\text{Eq. ratio} = 1.03 & : \\
\text{Eq. ratio} = 1.34 & : \\
\text{UNN-2 mechanism} & : \\
\text{GRI Mech. 3.0} & : \\
\text{Experiment Watson et al}[16] & : \\
\end{align*}
\]

N-heptane/syngas co-oxidation

N-C$_7$H$_{16}$/H$_2$ mixture

Fuel 22 Type 1
H$_2$/C$_7$H$_{16}$: 20%/80%
Eq.Ratio:1
Pressure: 55 bar

UNN-2 mechanism
- Creck Reduced mechanism [5]
- Chalmers Reduced mechanism [17]

N-C$_7$H$_{16}$/CH$_4$ mixture

Fuel 23 Type 1
CH$_4$/C$_7$H$_{16}$: 20%/80%
Eq.Ratio:0.5
Pressure: 55 bar

UNN-2 mechanism
- Creck Reduced mechanism [5]
- Chalmers Reduced mechanism [17]

CFD analysis

CFD analysis (cont.)

Pure hydrogen combustion

Ignition delay time

- The developed mechanism and GRI Mech. 3.0 [14] deviate especially during high temperatures and high eq.ratios.
- The deviation probably depends on the rate constants of specific hydrogen based reactions that were found to increase the reactivity of the mixture (especially rich mixtures) and control the formation of OH reactive radicals at high temperatures and pressure conditions.
- Further study is required for the investigation of the specific reactions that are responsible for that deviation and the optimization of their rate constants.

Final results - Scalars

**Fuel 24 Type 3**  Eq. Ratio: 0.8  $\Theta_{\text{inj}} = 8^\circ$ BTDC

<table>
<thead>
<tr>
<th>Time (deg ATDC)</th>
<th>8° BTDC</th>
<th>2° BTDC</th>
<th>1° ATDC</th>
<th>8° ATDC</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (K)</td>
<td>2200.</td>
<td>2100.</td>
<td>2000.</td>
<td>1900.</td>
</tr>
<tr>
<td></td>
<td>1800.</td>
<td>1700.</td>
<td>1600.</td>
<td>1500.</td>
</tr>
<tr>
<td></td>
<td>1400.</td>
<td>1300.</td>
<td>1200.</td>
<td>1100.</td>
</tr>
<tr>
<td></td>
<td>1000.</td>
<td>900.0</td>
<td>800.0</td>
<td></td>
</tr>
</tbody>
</table>

**Fuel 24 Type 6**  (Eq. Ratio: 0.6  $\Theta_{\text{inj}} = 17.5^\circ$ BTDC)

<table>
<thead>
<tr>
<th>Time (deg ATDC)</th>
<th>17.5° BTDC</th>
<th>10° BTDC</th>
<th>1° ATDC</th>
<th>9° ATDC</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (K)</td>
<td>2200.</td>
<td>2100.</td>
<td>2000.</td>
<td>1900.</td>
</tr>
<tr>
<td></td>
<td>1800.</td>
<td>1700.</td>
<td>1600.</td>
<td>1500.</td>
</tr>
<tr>
<td></td>
<td>1400.</td>
<td>1300.</td>
<td>1200.</td>
<td>1100.</td>
</tr>
<tr>
<td></td>
<td>1000.</td>
<td>900.0</td>
<td>800.0</td>
<td></td>
</tr>
</tbody>
</table>
Final results (Temperature)

**Fuel 24 Type 3**
- Eq. Ratio : 0.8
- $\theta_{\text{inj}}$ : 8° BTDC
- N-heptane : 2mg/ cycle

**Fuel 24 Type 6**
- Eq. Ratio : 0.6
- $\theta_{\text{inj}}$ : 17.5° BTDC
- N-heptane : 4 mg/cycle
### Conclusions

The developed mechanism contains the lowest number of reactions and species.

- It includes not only multicomponent syngas reactions but also n-heptane chemistry and NOx sub mechanism.

- It can be implemented in multidimensional CFD simulations with low level of complexity.

<table>
<thead>
<tr>
<th>Chemical Kinetics Mechanisms</th>
<th>Reactions</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-heptane/syngas/NOx Mechanism</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 Reduced syngas/NOx/n-heptane mechanism</td>
<td>276</td>
<td>75</td>
</tr>
<tr>
<td>2 Creck Reduced mechanism</td>
<td>1790</td>
<td>106</td>
</tr>
<tr>
<td>3 LLNL detailed mechanism</td>
<td>2827</td>
<td>654</td>
</tr>
<tr>
<td>4 Lu et al. Skeletal</td>
<td>842</td>
<td>188</td>
</tr>
</tbody>
</table>
Thank you for your attention.

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