Reduced Chemical Reaction Mechanisms: Experimental and HCCI Modelling Investigations of Autoignition Processes of n-Heptane in Internal Combustion Engines

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ABSTRACT
A skeletal (27 species and 21 reactions) chemical reaction mechanism for n-heptane is constructed from a semi-detailed n-heptane mechanism (57 species and 290 reactions) of the Chalmers University of Technology in Sweden. The construction of the reduced mechanisms is performed by using reduction methods such as the quasi-steady-state assumption and the partial equilibrium assumption. The inlet temperature and the equivalence ratio are varied and ignition delays are calculated from pressure curves, using the reduced n-heptane mechanism for several engine parameters adhering to HCCI conditions: inlet temperature (303 ~ 365 K) and equivalence ratio (0.2 ~ 0.4). Subsequently the reduced mechanism is successfully numerically validated against the Chalmers mechanism and another more detailed mechanism provided LLNL (Curran et al. with 561 species and 2539 reactions). Furthermore the results obtained from the reduced n-heptane mechanism are experimentally validated by experiments performed on a CFR engine, using the same parameters.

INTRODUCTION
In view of the environmental effects, strategy of the automobile industry implies developing new engines functioning with a low equivalence ratio, lower fuel consumption and consequently reducing CO2, NOx and particle emissions. Respecting the Euro IV emission norms in 2005 (Table 1), possibilities as the catalytic oxidation, the NOx traps and the particulate traps can be used, in other words: post-treatment. Concerning the emission reduction during the combustion process, HCCI Homogeneous Charged Compression Ignition) appears to be a good solution to respect the future Euro norms (Table 1).

<table>
<thead>
<tr>
<th>Norm</th>
<th>HC [g/km]</th>
<th>CO [g/km]</th>
<th>NOx [g/km]</th>
<th>Particles [g/km]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Euro II 1992</td>
<td>2.20</td>
<td>1.00</td>
<td>-</td>
<td>0.10</td>
</tr>
<tr>
<td>Euro III 2000</td>
<td>0.20</td>
<td>2.30</td>
<td>0.64</td>
<td>0.15</td>
</tr>
<tr>
<td>Euro IV 2005</td>
<td>0.10</td>
<td>1.90</td>
<td>0.50</td>
<td>0.08</td>
</tr>
<tr>
<td>Euro V 2008 or 2010</td>
<td>in Establishment</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Using a lean burn combustion process at lower temperatures and a premixed air-fuel mixture, the HCCI combustion allows for a higher thermal efficiency, less NOx emissions and less particulate-matter emissions [1]. Whereas diesel combustion is mainly controlled by turbulence during flame diffusion and gasoline combustion with a flame front propagation, the auto-ignition phenomenon in an HCCI engine is mainly controlled by chemical kinetics and its combustion progression is much more complicated. Much research [2,3,4,5,6,7] is performed in investigating this auto-ignition for many compounds. A great part of the HCCI investigations use the so-called Primary Reference Fuels such as iso-octane and n-heptane [8]. This due to the great interest in improving the engine efficiency and reducing their pollution. Hydrocarbon ignition can occur...
in two significantly different stages [2,3,4,9,10], which depends on the initial temperature (for example during n-heptane and n-decane combustion at low temperatures [2,11]).

HCCI CHEMISTRY
The first stage is initiated by a serie of reactions at the lower temperature zone (T < 700 K), of which the most important reactions are considered to be the formation of the heptyl radicals. The first reaction is the initiation reaction, in which n-heptane reacts with oxygen. After the H-abstraction step, the heptyl radical can subsequently react with molecular oxygen to form an alkyperoxy radical.

More intermediate peroxy species are formed. During this first stage, temperature and pressure increase slightly, causing the cool flame to occur. Then, the temperature continues to increase until reaching an intermediate temperature zone (700 – 1000 K) where small radicals such as HO$_2$ are formed. The HO$_2$ radicals react further with the fuel to form H$_2$O$_2$. Then OH, formed by the decomposition of H$_2$O$_2$, leads to the second stage combustion [12]. In this step, the OH radicals (far more important than other radicals formed from chain branching) consume the fuel (the cool flame ends), resulting in a sudden temperature rise and pressure increase (the second stage begins). Depending on the type of fuel and the thermodynamics evolution (of an engine, a RCM or stirred reactors), in some cases at a given pressure and for some low initial temperature (lower than ~750 K), the oxidation process slows down whereas the temperature increases. This is the main characteristic of the Negative Temperature Coefficient (NTC) regime. In this zone, the formation of HO$_2$ radicals becomes more important than the isomerisation reactions and the peroxy formations. HO$_2$ radicals are more stable than OH. Moreover, the propagation reaction with HO$_2$ is less exothermic than that with the OH radical [13]. Then, when the temperature is high enough for the OH reaction to become more important, the reaction rate increases with the temperature. After this region, at higher inlet temperatures (T > 900 K), the ignition takes place in a single stage. In this paper the cool flame delay defined as the number of crank angle degrees, from the start of the compression (BDC), to the moment where the net heat release reaches it’s first maximum. The second delay, is defined as the number of crank angle degrees, from the start of the compression, to the moment where the net heat release reaches it’s second maximum.

As is mentioned previously, the HCCI chemistry is mainly controlled by the chemical kinetics at lower temperatures that precede the auto-ignition. Indeed, the HCCI combustion process could be applied widely in engine applications if precise prediction of ignition timing for variable experimental conditions is involved. So it is of great importance to understand the underlying mechanisms that are responsible for the ignition delay. The first reactions that govern the combustion initiation, are the following:

C$_7$H$_{16}$ + O$_2$ → C$_7$H$_{15}$• + HO$_2$•
C$_7$H$_{16}$ + X• → C$_7$H$_{15}$• + XH

The X• in the second reaction is a radical. After the formation of heptyl radicals (C$_7$H$_{15}$•), these react further forming several peroxide radicals (C$_7$H$_{15}$OO•) starting with the reaction:

C$_7$H$_{15}$• + O$_2$ → C$_7$H$_{15}$OO•

and eventually the hydroxyl radical OH• [14], via a sequence of reactions. These peroxide radicals and the hydroxyl radical play an important role in the oxidation process [12,14], since the reactions concerning the formation of the peroxy radicals and the hydroxyl radical release the energy that are the cause of the temperature and pressure rises (in addition of the compression stroke). Finally the hydroxyl radical consumes rapidly n-heptane, resulting into a rapid increase in the temperature and eventually the auto-ignition [2].

H$_2$O$_2$ + M → OH• + OH• + M
C$_7$H$_{16}$ + OH• → C$_7$H$_{15}$• + H$_2$O

Here M denotes a third body, which could be any substance present in the cylinder. At higher temperatures (T > 1000 K), however, the reaction where n-heptane decomposes into two smaller radicals promotes the combustion process. This decomposition into smaller radicals and olefins govern the main combustion process which becomes a one-stage combustion [14,15].

EFFECTS OF THE PARAMETERS ON THE IGNITION DELAY
When implying HCCI combustion, the major problem that appears, is the control of the ignition delay. Several physical parameters affect the quality of the HCCI combustion and the ignition delay: mixture homogeneity, inlet temperature of air and fuel, fuel composition, kinetics of the fuel oxidation at lower temperatures and thermal effects (heat exchange, thermal loss to the wall, EGR ratio mixture quality) [2,11,14,16,17]. A better
understanding of the influence of these parameters on the ignition time is required, to have a more thorough knowledge of the HCCI combustion process and consequently of the application on an engine.
The main parameters, studied the most in the literature \([2,11,14,16,17,18]\), are the inlet temperature and the equivalence ratio. In order to determine the influence on ignition delay, Ogink and Golovitchev \([16]\) have performed modeling calculations on varying the inlet temperature \((600 \text{ K to } 1400 \text{ K})\) and pressure \((10 \text{ atm to } 40 \text{ atm})\). For iso-octane they have determined that a higher initial pressure and inlet temperature result into a lower ignition delay. Soyhan and Mauss \([17]\) have determined the influence of the inlet temperature on the ignition delay, but only at inlet temperatures higher than \(700 \text{ K}\). With respect to the influence of the inlet temperature on the ignition delay they have come to the same conclusion as Ogink and Golovitchev \([16]\). Gauthier et al. \([18]\) performed stoichiometric n-heptane/air measurements a low-pressure shock tube near \(2\) and \(11 \text{ atm}\) at temperatures above \(1200 \text{ K}\). To compare their data to the results of Fieweger et al. \([19]\) they normalized their data to \(13 \text{ bar}\), using a pressure scaling of \(P^{-0.66}\) based on the correlation of Horning et al. \([20]\). Gauthier found also like Fieweger that the ignition delay decreased at increasing temperature, as well as a pronounced NTC region around \(700\) to \(900 \text{ K}\). Depending on the experimental apparatus to measure the ignition delay (shock tube, RCM, reactors...), the application of these data to an engine is an extrapolation process which must be used with care. Most of the results are given in varying the temperature at a fixed pressure or varying the pressure at a fixed temperature, while in an engine both the temperature and pressure vary. The overall temperature evolution during the ignition process could be modified by a sort of a self combustion effect for instance if the dilution is not sufficient.
Specifically, to predict satisfactorily the auto-ignition delay in an engine, the pressure tendency or the rate of heat release, it is necessary to use a realistic modelling of the chemical process with a lower inlet temperature. Since a large number of intermediate species participate in a great number of elementary reactions during fuel oxidation, it is very difficult to add this entire mechanism in a Computational Fluid Dynamics (CFD) code. Therefore, it is necessary to reduce a detailed mechanism and to determine the validity of the reduced mechanism, prior to its utilization for predicting the aerodynamic effects in an engine cylinder using CFD codes.
This paper’s main interest involves producing a reduced mechanism that predicts accurately the ignition delay and pressure curves for several equivalence ratios \((0.2 \sim 0.4)\) and air inlet temperatures \((303 \sim 365 \text{ K})\). Specific engine parameters (cylinder capacity \(611 \text{ cm}^3\), initial pressure \(1 \text{ atm}\) and engine speed \(600 \text{ rpm}\)) are used. In addition to previous experiments \([16,17]\), very low temperatures are studied, since the goal of HCCI engines is to operate at lower temperatures.

In this paper, a description of the method used to reduce the n-heptane detailed chemical mechanism is presented and a validation of this mechanism on a CFR engine is also presented. The effects of the equivalence ratio and the inlet temperature on the ignition delay are presented as well.

**REDUCTION OF THE N-HEPTANE MECHANISM**

This section describes the reduction methodology of the n-heptane mechanism \([21]\), developed and provided by the Chalmers University of Technology in Sweden, containing 290 reactions and 57 species. This mechanism has previously been validated successfully at the Chalmers University of Technology in a reactor between \(10\) and \(40\) bar \([21]\). Reduction is performed using Aurora, provided in Chemkin. The reduction of the Chalmers mechanism is obtained by eliminating reactions in a manner to keep the same predictability as the initial Chalmers mechanism (the obtained model must be very accurate and only \(5\) % fluctuations on the ignition delays is allowed). The reduction is performed using a method developed by Peters in 1987 \([21,23,24]\), which comprises several steps \([13,24]\). Firstly, using the analysis of the conversion rate of the reactant species, the redundant species were removed \([22]\) from the Chalmers mechanisms. Secondly, by introducing the quasi-steady-state assumption \([23]\) and, thirdly, the partial equilibrium assumption \([22]\), obtaining 21 reactions and 27 species for the n-heptane mechanism (shown in the appendix). The quasi-steady-state assumption is a classical hypothesis in the domain of combustion chemistry. It consists of assuming an equilibrium between the production and consumption of certain intermediary species that are very reactive \([22,24]\) (on calculating the rate constants), with a short lifetime \([25]\) and in small quantities (due to the high reactivity). For example, a certain species’ concentration is very low \([24]\) and constant due to the fact that it is produced very slowly and
consumed very rapidly. Here this species can be eliminated and the two concerning reactions can be merged into one, hereby eliminating one [22]. The partial equilibrium assumption is also a classical hypothesis whereby an equilibrium is assumed between the reaction rates in the direct and the inverse direction of certain reversible reactions that are very rapid [22,24]. This approach (or even just the quasi-steady-state assumption alone) proved to be successful for the construction of reduced chemical kinetic schemes [22,23,24,25] for the combustion of several hydrocarbons [14,26].

RESULTS AND DISCUSSION
NUMERICAL VALIDATION OF THE REDUCED N-HEPTANE MECHANISM
For the calculations a HCCI internal combustion engine model in Chemkin is used, having the same engine characteristics as presented in the section experimental set-up later on. To check the validity of the reduced mechanism, it was not only compared to the Chalmers n-heptane mechanism, but also to the more detailed mechanism provided by LLNL [27] by Curran et al. in USA (2539 reactions and 561 species). Figure 1 shows the cool flame and the final ignition delay values of n-heptane, calculated using the reduced n-heptane mechanism (n-hept21) and compared with the ones calculated by the detailed Chalmers and Curran n-heptane mechanisms.

Figures 2 and 3 show that the pressure curves of the reduced mechanism of n-heptane correspond well with those of the detailed mechanisms of Chalmers and Curran. The two numerical validations (ignition delay and pressure curves) are two classical criteria. One could complete this approach by introducing a comparison involving the heat release or the pollutants’ emissions. The next paragraph expands the validation procedure by means of experiments performed on a CFR engine.

EXPERIMENTAL VALIDATION BY A CFR ENGINE

Experimental set-up

Figure 1: Comparison different mechanisms with respect to the cool flame and final ignition delays of n-heptane combustion at a compression ratio of 10.2 and an equivalence ratio of 0.39, with at each delay the ignition temperature.

Figure 2: Comparison different mechanisms with respect to the pressure curves, with a compression ratio of 12, an equivalence ratio of 0.2 and an inlet temperature of 365 K for n-heptane.

Figure 3: Comparison different mechanisms with respect to the pressure curves, with a compression ratio of 18, an equivalence ratio of 0.3 and an inlet temperature of 350 K for n-heptane.
Figure 4: Schematic of the experimental set-up of the CFR engine

Figure 4 shows the experimental set-up of the CFR engine on which the experiments have been performed. In this paper, two parameters are mainly studied, the effects of the equivalence ratio and the inlet temperature. Table 2 shows characteristics of this CFR engine.

Table 2: CFR engine description

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compression ratio</td>
<td>4 ~16</td>
</tr>
<tr>
<td>Bore</td>
<td>82.55 mm</td>
</tr>
<tr>
<td>Stroke</td>
<td>114.5 mm</td>
</tr>
<tr>
<td>Displacement volume</td>
<td>611 cm³</td>
</tr>
<tr>
<td>Engine connecting rod to crank radius ratio</td>
<td>3.26</td>
</tr>
<tr>
<td>Exhaust valve open</td>
<td>140 °ATDC</td>
</tr>
<tr>
<td>Exhaust valve close</td>
<td>15 °ATDC</td>
</tr>
<tr>
<td>Intake valve open</td>
<td>10 °ATDC</td>
</tr>
<tr>
<td>Intake valve close</td>
<td>146 °BTDC</td>
</tr>
</tbody>
</table>

The compression ratio was always set at 10.2 for the experiments in this study.

Comparison experimental results with modelling results

This section shows the experimental validation of the reduced n-heptane mechanism by means of the experiments performed on the CFR engine. The effects of residual gasses in the CFR engine were compensated in the calculations by adding a mixture of N2, CO2 and O2 at a temperature of 1000 K consisting of a mass fraction of 6% of the initial fuel/air mixture.

Figure 5: In-cylinder pressure and the comparison of experimental and modeling heat release. Experimental conditions: equivalence ratio 0.4 – inlet temperature 45 and 70 °C
Figure 6: Comparison of the calculations and the experimental results regarding the cool flame delays, the final ignition delays: Inlet temperature (a) 45 °C (b) 70°C

Figure 5 and 6 show the experimental validation of the n-heptane mechanism. The compression ratio is held at 10.2, while the inlet temperature for these results is chosen to be 45 or 70 °C, as is indicated in each of the figures. The fuel used is n-heptane. The pressure and the heat release curves presented are obtained with an equivalence ratio held at 0.4.

The pressure and the heat release curves show a good comparison between the n-heptane reduced model and the experiments on the CFR engine. The heat release shows a small discrepancy between the modeling and the experimental results, because of the following reasons: the reduction method was focused on the ignition delay and the cool flame phase, the wall heat transfer modelling is not yet well fitted in Chemkin and Chemkin simulates the cycle only in one homogeneous zone and does not take into account the real physical processes.

In Figure 6, the cool flame delays and the final ignition delays, calculated by the reduced n-heptane mechanism seem to correspond very well with the experimental results, especially at higher equivalence ratios. At lower equivalence ratios, the combustion is probably not optimal, a fact of which the mechanism does not take account. As a matter of fact, again the mechanism considers an ideal homogeneous mixture in the cylinder, which is not the case in the experiments.

In this section the reduced n-heptane mechanism is both numerically and experimentally validated and could be used for other purposes as the usage in a CFD code to examine the aerodynamics influence on the combustion process. The next section summarizes the trends that were observed from the experimental results obtained from the CFR engine.

EFFECTS OF THE PHYSICAL PARAMETERS ON THE IGNITION DELAYS

Figure 7 shows the cool flame delays and the final ignition delays obtained using n-heptane as the fuel. The compression ratio is held at 10.2, while the influence of the equivalence ratio and the inlet temperature on the ignition delays is examined. The equivalence ratio plays a role in the amount of fuel present for the formation of the peroxides, but as the formation of the peroxides does not need much fuel, the equivalence ratio does not influence much the cool flame delay. Nevertheless an increase in the equivalence ratio results into a decrease in the cool flame delay, because there is simply more fuel and thus more energy which cause the kinetics of the formation of the peroxides to accelerate, even slightly. As for the inlet temperature, it is clear that a higher inlet temperature accelerates the kinetics and thus decreases the cool flame delay, in the same way as it decreases the final ignition delay. The final ignition delay decreases when the equivalence ratio is increased, since this, as is the case for the cool flame delay – only much stronger –, provides more energy and enhances the chemical kinetics.
As figure 8 shows the maximum pressure and heat release are hardly influenced by the inlet temperature but rather by the equivalence ratio as figure 9 shows. This implies that the energy and power or work delivered to the piston is mainly delivered by the fuel, while the inlet temperature does not seem to play a major role for that matter. It appears from figure 8 that with the inlet temperature the auto-ignition timing could be predicted. The difference between the cool flame and the final ignition stays practically the same. So the inlet temperature can be used as a tool for choosing the start of the ignition, from the cool flame on. Figures 8 and 9 show also that there is a slow combustion right after the two ignitions, depicted by the long curve after the final ignition. The equivalence ratio seems to alter the final ignition delay much more than the cool flame delay. So the energy content and duration between the cool flame and the final ignition is largely influenced by the equivalence ratio and the equivalence ratio could be used as a tool for choosing the timing between the start of the ignition, the cool flame, and the final ignition.
CONCLUSION

The skeletal (27 species, 29 reactions) reduced chemical reaction mechanisms for n-heptane is constructed successfully from a detailed n-heptane mechanism (57 species and 290 reactions).

For HCCI conditions (equivalence ratio of 0.2 ~ 0.4 and inlet temperatures of 303 ~ 365 K) the calculated cool flame delays and final ignition delays by the reduced n-heptane mechanism as well as the pressure curves and the heat release curves are in good agreement with those obtained with the detailed Chalmers n-heptane mechanism and the detailed Curran n-heptane mechanism. Concerning the comparison of the reduced n-heptane mechanism with the CFR experimental results, the mechanism is successfully validated, though at equivalence ratios lower than ~ 0.25 a small difference is observed between the calculations and the experiments. This is probably due to a bad combustion, of which the mechanism does not take account. Nevertheless, generally, in the aforementioned conditions, the mechanism’s calculations correspond very well with the experimental results with regard to the ignition delays, the pressure curves and the heat release curves. The reduced n-heptane mechanism is considered both numerically and experimentally validated for HCCI purposes and can be perfectly used for future aerodynamics applications in CFD codes.

Concerning the ignition delay it is shown that it decreased with
- an increasing temperature,
- an increasing equivalence ratio.

However, fuel composition can also play an important role in the ignition and its effects will be studied for several mixtures of n-heptane and iso-octane. In a previous work a reduced mechanism of iso-octane has been validated numerically and experimentally. The possibility of a composition of these two reduced mechanisms will be investigated for a construction of a n-heptane/iso-octane mixture mechanism. A brief study of emissions emitted by the engine will be investigated as well.

REFERENCES

7 P. Guibert, S. Mokhtari, C. Morin, Experimental analysis of auto-ignition generated combustion AIGC, MTZ, Part II, 2004
9 H. Li, D.L. Miller, N.P. Cernansky 1996 Society of Automotive Engineers SAE-960498
### APPENDIX – REACTION SCHEME OF THE REDUCED N-HEPTANE MECHANISM

| Reaction number | Reaction | A \( \times 10^b \) | Ea \[ J/mole \] | RL | Limiting
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C7H16 + O2 =&gt; C7H15 + 2HO2</td>
<td>2.80E+14</td>
<td>0.00</td>
<td>197533</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>C7H16 + OH =&gt; C7H15 + H2O</td>
<td>4.80E+09</td>
<td>1.30</td>
<td>2891</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>C7H16 + HO2 =&gt; C7H15 + H2O2</td>
<td>1.00E+13</td>
<td>0.00</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>C7H15 + O2 = C7H15O2</td>
<td>2.00E+12</td>
<td>0.00</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>C7H15O2 = C7H14O2H</td>
<td>6.00E+11</td>
<td>0.00</td>
<td>85327</td>
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</tr>
<tr>
<td>6</td>
<td>C7H14O2H + O2 = C7H14O2HO2</td>
<td>2.34E+11</td>
<td>0.00</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>C7H14O2HO2 =&gt; C7KET21 + OH</td>
<td>2.97E+13</td>
<td>0.00</td>
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<tr>
<td>8</td>
<td>C7KET21 = C5H11 + CO + CH2O + OH</td>
<td>1.00E+16</td>
<td>0.00</td>
<td>177520</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>C5H11 =&gt; C2H5 + C3H6</td>
<td>3.20E+13</td>
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<tr>
<td>10</td>
<td>C3H6 + OH =&gt; CH3CHO + CH3</td>
<td>3.50E+11</td>
<td>0.00</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>CH3CHO + OH + M = CH3 + CO + M + H2O</td>
<td>1.80E+17</td>
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<tr>
<td>12</td>
<td>CH3O + M = CH2O + H (+M)</td>
<td>2.00E+13</td>
<td>0.00</td>
<td>114802</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>CH3 + HO2 =&gt; CH3O + OH</td>
<td>4.30E+13</td>
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<td>0</td>
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<tr>
<td>14</td>
<td>CO + OH =&gt; CO2 + H</td>
<td>3.51E+07</td>
<td>1.30</td>
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<tr>
<td>15</td>
<td>O + OH =&gt; O2 + H</td>
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<td>0</td>
<td></td>
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<tr>
<td>16</td>
<td>H + O2 + N2 =&gt; HO2 + N2</td>
<td>2.60E+19</td>
<td>41.24</td>
<td>0</td>
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<tr>
<td>17</td>
<td>HO2 + HO2 =&gt; H2O2 + O2</td>
<td>2.00E+12</td>
<td>0.00</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>OH + OH (+M) = H2O2 (+M)</td>
<td>7.60E+13</td>
<td>40.37</td>
<td>0</td>
<td></td>
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<tr>
<td>19</td>
<td>CH2O + OH + O2 =&gt; H2O + HO2 + CO</td>
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<td>1.18</td>
<td>41871</td>
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<tr>
<td>20</td>
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<td>0.00</td>
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<td>2.00E+10</td>
<td>0.00</td>
<td>49211</td>
<td></td>
</tr>
</tbody>
</table>

The table contains the rate coefficients for each reaction, along with their activation energies and low-pressure limits. The mechanism is expressed as a product of reactant coefficients, with enhancement factors for various species. The table also includes the reaction numbers and the corresponding rate expressions.

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### APPENDIX – REACTION SCHEME OF THE REDUCED N-HEPTANE MECHANISM


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