ROLE OF CHEMICAL KINETICS ON THE DETONATION PROPERTIES OF HYDROGEN / NATURAL GAS / AIR MIXTURES

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ABSTRACT
The first part of the present work is to validate a detailed kinetic mechanism for the oxidation of hydrogen – methane – air mixtures in a detonation waves. A series of experiments on auto-ignition delay times have been performed by shock tube technique coupled with emission spectrometry for H2 / CH4 / O2 mixtures highly diluted in argon. The CH4/H2 ratio was varied from 0 to 4 and the equivalence ratio from 0.4 up to 1. The temperature range was from 1250 K to 2000 K and the pressure behind reflected shock waves was between 0.15 and 1.6 MPa. A correlation was proposed between temperature (K), concentration of chemical species (mol m⁻³) and ignition delay times. The experimental auto-ignition delay times were compared to the modelled ones using four different mechanisms from the literature: GRI [22], Marinov et al. [23], Hughes et al. [24], Konnov [25]. A large discrepancy was generally found between the different models. The Konnov’s model that predicted auto-ignition delay times close to the measured ones has been selected to calculate the ignition delay time in the detonation waves. The second part of the study concerned the experimental determination of the detonation properties, namely the detonation velocity and the cell size. The effect of the initial composition, hydrogen to methane ratio and the amount of oxygen in the mixture, as well as the initial pressure on the detonation velocity and on the cell size were investigated. A correlation was established between the characteristic cell size and the ignition delay time behind the leading shock of the detonation. It was clearly showed that methane has an important inhibitor effect on the detonation of these combustible mixtures.

1.0 INTRODUCTION
One of the main problems that faces industrial countries is the reduction of atmospheric pollutant emissions. Since almost 85% of the total energy consumption of the word is obtained by using fossil fuels (coal, petroleum, natural gas), one has to take into account the green house effect of the main combustion products such as CO, CO₂, NOx and soot particles. These pollutants can be reduced by using biofuels or hydrogen enriched fuels synthesized from non pollutant sources. Natural gas, compared to other current fuels, is responsible for relatively low emission in terms of CO₂, PAH’s and soot particles and from the economical point of view represents a good candidate for internal combustion engines due to its high octane number which makes it eligible for spark ignition engines. One way to enhance natural gas reactivity is to add hydrogen which will decrease the auto-ignition delay times. It will also increase the flammability and stability ranges of the flame and the operating conditions can then be shifted towards leaner conditions [1-4]. This behavior of these mixtures could be of a great interest for new kinds of car engines (for example HCCI). However, in order to make hydrogen suitable many problems have to be solved: production and storage have to be secured, economically interesting and be adapted for multiple uses such as public transportation. The presence of hydrogen in combustible mixtures increases the risk of explosion and detonation, especially in confined environment, this risk has to be assessed.

Several studies can be found in the literature concerning the auto-ignition delay times of H2 / O2 based mixtures. The oldest one was performed by Schott et al. [5] who measured ignition delay times of H2/O2/Ar behind incident shock waves for temperatures between 1085 and 2700 K at a pressure of
101.3 kPa. Skinner and Ringrose [6] measurements of auto-ignition delay times were limited to a narrow range of temperature, between 965 and 1076 K and for only one reflected shock pressure of 506.5 kPa. At low reflected shock pressures, between 23.6 and 38.3 kPa, Asaba et al. [7] determined auto-ignition delay times at an equivalence ratio of 0.5 in reflected shock temperature range of 1500 – 2700 K. At high pressures, between 131.7 and 506.5 kPa, Fujimoto et al. [8] performed measurements at lower temperature, 700 – 1300 K, for a stoichiometric mixture. For very lean mixture (an equivalence ratio of 0.25), one can find only the work of Hasegawa et al. [9] which was done for reflected shock temperatures between 920 and 1650 K and for reflected shock pressures around 515.7 kPa. Hidaka et al. [10] study was performed in the following reflected shock conditions, temperature between 1250 and 1650 K and pressures between 160 and 280 KPa. For pressures around the atmospheric one and for equivalence ratios of 1 and 1.47, Petersen et al. [11] have determined auto-ignition delay times for temperature lying between 1010 and 1750 K. For less diluted mixtures, Cheng et al. [12] have measured auto-ignition delay times for reflected shock temperatures ranging from 1010 and 1430 K at a pressure close to 203 kPa. The only study concerning H₂/O₂/Ar auto-ignition delay times at high pressure, from 33 atm up to 87 atm, was done by Petersen et al. [13] for an equivalence ratio of 1 for the temperature range 1190 – 1880 K.

Only a limited number of studies concerned hydrogen / air mixtures, for reflected shock pressure around 2 atm, Bhaskaran et al. [14] and Slack [15] have conducted measurements for temperatures ranging between 980 and 1330 K. More recently, Wang et al. [16] have studied the effect of water vapor on the auto-ignition delay times of hydrogen / air mixtures at pressures ranging from 3.36 and 16.63 atm and for temperatures comprised between 950 and 1330 K.

As far as binary mixtures of methane and hydrogen are concerned, the only study available in the literature was performed by Cheng et al. [12] who established an expression of the auto-ignitions delay times of CH₄/H₂/O₂ as a function on the auto-ignition delay times expression for each mixture H₂/O₂ and CH₄/O₂ for temperatures varying between 800 and 2400 K, pressures between 1 and 3 atm and for an equivalence ratio between 0.5 and 1. These expressions are:

\[
\tau_{CH_4}(\mu s) = 1.19 \cdot 10^{-12} \cdot [CH_4]^{0.48} \cdot [O_2]^{-1.94} \cdot \exp\left(\frac{23316}{T(K)}\right),
\]

\[
\tau_{H_2}(\mu s) = 1.54 \cdot 10^{-4} \cdot [H_2]^{0.14} \cdot [O_2]^{-0.56} \cdot \exp\left(\frac{8643}{T(K)}\right)
\]

with [X] the species X concentration expressed in mol.cm⁻³.

The expression of the mixture containing methane and hydrogen is given by:

\[
\tau_{CH_4+H_2}(\mu s) = \tau_{CH_4}^{(1-e)} \cdot \tau_{H_2}^{e},
\]

with \(e = \frac{X_{H_2}}{X_{CH_4} + X_{H_2}}, \) \(X_{H_2}\) et \(X_{CH_4}\) are the molar fraction of hydrogen and methane in the mixture.

### 2 EXPERIMENTAL SETUP AND METHODOLGY

#### 2.1 Experimental setup

For the auto-ignition study, the experiments were performed in 2 different shock tubes. A pyrex tube (50 mm i.d.) with a low pressure section of 9 m long and a metallic high pressure section of 2 m long. The second shock tube is a stainless steel shock tube of 7.15 m. The high pressure section (128.2 mm i.d.) is 0.9 m long while the low pressure section is 4 m long (78 mm i.d.). The pyrex tube and the
stainless steel tube were used for the low pressure and high pressure studies respectively. The last section of each tube is equipped with 4 pressure transducers (equally spaced by 150 mm) mounted flush with the inner surface of the tube, the last one being 15 mm before the shock tube end wall. At the same plane as the last pressure transducer, a fused silica window (9 mm optical diameter and 6 mm thickness) is mounted across a UV-sensitive photomultiplier equipped with a narrow-band filter centered on 306 nm which is characteristic of OH emission. The shock wave velocity is deduced from the pressure jump monitored by the pressure transducers. By using the classical procedure, the temperature and pressure behind the incident and reflected shock waves are deduced [17]. Each shock tube and associated tubing is connected with 2 primary vacuum pump, which allows the whole experimental setups to be vacuumed below 1 Pa before every run. The high pressure gas used is He (purity > 99.995 %) distributed by AIR LIQUIDE.

For the detonation work a third shock tube was used (stainless-steel, 78 mm i.d.) which has a 1 m long driver section filled with helium, and a test section, about 4.50 m long, in which the reactive mixtures are introduced initially at ambient temperature and at the total pressure of 10 and 20 kPa. The last section of the driven section, to get the maximum possible pre-detonation length possible L_{DDT}, here at about 3.20 m, is equipped with 4 piezoelectric pressure transducers, mounted flush with the inside wall, to measure either shock wave speed V, or detonation velocity D_{exp}. A soot foil, put against the wall of the section which follows the transducers, is used to record the cellular structure width \lambda_{exp}.

The hydrocarbons used were hydrogen (purity > 99.995), oxygen (purity > 99.95), methane (purity > 99.995). The hydrocarbon / Oxygen / Argon mixtures were prepared in a mixing tank using the partial pressure method. The experimental conditions, obtained behind reflected shock waves, are summarized in table 1.

<table>
<thead>
<tr>
<th>Mixtures</th>
<th>CH₄ ( % \text{mol} )</th>
<th>H₂ ( % \text{mol} )</th>
<th>O₂ ( % \text{mol} )</th>
<th>Ar ( % \text{mol} )</th>
<th>( \Phi )</th>
<th>( P_2 ) (kPa)</th>
<th>( T_5 ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0.000</td>
<td>0.444</td>
<td>0.556</td>
<td>99</td>
<td>0.4</td>
<td>209 - 233</td>
<td>1160 - 1520</td>
</tr>
<tr>
<td>S2</td>
<td>0.000</td>
<td>0.600</td>
<td>0.400</td>
<td>99</td>
<td>0.75</td>
<td>197 - 230</td>
<td>1180 - 1360</td>
</tr>
<tr>
<td>S3</td>
<td>0.000</td>
<td>0.666</td>
<td>0.333</td>
<td>99.001</td>
<td>1</td>
<td>174 - 240</td>
<td>1180 - 1345</td>
</tr>
<tr>
<td>S4</td>
<td>0.107</td>
<td>0.160</td>
<td>0.733</td>
<td>99</td>
<td>0.4</td>
<td>162 - 220</td>
<td>1087 - 1660</td>
</tr>
<tr>
<td>S5</td>
<td>0.156</td>
<td>0.123</td>
<td>0.611</td>
<td>99</td>
<td>0.75</td>
<td>146 - 214</td>
<td>1270 - 2015</td>
</tr>
<tr>
<td>S6</td>
<td>0.1905</td>
<td>0.072857</td>
<td>0.5238</td>
<td>99</td>
<td>1</td>
<td>171 - 200</td>
<td>1370 - 1897</td>
</tr>
<tr>
<td>S7</td>
<td>0.1524</td>
<td>0.0381</td>
<td>0.8095</td>
<td>99</td>
<td>0.4</td>
<td>157 - 211</td>
<td>1354 - 1717</td>
</tr>
<tr>
<td>S8</td>
<td>0.296</td>
<td>0.074</td>
<td>0.63</td>
<td>99</td>
<td>1</td>
<td>164 - 221</td>
<td>1394 - 1930</td>
</tr>
</tbody>
</table>

2.2 Methodology

The ignition delay time is defined as the time between the passage of the reflected shock wave, indicated by pressure jump, monitored by pressure transducer, and 50 % of OH emission signal at 306 nm (Fig. 1). In case of less diluted mixtures, the OH emission corresponds to the run-away of the explosive reaction detected by a small pressure signal increase. The error on the temperature is estimated to be less than 1 % while the one on the pressure is 1.3 %. Concerning the error on the auto-ignition delay time, the estimated error depends on the temperature range and is the highest on the high temperature side; it varies between 2 to 14 %.
Figure 1. Signal examples recorded during the oxidation of a binary mixture of methane and hydrogen behind reflected shock waves. $P_5$ and $T_5$ are respectively the pressure and the temperature behind the reflected shock wave and $\Phi$ the equivalence ratio.

2.3 Modeling

The main objective of the present work is to determine the auto-ignition delay time behind a plane shock wave propagating in a combustible gaseous mixture. To do so, calculations have been performed using different codes of the CHEMKIN library [18], first the detonation properties such as Chapman-Jouguet pressure, temperature and detonation velocity are evaluated using EQUIL code [19], the second step concerns the determination of ZND temperature and pressure using the detonation velocity and the initial conditions as inputs to the SHOCK code [20]. Finally, SENKIN [21] code is used for the evaluation of auto-ignition delay times.

Since the aim of the present work is to choose a detailed chemical mechanism for the determination of auto-ignition delay times behind the leading shock, several mechanisms from the literature are used in order to compare the auto-ignitions delay times derived from the modelling to the measured ones. The four following mechanisms were considered:

- GRI [22], which stands for Gaz Research Institute [22] which considers 53 species and 325 reactions,
- LLNL [23], the Lawrence Livermore National Laboratory mechanism [23] in which 155 species and 689 reactions are involved
- LEEDS [24], developed by Hughes et al. [24], which has 37 species and 175 reactions.
- Konnov [25], developed by Konnov [25] which takes into account 127 species and 1027 reactions.

3 MODELING RESULTS

3.1 Chapman-Jouguet Parameters evaluation

All the evaluations have been performed at an initial temperature of 298 kPa and for 2 different initial pressures, 10 and 100 kPa. As one can see on Fig. 2, for an equivalence ratio of 0.75 an increase of the initial pressure from 10 to 100 kPa induces an increase in the 3 detonation characteristics, namely $P_{CJ}$, $T_{CJ}$ and $V_{CJ}$ which assesses that the sensitivity of the considered mixtures increases with the initial pressure. From this figure one can see also that increasing the methane over hydrogen ratio in the mixture induces a drop in the temperature $T_{CJ}$ as well as for the detonation velocity $V_{CJ}$. 
Figure 2. Evolution of the CJ-parameters versus the methane content in the mixture for 2 different initial pressure, 10 and 100 kPa and an equivalence ratio of 0.75. The mixture was initially at 298 K.

The predicted $T_{CJ}$ and $V_{CJ}$ are lower in the case of the GRI species than in the case of LEEDS species and this is due to the fact that the 2 mechanisms don’t take into account the same species and this induces different values.

Adding methane to the mixture has an inhibitor effect on the sensitivity of the mixture to detonation for all the investigated equivalence ratios (Fig. 3). An increase of the equivalence ratio is responsible also of higher values for $T_{CJ}$, $V_{CJ}$ and $P_{CJ}$ and then promotes the detonation.

Figure 3. Evolution of the CJ-parameters versus the methane content in the mixture for 2 different initial pressure, 10 and 100 kPa and 3 different equivalence ratios, 0.4, 0.75 and 1. The mixture was initially at 298 K.

3.2 ZND Parameters evaluation

After the calculation of the CJ parameters have been performed, the ZND parameters can be deduced. As one can see in Fig. 4, $P_{ZND}$ and $T_{ZND}$ increase considerably as the initial pressure is raised from 10 to 100 kPa. The fact that the GRI and LEEDS mechanisms do not consider the same species has a big impact on the ZND parameters.

Adding methane to the combustible mixture is responsible for a decrease of $T_{ZND}$ for all the investigated conditions (Fig. 5). This is not the case for $P_{ZND}$ which remains almost constant in the case of the 0.4 equivalence ratio mixtures and increases only slightly for the 2 other equivalence ratios at an initial pressure of 100 kPa.

Regarding the effect of the oxygen on ZND parameters, from these results one can see that $T_{ZND}$ increases with the equivalence ratio for the 2 studied initial pressures, while $P_{ZND}$ is not affected by the oxygen content of the mixture at low pressure and increases with the equivalence ratio at 100 kPa.
Figure 4. Evolution of the ZND-parameters versus the methane content in the mixture for 2 different initial pressures, 10 and 100 kPa and an equivalence ratio of 0.75. The mixture was initially at 298 K.

Figure 5. Evolution of the ZND-parameters versus the methane content in the mixture for 2 different initial pressure, 10 and 100 kPa and 3 different equivalence ratios, 0.4, 0.75 and 1. The mixture was initially at 298 K.

3.3 Auto-ignition delay times evaluation for CH₄/H₂/O₂ mixtures

The auto-ignition delay times have been evaluated once the temperature and pressure behind the leading shock have been calculated. Since a short delay behind the leading shock is characteristic of an easy detonable mixture, one can see that decreasing the amount of methane in the mixture decreases drastically the auto-ignition delay time (Fig. 6) for all the investigated conditions in terms of pressure and equivalence ratio.

As one can see on Fig. 7, at an initial pressure of 10 kPa, the GRI mechanism and LEEDS mechanism predict the same auto-ignition delay times and the values given by LLNL are higher than the 2 others. The difference between LLNL and the 2 others increases when the mixture is leaner and when the methane content increases as well. The same results are obtained when the initial pressure is raised to 100 kPa (Fig. 8). A good agreement is found between GRI and LEEDS while LLNL is farther.
Figure 6. Evolution of the auto-ignition delay time versus the methane content in the mixture for 2 different initial pressure, 10 and 100 kPa and 3 different equivalence ratios, 0.4, 0.75 and 1. The mixture was initially at 298 K.

Figure 7. Evolution of the auto-ignition delay time versus the methane content in the mixture for an initial pressure of 10 kPa and 3 different equivalence ratios, 0.4, 0.75 and 1. Comparison between 3 models. The mixture was initially at 298 K.

Figure 8. Evolution of the auto-ignition delay time versus the methane content in the mixture for an initial pressure of 100 kPa and 3 different equivalence ratios, 0.4, 0.75 and 1. Comparison between 3 models. The mixture was initially at 298 K.

The 3 different detailed mechanisms predicts the minimum auto-ignition delay time for stoechiometric mixtures and for an initial pressure of 100 kPa.
4 EXPERIMENTAL RESULTS

4.1 Auto-ignition delay times measurements for CH₄/H₂/O₂ mixtures

Auto-ignition delay times have been measured for a wide range of temperature, equivalence ratio and methane to hydrogen ratio. The experimental conditions are reported in table 1. By plotting the auto-ignition delay time as a function of the temperature inverse (Fig. 9) one can see that it varies exponentially with the temperature. The longest delay are obtained for the leaner mixtures, oxygen promotes the oxidation of hydrogen based mixtures and this more pronounced when the mixture contains methane.

![Figure 9](image-url)

Figure 9. Evolution of the auto-ignition delay time versus the temperature inverse for different conditions of methane to hydrogen ratio and equivalence ratio

For a given equivalence ratio (Fig. 10), adding methane has a dramatic effect on the auto-ignition delay time which increases drastically reducing then the sensitivity of the mixture to detonation. When the pressure behind the reflected shock wave is raised up to around 1500 kPa, and when the mixture is constituted of {0.16 %H₂ + 0.107%CH₄ + 0.733% O₂ + 99% Ar} the auto-ignition delay times are strongly decreased (Fig. 11).

![Figure 10](image-url)

Figure 10. Evolution of the auto-ignition delay time versus the temperature inverse for different conditions of methane to hydrogen ratio and equivalence ratio
Figure 11. : Evolution of the auto-ignition delay times versus the temperature inverse for \{0.16 \%H_2 + 0.107\%CH_4 + 0.733\% O_2 + 99\% Ar\} mixture at an equivalence ratio of 0.4 and for 2 different pressure ranges.

A multiple regression correlation was applied on the experimental results in order to obtain a modified Arrhenius expression of the auto-ignition delay time, \( \tau_i \), as a function of the initial conditions of temperature, pressure and concentrations, equation (3) is valid for H_2 / O_2 / Ar mixtures while equation (4) is valid for CH_4 / H_2 / O_2 / Ar mixtures:

\[
\tau_{H_2} (\mu s) = 1.14 \times 10^{-2} \cdot [H_2]^{-0.405} \cdot [O_2]^{-0.649} \cdot \exp \left( \frac{9815}{T(K)} \right) \quad (3)
\]

\[
\tau_{CH_4+H_2} (\mu s) = 5.96 \cdot [CH_4]^{0.351} \cdot [H_2]^{0.124} \cdot [O_2]^{-1.103} \cdot \exp \left( \frac{12177}{T(K)} \right) \quad (4)
\]

where \( \tau_i \) is in second, the concentrations in mol/m^3, the temperature in K.

The average error between the experimental data and the correlated ones is equal to 14 %. As expected from the variation of the delay time versus the fuel or the oxygen concentrations, in the case of H_2 / O_2 / Ar mixtures negative exponents both over the fuel and the oxygen concentrations were derived, which expresses the promoter effect of the fuel and the oxygen over its own oxidation. In the case of CH_4 / H_2 / O_2 / Ar a positive exponent over the fuel concentration was derived, which expresses the inhibitor effect of the fuel over its own oxidation, while a negative one was derived for the oxygen concentration assessing the promoter effect of oxygen during the oxidation process.

4.2 Auto-ignition delay times modeling for CH_4/H_2/O_2 mixtures

As it was stated before, 4 different mechanisms were used in order to model the auto-ignition delay times for the different conditions that were studied experimentally. As one can see in Fig. 12, when the mixture contains only hydrogen an oxygen highly diluted by argon, all the simulated auto-ignition delay times are much higher than the measured ones at the exception of Konnov’s one which is the closest to the experiments.

When the methane to hydrogen ratio is set to 0.66, the agreement between simulations and measurements is improved (Fig. 13). Konnov’s mechanism remains the most reliable in the whole domain investigated in this study.
When increasing further the methane concentration in the mixture a better agreement is found between the simulations and the experiments for an equivalence ratio of 1, while for the very lean mixtures (equivalence ratio of 0.4) only Konnov’s mechanism gives correct values.

4.3 Detonation Study of CH₄/H₂/O₂ mixtures

Experiments were performed in order to determine the detonation properties of different mixtures of CH₄/H₂/O₂, the conditions are summarized in table 2.
Table 2. Experimental conditions for the detonation study.

<table>
<thead>
<tr>
<th>CH₄/CH₄+H₂</th>
<th>x_H₂</th>
<th>x_CH₄</th>
<th>x_O₂</th>
<th>X_N₂</th>
<th>Φ</th>
<th>P₁ (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.296</td>
<td>0</td>
<td>0.148</td>
<td>0.556</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>0</td>
<td>0.667</td>
<td>0</td>
<td>0.333</td>
<td>0</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>0</td>
<td>0.600</td>
<td>0</td>
<td>0.400</td>
<td>0</td>
<td>0.75</td>
<td>10</td>
</tr>
<tr>
<td>0.2</td>
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<td>0.0416</td>
<td>0.166</td>
<td>0.6257</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>0.2</td>
<td>0.444</td>
<td>0.1111</td>
<td>0.444</td>
<td>0</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>0.2</td>
<td>0.444</td>
<td>0.1111</td>
<td>0.444</td>
<td>0</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>0.4</td>
<td>0.285</td>
<td>0.1905</td>
<td>0.5238</td>
<td>0</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>0.4</td>
<td>0.243</td>
<td>0.1622</td>
<td>0.5946</td>
<td>0</td>
<td>0.75</td>
<td>10</td>
</tr>
<tr>
<td>0.6</td>
<td>0.166</td>
<td>0.25</td>
<td>0.5833</td>
<td>0</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>0.6</td>
<td>0.139</td>
<td>0.2093</td>
<td>0.6512</td>
<td>0</td>
<td>0.75</td>
<td>10</td>
</tr>
</tbody>
</table>

The detonation velocity was measured via several pressure transducers and the average velocity \( D_{\text{exp}} \) is given in Table 3. The cell size, \( \lambda \), was also measured using the soot foil technique. The variation of the average cell size is reported in Fig. 15. As one can see, adding methane to the mixture has an inhibiting effect over the detonation sensitivity and the same behaviour is observed whether the equivalence ratio is equal to 0.75 or 1. Moreover, as it is predicted the stoechiometric mixtures are more sensitive to detonation than lean mixtures.

Table 3. Average detonation velocity measured in the shock tube.

<table>
<thead>
<tr>
<th>CH₄/CH₄+H₂</th>
<th>x_H₂</th>
<th>x_CH₄</th>
<th>x_O₂</th>
<th>X_N₂</th>
<th>Φ</th>
<th>P₁ (kPa)</th>
<th>( D_{\text{exp}} ) (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>0.444</td>
<td>0.1111</td>
<td>0.444</td>
<td>0</td>
<td>1</td>
<td>100</td>
<td>2870</td>
</tr>
<tr>
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<td>0.1111</td>
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<td>100</td>
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<td>0.600</td>
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<tr>
<td>0.6</td>
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<td>0</td>
<td>0.75</td>
<td>100</td>
<td>2189</td>
</tr>
</tbody>
</table>

![Figure 15](image-url): Evolution of the cell size versus methane content in the mixture for 2 different equivalence ratios.
4 CONCLUSION

A large series of experiments have been performed on the auto-ignition delay times of mixtures containing methane and hydrogen. New data sets were obtained for these mixtures that were not available in the literature before. Regarding the detonation study, as far as we know, characterizing the effect of methane addition to hydrogen, on the detonation parameters, is totally new. The literature provides several mechanisms for the methane combustion and necessarily it contains the sub-mechanism of hydrogen combustion. As we have shown, these mechanisms do not agree on the auto-ignition delay times predictions and especially when methane is added to the mixtures. A comparison between the experiments and the simulations allowed us to discriminate between the different mechanisms and finally Konnov’s mechanism seems to be the most reliable.

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