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Investigation of the Effect of Hydrogen and Methane on Combustion of Multicomponent Syngas Mixtures using a Constructed Reduced Chemical Kinetics Mechanism

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Abstract: This study investigated the effects of H_2 and CH_4 concentrations on the ignition delay time and laminar flame speed during the combustion of CH_4/H_2 and multicomponent syngas mixtures using a novel constructed reduced syngas chemical kinetics mechanism. The results were compared with experiments and GRI Mech 3.0 mechanism. It was found that mixture reactivity decreases and increases when higher concentrations of CH_4 and H_2 were used, respectively. With higher H_2 concentration in the mixture, the formation of OH is faster, leading to higher laminar flame speed and shorter ignition delay time. CH_4 and H_2 concentrations were calculated at different pressures and equivalence ratios, showing that at high pressures CH_4 is consumed slower, and, at different equivalence ratios CH_4 reacts at different temperatures. In the presence of H_2, CH_4 was consumed faster. In the conducted two-stage sensitivity analysis, the first analysis showed that $H_2/CH_4/CO$ mixture combustion is driven by H_2-based reactions related to the consumption/formation of OH and CH_4 recombination reactions are responsible for CH_4 oxidation. The second analysis showed that similar CH_4-based and H_2 -based reactions were sensitive in both, methane- and hydrogen-rich H_2/CH_4 mixtures. The difference was observed for reactions $CH_2O + OH = HCO + H_2O$ and $CH_4 + HO_2 = CH_3 + H_2O_2$, which were found to be important for CH_4-rich mixtures, while reactions $OH + HO_2 = H_2O + O_2$ and $HO_2 + H = OH + OH$ were found to be important for H_2-rich mixtures.

Keywords: syngas; chemical kinetics mechanism; reaction sensitivity analysis; laminar flame speed; ignition delay time; digital analysis of reactive systems (DARS)

1. Introduction

Increasingly serious environmental problems, due to the harmful exhaust gas emissions produced by the combustion of fossil fuels, along with ongoing fluctuations in crude oil prices, have prompted researchers and engine manufacturers to search for new, environmentally friendly and sustainable fuels [1,2]. Synthesis gas (syngas) is seen as a possible solution as it is produced via the gasification of coal or biomass and produces lower levels of emissions during its combustion in comparison with traditional fossil fuels. Syngas fuels consist of different components such as H_2, CO, CH_4, CO_2 and H_2O. The concentration of each component in the syngas is strongly depended on the type of feedstock and the gasification procedure that is used for its production [3].

For example, the hydrogen concentration in a syngas mixture can vary from 25% to 80% depending on the gasification process and the feedstock type used [4]. This variation of the concentration of the different gases in the syngas has a direct effect on important combustion characteristics such as the laminar flame speed, the ignition delay time and the exhaust gas emissions and in general

on the combustion stability. This has posed a great challenge to engine manufacturers in the sense that combustion chambers must be able to support the combustion of fuels with high compositional variations [5].

During the recent years, the combustion of syngas fuels has been of great interest, mostly due to the chemical and thermal characteristic of CH_4 and H_2 [6]. In general, mixtures with a high concentration of methane, for example natural gas, produce lower emissions than diesel and petrol during their combustion. However, natural gas is not a sustainable energy source and it currently has a long-term demand [6,7]. Both of these factors have intensified the research on finding a sustainable and renewable resource that will be able to replace natural gas or high methane mixtures. Syngas mixtures are characterized as potential replacements of natural gas but unlike natural gas, have not been given much consideration and only a few experimental and numerical studies can be found investigating the effects of individual syngas components, such as CH_4 and H_2, on their combustion characteristics. Ilbas et al. [8] experimentally analysed the laminar burning velocities of hydrogen-air and hydrogen-methane-air mixtures at various equivalence ratios (0.8–3.2). The authors showed that the burning velocity as well as the flammability limits increased significantly by increasing the hydrogen concentration in the hydrogen-methane mixtures. Moreover, the authors suggested that mixtures of 70% methane and 30% hydrogen could be a possible solution and can be used as an alternative fuel for different existing combustion plants.

Mathieu et al. [9] investigated experimentally the ignition of fuel blends representative of a syngas produced from biomass (0.09%mol CH_4/0.296%mol CO/0.157%mol CO_2/0.3%mol H_2/0.2%mol H_2O/0.95%mol O_2/98%mol AR). The authors showed that the higher concentration of CO does not affect the combustion process, while the higher concentration of CH_4 reduces the reactivity of the mixture and increases the ignition delay time. They concluded that simple H_2/CO mixtures are not fully adequate to represent real syngas fuels, since concentration of CH_4 has a significant effect on the thermochemical properties of the mixtures and affects the fuel oxidation, the ignition of the fuel and the general combustion process. In another research, Watson et al. [9], performed experimental studies comparing the combustion characteristics and the emissions of multicomponent syngas mixtures, which consisted of CH_4/CO_2/CO/H_2 and pure methane. The authors showed that for lean mixtures (equivalence ratios lower than 1.0), multicomponent syngas fuels produced lower NOx emissions than fuels containing only methane. They made the statement that fuels with high hydrogen content (and relatively low methane content) were more appropriate for lean burn applications because of the excess air that will keep the temperatures at moderated levels and reduce the produced NOx emissions [10–12]. Gersen et al. [13] conducted an experimental study for the investigation of H_2/CO/CH_4 syngas combustion at pressures of 20 to 80 bar, equivalence ratios 0.5 and 1.0 and temperatures between 900–1100 K. The authors investigated the effect of the syngas components on the ignition delay time by varying their concentrations. Their results were identical with the results obtained by Mathieu et al. [9]. They found that CO has a very small effect on the ignition delay time but increased concentration of CH_4 reduced the reactivity of the mixture and increased the ignition delay time. They showed that by increasing H_2 concentration, ignition delay time was reduced and the combustion intensity increased.

Pio et al. [14], performed an investigation of the laminar burning velocity of different mixtures of hydrogen and methane at low temperatures. The authors compared numerical results obtained by using detailed chemical kinetics mechanisms with experimental data available in the literature. According to the authors, increasing the concentration of hydrogen affects the chemical kinetics and more specifically the activation energy. They showed that the combustion regime dominated by methane for mixtures containing hydrogen content >60% is correlated with the limitations presented during hydrogen formation when hydrogen is used as intermediate species in the decomposition chemical path of methane. Furthermore, the authors performed a sensitivity analysis study and they showed that the reaction paths responsible for the production of important species such as H, are affected by the initial conditions and more specifically the low temperatures.

Recently, Salzano et al. [15] investigated the effect of hydrogen concentration on the premixed flame structure of methane/hydrogen/air mixture at various equivalence ratios and fuel compositions using experimental and numerical results. The authors concluded that the reaction zone thickness of methane/air mixtures was reduced drastically when hydrogen was added at 298 K. In conducted sensitivity study, the authors showed that the addition of hydrogen resulted in higher sensitivity coefficient for reaction $H + O_2 = O + OH$, while for pure mixtures under similar conditions, a smaller sensitivity coefficient was observed. This indicates that kinetics paths and the interactions between species play a major role in the combustion process. Finally, the authors made a statement that increasing the amount of carbon atoms in the fuel significantly reduces hydrogen concentration.

Different experimental studies are available in the literature regarding the effects of H_2 and CH_4 on syngas combustion [16–18] but there is still a need for more detailed analysis of the syngas combustion chemistry. Analysis of the combustion chemistry and investigation of the important reactions that are affected, not only by the concentration of methane and hydrogen but also by the temperature variations, is critical for the identification and the analysis of the factors that affect syngas combustion characteristics and are responsible for combustion instabilities.

Therefore, in this paper, a numerical investigation of the effects of methane and hydrogen on the combustion of multicomponent syngas mixtures has been performed. First, the effects of methane and hydrogen concertation on laminar flame speed and ignition delay time have been investigated. CH_4 and H_2 concentration profiles during the combustion of different multicomponent mixtures have been calculated at different initial conditions (pressures and equivalence ratios). Numerical results obtained using a reduced syngas chemical kinetics mechanism developed earlier [19] and the detailed GRI Mech. 3.0 [20] are compared against experimental results available in the literature. The reduced syngas mechanism [19] consists of 31 reactions and includes H_2/CO and CH_4 chemical pathways. Then, a detailed chemical analysis has been performed using the reduced syngas mechanism for the identification of the important reactions that have been triggered due to the changes in the mixture composition, which are responsible for decreasing/increasing the reactivity of the mixture.

The difference of this study from the study in Reference [19] is that the aim of the study in Reference [19] was the development of a reduced mechanism that was used in 0D, 1D and 3D analysis of multicomponent syngas combustion in a micro-pilot ignited dual fuel engine. In this paper, the mechanism proposed in Reference [19] was used for a different type of analysis as we focused specifically on the investigation of the effects of CH_4 and H_2 concentration on ignition delay time and laminar flame speed and the analysis of the combustion chemistry. In contrast to the other published studies, this paper has analysed a two-stage chemical kinetics with the specific focus on, the first, methane oxidation and the second, the comparison of the chemical interactions during the combustion of methane-rich H_2/CH_4 and hydrogen-rich H_2/CH_4 mixtures.

2. Chemical Kinetics Mechanism

During this study, a CFD compatible, reduced syngas chemical kinetics mechanism that was developed in a previous research [19] for the simulation of dual-fuel engine combustion at various engine conditions was used, see Table 1. For the mechanism development, the reduced mechanism proposed by Azimov et al. [21] was used as a reference point and was then re-developed and updated. During the development procedure, a chemical detailed analysis was conducted for the investigation of important hydrogen, methane and carbon based reactions that were found significantly affect the accuracy of the mechanism and the accurate simulation of the combustion process. Therefore, such reactions have been incorporated into the reduced mechanism and their rate constants have been updated. Then the reduced mechanism was tested against experimental and numerical results obtained from the literature in terms of in-cylinder pressure, ROHR, ignition delay time and laminar flame speed for various syngas mixtures. Full details about the development, validation and testing procedures that were followed for the reduce mechanism development can be found in Reference [19]. The mechanism

consists of 31 reactions and includes important hydrogen-based, methane-based and carbon-based reactions. It can be used for the simulation of various multicomponent syngas mixtures.

Table 1. Reduced chemical kinetics mechanism [19] used in this study.

	Reactions	A (cal-cm-sec-K)	n	E (cal/mol)	Ref.
R1	$CH_4 + O_2 = CH_3 + HO_2$	3.98×10^{13}	0.0	56,855.5	[22]
R2	$CH_4 + HO_2 = CH_3 + H_2O_2$	0.964×10^{11}	0.0	24,629.4	[22]
R3	$CH_4 + OH = CH_3 + H_2O$	1.60×10^{7}	1.83	2771.1	[23]
R4	$CH_3 + O_2 = CH_2O + OH$	3.30×10^{11}	0.0	8934.4	[22]
R5	$CH_2O + OH = HCO + H_2O$	3.90×10^{10}	0.0	406.1	[22]
R6	$CO + O (+M) = CO_2 (+M)$	9.04×10^{12}	0.89	3800.0	[23]
	/LOW / 0.2070×10^{27} −3.340 7610.0 /M/ H_2O/12.00/ H_2/2.00/ CO/1.50/ CO_2/2.00/ AR/0.50/				
R7	$CO + OH = CO_2 + H$	0.9600×10^{12}	0.14	7352.0	[23]
R8	$CO + OH = CO_2 + H$	0.7320×10^{11}	−1.00	−16.0	[23]
R9	$CO + HO_2 = CO_2 + OH$	0.1200×10^{18}	0.00	17,000.0	[23]
R10	$CO + H_2O = CO_2 + H_2$	0.2000×10^{9}	0.00	38,000.0	[23]
R11	$HCO (+M) = CO + H (+M)$	0.3000×10^{14}	0.03	23,000.0	[23]
	/M/ H_2O/5.00/ CO_2/3.00/ H_2/1.90/ CO/1.90/				
R12	$HCO + O = CO_2 + H$	0.3000×10^{14}	0.00	0.0	[23]
R13	$HCO + H = H_2 + CO$	0.1000×10^{13}	0.00	0.0	[23]
R14	$HCO + OH = H_2O + CO$	0.5000×10^{14}	0.00	0.0	[23]
R15	$HCO + HO_2 = H_2O_2 + CO$	0.4000×10^{12}	0.00	0.0	[23]
R16	$HCO + HO_2 => H + OH + CO_2$	0.3000×10^{14}	0.00	0.0	[23]
R17	$O_2 + CO = CO_2 + O$	0.2530×10^{10}	0.00	0.0	[23]
R18	$O_2 + HCO = HO_2 + CO$	0.1000×10^{15}	0.00	47,700.0	[23]
R19	$OH + OH (+M) = H_2O_2 (+M)$	0.7400×10^{14}	−0.370	0.0	[23]
	/LOW / 0.2300×10^{19} −0.900 −1700.0 /TROE/ 0.7346 94.00 1756.0 5182.0 /M/ H_2/2.00 /H_2O/6.00/ CO/1.50/ CO_2/2.00/ AR/0.70/				
R20	$H + O_2 = OH + O$	3.52×10^{16}	−0.7	17,061.4	[24]
R21	$H_2 + O = OH + H$	5.06×10^{4}	2.67	6287.6	[25]
R22	$H_2 + OH = H_2O + H$	1.17×10^{9}	1.3	0.0	[26]
R23	$H + O_2 (+M) => HO_2 + (M)$	4.6×10^{12}	0.4	0.0	[27]
	/LOW / 1.737×10^{19} −1.23 0.0 /M/ AR/0.0/ H_2/1.3/ H_2O/10.0/ CO/1.9/ CO_2/3.8/				
R24	$H + H + (M) => H_2 + (M)$	1.30×10^{18}	−1	0.0	[25]
	/M/ H_2/2.5/ H_2O/12.0/ CO/1.9 /CO_2/3.8/ AR/0.5/				
R25	$H + OH (+M) => H_2O (+M)$	4.00×10^{22}	−2	0.0	[25]
	/M/ H_2/2.5/ H_2O/12.0/ CO/1.9/ CO_2/3.8/ AR/0.38/				
R26	$HO_2 + H => OH + OH$	7.08×10^{13}	0.0	298.8	[28]
R27	$HO_2 + H = H_2 + O_2$	1.66×10^{13}	0.0	821.8	[27]
R28a	$HO_2 + OH = H_2O + O_2$	2.89×10^{13}	0.0	−500	[29]
R28b	$HO_2 + OH = H_2O + O_2$	2.456×10^{13}	0.0	−497	[27]
R29	$HO_2 + HO_2 = H_2O_2 + O_2$	1.300×10^{11}	0.00	-1.630×10^{3}	[27]
R30	$H_2O_2 + H = H_2 + HO_2$	7.7×10^{12}	0.0	3755	[29]
R31	$O + H_2O = OH + OH$	2.97×10^{6}	2.02	1.340×10^{4}	[28]

3. Modelling Approach

As already highlighted, multicomponent syngas mixtures produced from biomass, include a small amount of CH_4 that has a significant effect on the combustion characteristics, such as the laminar

flame speed and ignition delay time. In order to investigate the effects of CH_4 on syngas combustion, a two-stage process was conducted. For the first stage, zero and one-dimensional simulations were performed for testing the reduced mechanism on simulating laminar flame speed and ignition delay times of different CH_4/H_2 and $H_2/CO/CH_4$ mixtures and the investigation of the effects of CH_4 and H_2 on ignition delay time and laminar flame speed. For the mechanism validation, the numerical results from the reduced mechanism [19] were compared against numerical results obtained using the detailed GRI Mech. 3.0 [20] and experimental measurements obtained from the literature. The effects of temperature, pressure and equivalence ratio on methane and hydrogen oxidation were investigated by calculating the methane and hydrogen concentrations profiles during the combustion of different H_2/CH_4 mixtures at various initial conditions. The second stage includes two reaction sensitivity analysis. For the first, important reactions affecting $H_2/CO/CH_4$ syngas combustion at different equivalence ratios were analysed, while for the second, important methane-based and hydrogen-based reactions affecting CH_4-rich and H_2-rich H_2/CH_4 mixtures were compared and discussed.

Zero and one-dimensional simulations as well as sensitivity analysis were performed using Digital Analysis of Reactive systems (DARS) software [30]. DARS has been built with the specific purpose of enabling detailed chemical kinetics analysis of engineering applications, with particular focus on internal combustion engines. It incorporates a suite of reactor models and reaction mechanisms for the detailed investigation of combustion chemistry.

3.1. Ignition Delay Time

For the simulation of the ignition delay times in conditions relevant to rapid compression machine (RCM), the constant volume reactor implemented in DARS was used by assuming adiabatic conditions [31]. The ignition delay times were calculated based on the slope of the in-cylinder pressure tracers and the maximum slope of the OH concentration. Many authors have studied the relationship between the formation of OH radicals and the in-cylinder temperature changes [32,33]. They showed that the concentration of OH increases with temperature and therefore can be used as an indicator of the combustion initiation [32–34].

3.2. Laminar Flame Speed

Laminar flame speed simulations have been performed using the one-dimensional premixed laminar flame propagating module incorporated in DARS [35]. According to previous studies, thermal diffusion and radiation factors have a significant effect on the accuracy of the simulations [22]. Keromnes et al. [27] showed that, for stoichiometric mixtures, the calculated laminar flame speed increased by 8% if the thermal diffusion and radiation factors are excluded from the simulations. Therefore, for better accuracy, it was decided to include both of these factors in all of the simulations. The convergent solution was adjusted to be obtained by using 400 grid points.

3.3. Species Concentration Profiles

The concentration profiles of methane and hydrogen during the combustion of different H_2/CH_4 fuels were calculated using the constant volume module available in DARS. The mole fractions of hydrogen and methane were calculated at different temperatures, pressures and equivalence ratios. The initial and boundary conditions used during the simulations were taken directly from the experimental investigations, allowing a direct comparison of the simulated results with the experimental measurements.

3.4. Sensitivity Analysis

Sensitivity analysis is a well -established method for the detailed analysis of complex chemical kinetic systems, investigation of the most sensitive reactions and species and the reduction of detailed mechanisms [36–38]. Each specie is rated based on its own contribution to the formation and the consumption of other important species [32]. Therefore, it can be said that sensitivities are transported

through the chemical kinetic mechanism. For each individual species, sensitivity is used to describe how sensitive a specie is towards a chosen parameter A and is calculated by the summary of the reaction sensitivities (p) in which the species will take part [36,37]:

$$S^{p}_{A,i} = \sum_{k=1}^{N_r} \frac{d\Psi_A}{dr_k} \cdot \frac{u'_{i,k}}{c_i} \cdot r_k \quad (1)$$

Here $S^{p}_{A,i}$ is the summary of the reaction sensitivities and contains the information on how sensitive an arbitrary parameter, A, in the vector of unknowns, $d\Psi_A$, is to species i. Where, k is the reaction rate, w is the production rate, r_k is the internal energy of reaction k and c_i is the concentration of species i. It is important to mention here that the arbitrary parameter, A, could be an important combustion parameter such as the pressure or temperature or the flow rate of certain species [37].

4. Fuel Mixtures Used in This Study

Experimental results for various CH_4/H_2 as well as $H_2/CO/CH_4$ syngas mixtures were collected from the literature and used for mechanism testing. The investigation of the effects of CH_4 and H_2 concentration on laminar flame speed and ignition delay time, the calculation of CH_4 and H_2 concentration profile time and finally, for reaction sensitivity analysis. All of the syngas mixtures used during this study are presented in Table 2 with the range of equivalence ratios, initial pressures and temperatures.

Table 2. Syngas blends used during this study.

No.	Fuel Mixture	Model	Initial Pressure (bar)	Initial Temperature (K)	Composition in Volume Fractions (%)		Eq. Ratio	Ref.
Fuel 1	CH_4/H_2	Ignition delay time	5, 10, 20	1050–1820	Type1 Type 2 Type3 Type4	80/20 60/40 40/60 20/80	0.5	[39]
Fuel 2	CH_4/H_2	Laminar Flame speed	1	298	Type 1 Type 2 Type 3	80/20 50/50 10/90	0.5–1.3	[40]
Fuel 3	CH_4/H_2	Laminar Flame Speed	1	300	Type 1 Type 2 Type 3	100/0 85/15 70/30	0.65–1.1	[41,42]
Fuel 4	$CH_4/H_2/CO$	Laminar Flame speed	1	295	Type1 Type 2	20/40/40 40/30/30	0.75–1.3	[43]
Fuel 5	CH_4/H_2	Species concentration profiles	1, 10 1	900–1450 950–1125	Type 1 Type 2	100/0 50/50	0.1, 0.6 and 1.5 0.1 and 0.6	[44]
Fuel 6	$CH_4/H_2/H_2O/CO/CO_2/N_2$	Species concentration profiles	1.3	990	Type 1 Type 2	14/16/25/19/14/12 14/32/18/12/12/12	0.5	[45]
Fuel 7	$H_2/CO/CH_4$	Reaction sensitivity analysis	10	1125	30/30/40		0.5, 1.0 and 1.5	[43]
Fuel 8	CH_4/H_2	Reaction sensitivity analysis	10	1100	Type 1 Type 2	20/80 80/20	0.5	[40]

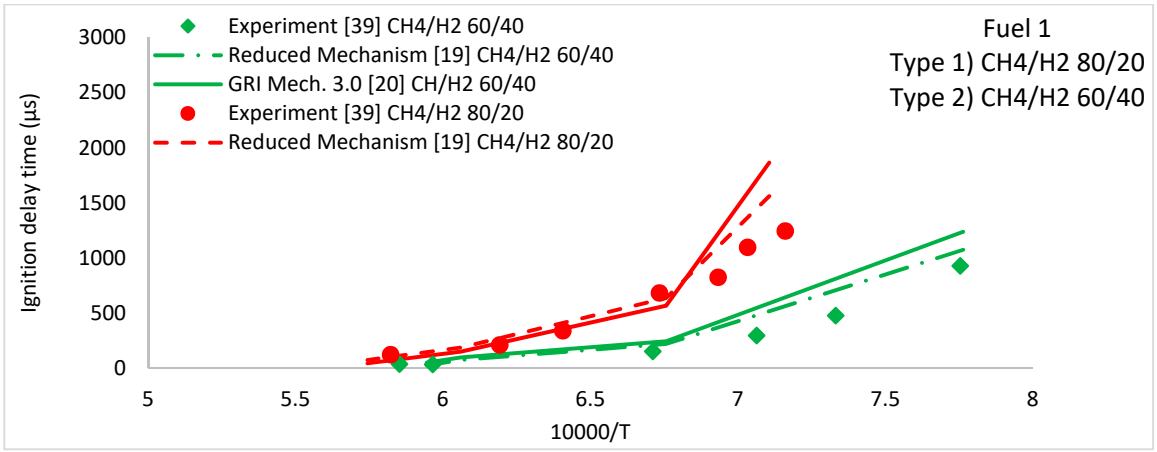
5. Results and Discussion

5.1. Ignition Delay Time

CH_4/H_2 Fuel Mixture

The effect of CH_4 and H_2concentration on ignition delay time was investigated using the experimental measurements from Zhang et al. [39], Fuel 1, Table 2. The comparisons are presented in the Figure 1 for pressure 5 bar, Figure 2 for pressure 10 bar and Figure 3 for pressure 20 bar. The results show that the reduced mechanism [19] and GRI Mech.3.0 [20] accurately simulate the effect

of temperature and mixture composition on the ignition delay time compared to the experimental results, especially for high methane mixtures (CH_4/H_2 60/40% and 80/20%). However, for high H_2 mixtures, GRI Mech. 3.0 [20] is higher at all of the tested temperatures for both mixtures (CH_4/H_2 80/20% and 40/60%). For example, at lower temperatures (1150 K) the ignition delay time using GRI Mech. 3.0 [20] is 1715 µs for H_2 60% while for the same conditions the experimental ignition delay time is 1300 µs. Moreover, for H_2 80% and temperature 1100 K, the ignition delay time using GRI Mech.3.0 [20] is 1100 µs while the experimental ignition delay time is 450 µs. This discrepancy is because GRI Mech. 3.0 was initially constructed for the simulation of natural gas mixtures (methane compositions higher than 50%).



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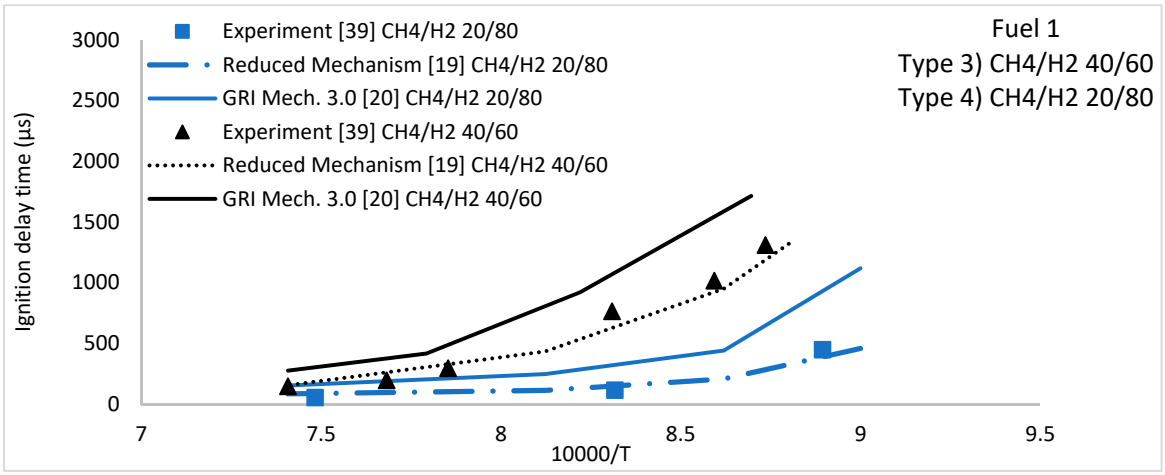
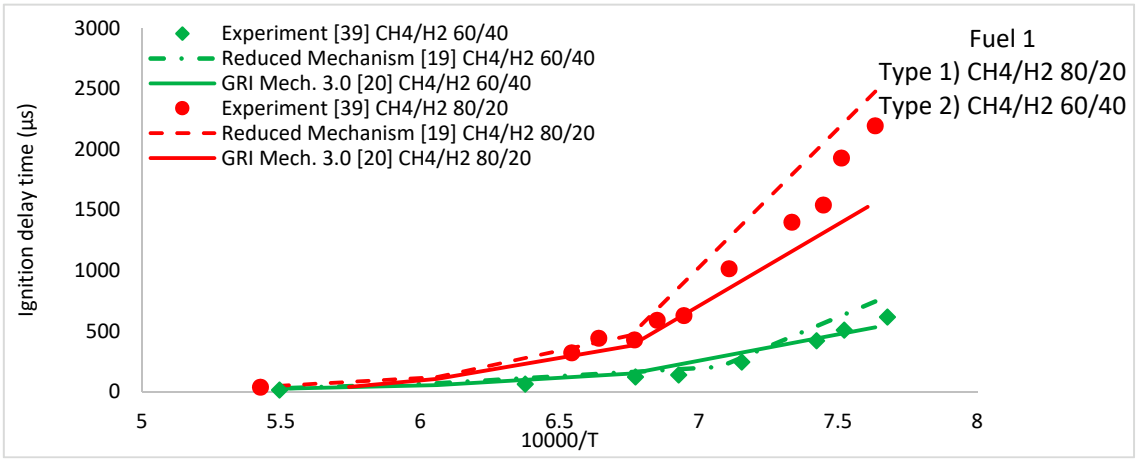


(**b**)

Figure 1. Comparison of the calculated ignition delay time by using the reduced mechanism [19] and GRI Mech. 3.0 [20] and the experimental measurements from Reference [39] for (**a**) Fuel 1 Type 1 and Type 2; and (**b**) Fuel 1 Type 3 and Type 4 at pressure 5 bar and equivalence ratio 0.5.



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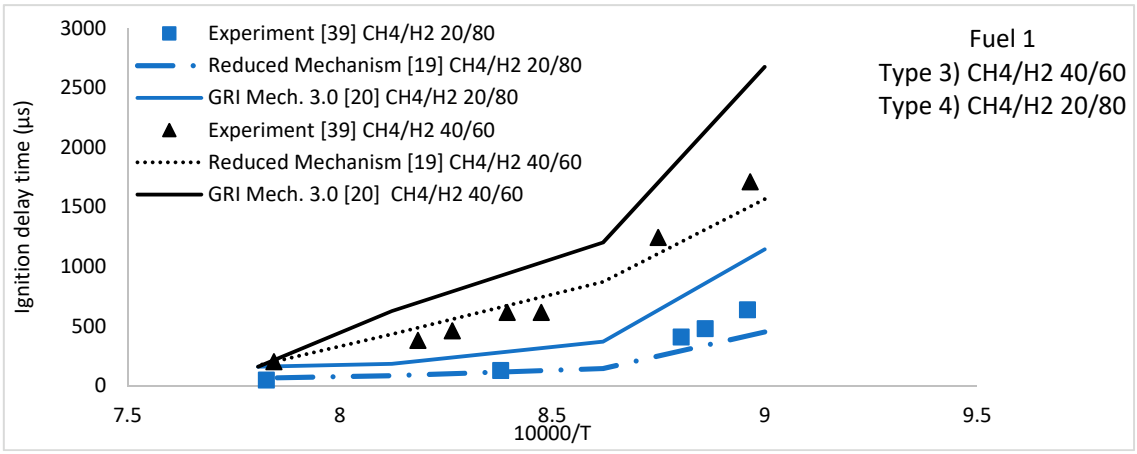
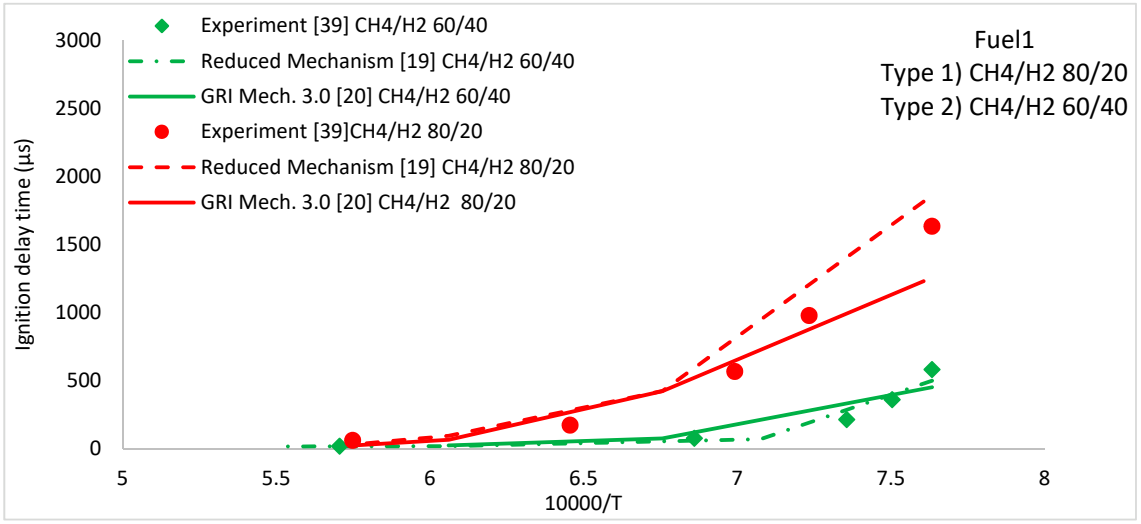


(**b**)

Figure 2. Comparison of the calculated ignition delay time by using the reduced mechanism [19] and GRI Mech. 3.0 [20] and the experimental measurements from Reference [39] for (**a**) Fuel 1 Type 1 and Type 2; and (**b**) Fuel 1 Type 3 and Type 4 at pressure 10 bar and equivalence ratio 0.5.

For all of the conditions tested, a significant decrease of the ignition delay with increase in temperature was observed. This is because the auto-ignition temperature of the fuel mixture is reached faster when the temperature is higher [39]. The effect of CH_4 and H_2 concentrations on ignition delay time can be seen: the higher the amount of CH_4 in the mixture, the longer the ignition delay time, while the higher the amount of H_2, the faster the reactivity of the mixture. This phenomenon is more obvious at lower temperatures, in which, the ignition delay time and the reactivity of the mixture are strongly dependent on the mixture composition [40]. For example, at pressure 5 bar (Figure 1), the ignition delay time of CH_4/H_2 80/20% at 1400 K, is 640 µs in comparison with the ignition delay time of CH_4/H_2 20/80% at similar initial conditions (pressure, temperature and equivalence ratio), which is 3 times shorter, 210 µs.



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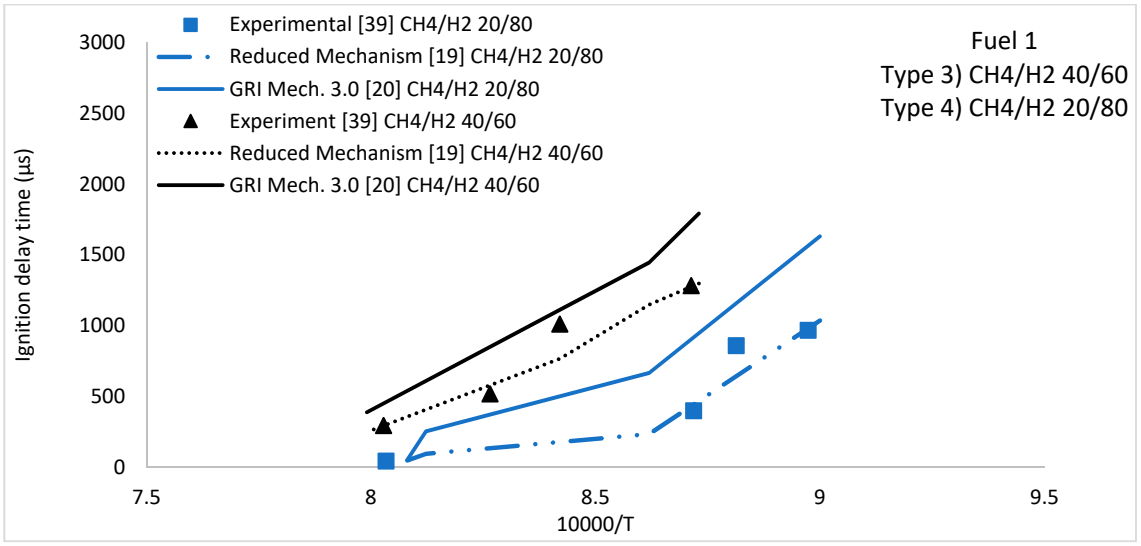

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Figure 3. Comparison of the calculated ignition delay time by using the reduced mechanism [19] and GRI Mech. 3.0 [20] and the experimental measurements from Reference [39] for (**a**) Fuel 1 Type 1 and Type 2; and (**b**) Fuel 1 Type 3 and Type 4 at pressure 20 bar and equivalence ratio 0.5.

5.2. Laminar Flame Speed

5.2.1. H_2/CH_4 Fuel Mixture

In terms of laminar flame speed, in order to validate the performance of the reduced mechanism [19] and GRI Mech. 3.0 [20] and investigate the effect of CH_4 concentration and equivalence ratio on the mixtures reactivity, the experimental measurements from Donohoe et al. [40], Fuel 2, Table 2, were used. These authors measured the laminar flame speed of different H_2/CH_4 mixtures (20/80%, 50/50% and 90/10%) at pressure 1 bar, temperature 298 K and a range of equivalence ratios of 0.5–1.3. The results are presented in Figure 4. It can be seen that both mechanisms accurately simulate the experimental results obtained using fuel mixtures with CH_4 content 50% and 80%. However, for H_2 90%, GRI Mech. 3.0 shows a significant deviation with the experimental results, while the reduced mechanism is close to the experiment. For example, the maximum laminar flame speed reached at equivalence ratio 1.3 using the reduced mechanism is 341 m/s while the experimental maximum laminar flame speed at

the same equivalence ratio is 330 m/s. On the other hand, by using GRI Mech. 3.0 [20], the maximum laminar flame speed at equivalence ratio 1.3 is 375 m/s. This is in agreement with the results observed from the ignition delay comparison, in which GRI Mech. 3.0 showed a significant deviation with the experimental results when mixtures with high H_2 content were used.

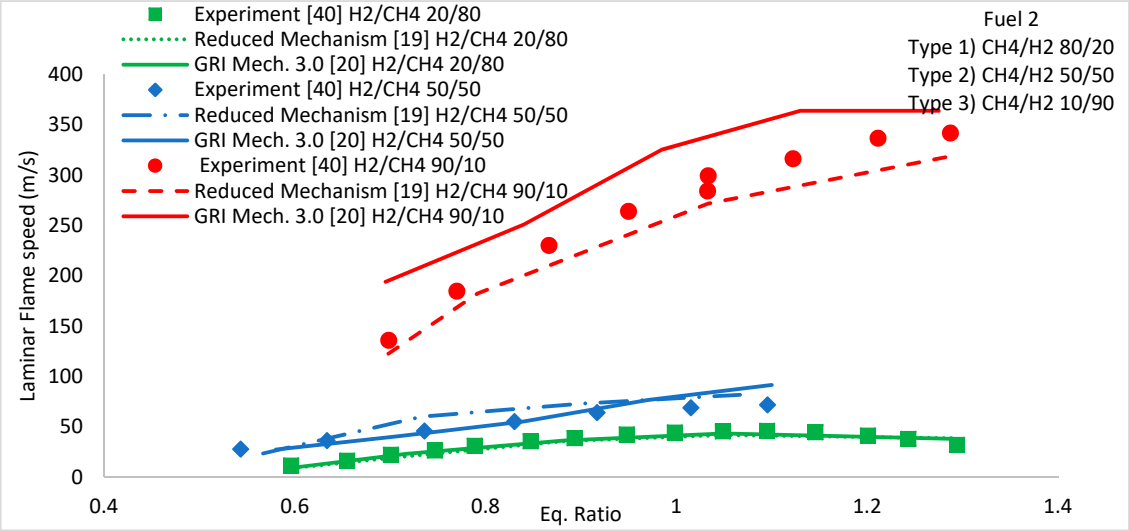


Figure 4. Comparison of the calculated laminar flame speed using the reduced mechanism [19] and GRI Mech. 3.0 [20] and the experimental measurements from Reference [40] for Fuel 2 (H_2/CH_4 20/80%, 50/50% and 90/10%) at pressure 1 bar, eq.ratio 0.5–1.3 and temperature 298 K.

Furthermore, according to the results, the richer the mixture and therefore the higher the equivalence ratio, the higher the intensity of the mixture and therefore the higher the laminar flame speed. Additionally, the higher the amount of CH_4 in the mixture, the lower the reactivity of the mixture and therefore the lower the laminar flame speed. However, this phenomenon is not only correlated with the higher concentration of CH_4 but also with the reduction of H_2. Different authors have highlighted the importance of the higher concentration of H_2 on the reactivity of the mixture [46–48]. By increasing the amount of H_2 in the mixture and therefore reducing CH_4, the formation rate of highly reactive OH radicals is greater and therefore the reactivity of the mixture is faster.

For further investigation of the effect of CH_4 and H_2 concentration on laminar flame speed, the experimental results obtained by Hermanns et al. [41] for pure methane (CH_4 100%) and CH_4/H_2 85/15% and by Coppens et al. [42] for CH_4/H_2 70/30% were used. Both authors measured laminar flame speeds at pressure 1 bar, temperature 300 K and equivalence ratios between 0.6-1.5. The results are presented in Figure 5 and show that both the reduced mechanism [19] and GRI Mech. 3.0 [20] accurately reproduce the experimental results and capture the effects of equivalence ratio and CH_4 and H_2 concentrations on laminar flame speed. Similar to the results of Figure 4, the higher the equivalence ratio, the higher the laminar flame speed. While on the other hand, the higher the concentration of CH_4 and therefore the lower the concentration of H_2 in the mixture, the lower the laminar flame speed. For example, the maximum laminar flame speed for 100% CH_4 is approximately 40 m/s, while for 70% CH_4, the maximum laminar flame speed increases to 50 m/s.

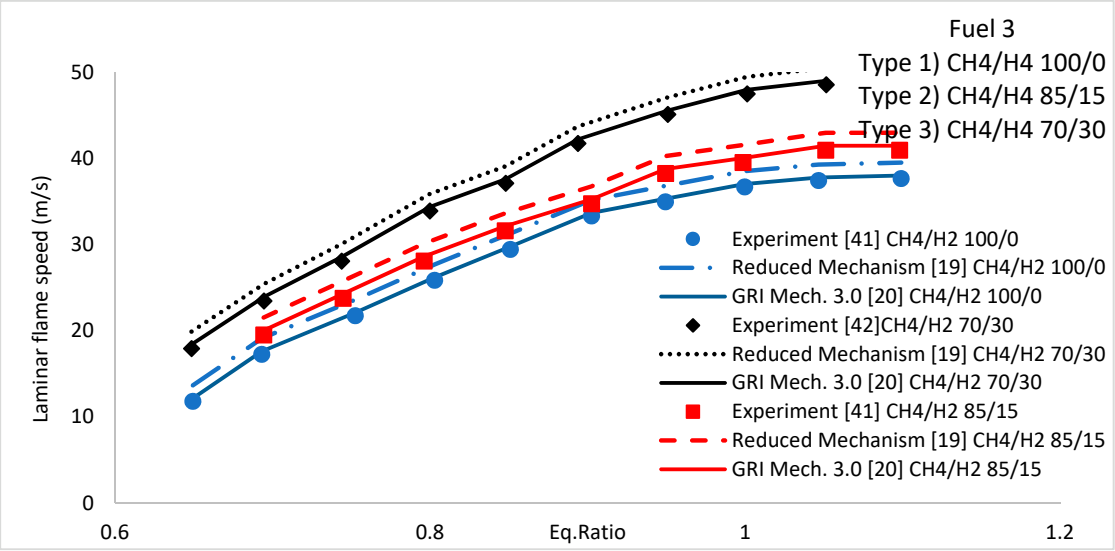


Figure 5. Comparison of the calculated laminar flame speed using the reduced mechanism [19] and GRI Mech. 3.0 [20] and the experimental measurements from References [41,42] for Fuel 3 (CH_4/H_2 100/0%, 70/30% and 85/15%) at pressure 1 bar, eq.ratio 0.65–1.1 and temperature 300 K.

5.2.2. $H_2/CO/CH_4$ Fuel Mixture

The last set of experimental laminar flame speed measurements were obtained from Lapalme et al. [43], Fuel 4, Table 2. The results of the comparison between the numerical and experimental results are presented in Figure 6. The reduced mechanism [19] captures the effect of CH_4 concentration and shows a good match with the experimental results at all equivalence ratios for both mixtures. On the other hand, GRI Mech. 3.0 [20] performs very well for both mixtures at lean equivalence ratios but for equivalence ratios higher than 1.0 the numerical results deviate from the experimental measurements.

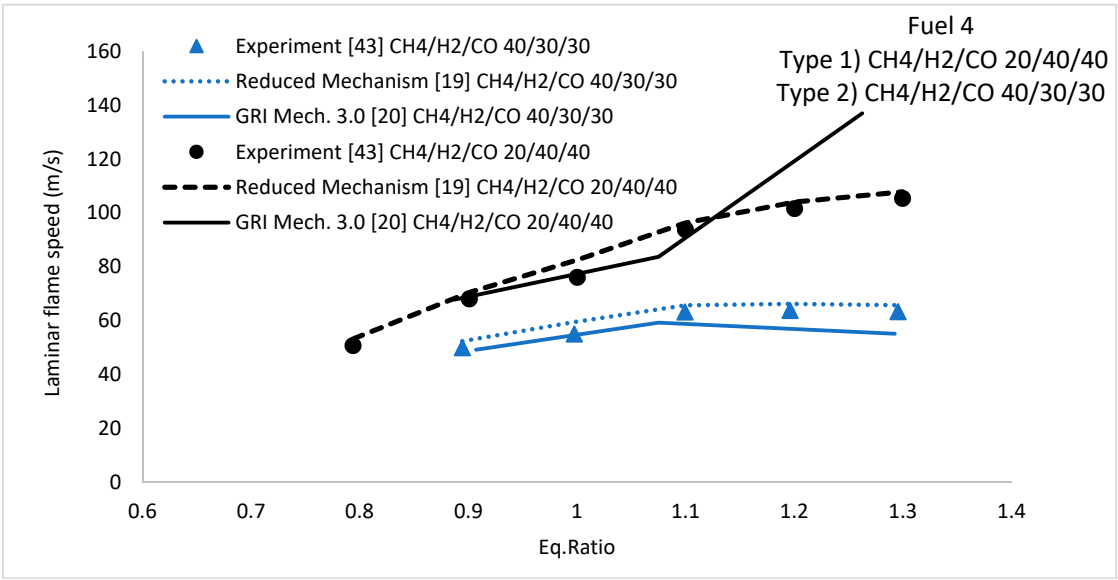


Figure 6. Comparison of the calculated laminar flame speed using the reduced mechanism [19] and GRI Mech. 3.0 [20] and the experimental measurements from Reference [43] for Fuel 4 (CH_4/H_2/CO 40/30/30% and 20/40/40%), at pressure 1 bar, eq.ratio 0.7–1.3 and temperature 295 K.

The effect of CH_4 concentration is similar to the effect observed previously for the comparisons presented in Figures 4 and 5. The maximum laminar flame speed for CH_4/H_2/CO 40/30/30% is

approximately 65 m/s, while for $CH_4/H_2/CO$ 20/40/40% is approximately 110 m/s. This phenomenon cannot only be attributed to the amount of CH_4 included in the mixture but also to the higher concentration of H_2. The higher concentration of H_2 increases the reactivity of the mixture and therefore increases the laminar flame speed.

5.3. Species Concentration Profiles

In order to investigate the oxidation of the fuel during the combustion of different CH_4/H_2 mixtures at different combustion conditions, different species concentrations were calculated using the reduced mechanism and compared with experimental measurements obtained from Cong et al. [44]. These authors measured the species concentrations by using a jet-stirred reactor at constant residence time of 120 ms at pressure 1 atm and 250 ms at pressure 10 atm. They pre-heated the fuel before injection while the flow rates were regulated by using thermal controllers. In order to reduce the uncertainties and produce accurate results, a similar approach was used during the simulations setting initial premixed temperature and fuel temperature similar to those used in experiments of [44]. In DARS, the fuel temperature was set to 400 K to achieve the ignition. By boosting and preheating, the mixture it was possible to obtain flame at very low equivalence ratio.

First, CH_4 concentration profiles were calculated for the combustion of CH_4/H_2 100/0% mixture at pressures 1 and 10 bar, temperatures ranging between 900–1450 K and equivalence ratios of 0.1, 0.6 and 1.5. The results are presented in Figure 7, for pressure 1 bar and Figure 8, for pressure 10 bar. As can be seen from the results, the reduced mechanism [19] simulates with relatively low deviation from the experimental results, the concentration profiles of methane at all of the tested conditions, accurately capturing the effect of pressure, equivalence ratio and temperature on methane consumption. At pressure 10 bar, methane is consumed more gradually, enhancing the reactivity of the mixtures in comparison with 1 bar in which it is consumed sharply and rapidly. According to Cong et al. [44], at high pressures, recombination reactions affecting the formation of methane and the metathesis of methane and OH are more important and lead to lower reactivity of methane.

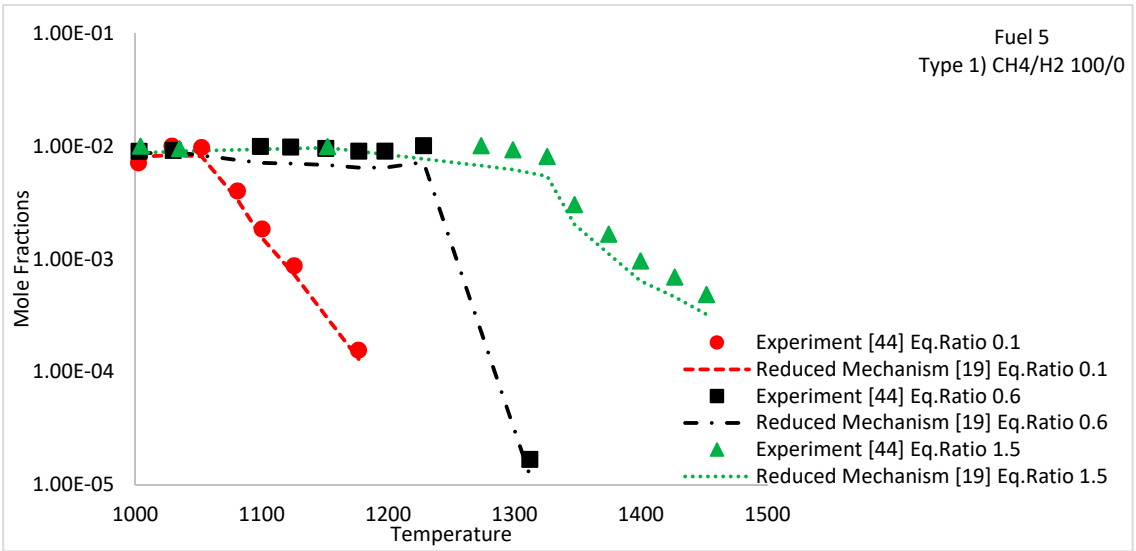


Figure 7. Comparison of the calculated CH_4 profiles by using the reduced mechanism [19] and the experimental measurements from Reference [44] for 100% methane mixture at pressure 1 bar, temperatures 900–1450 K and eq.ratios 0.1, 0.6 and 1.5.

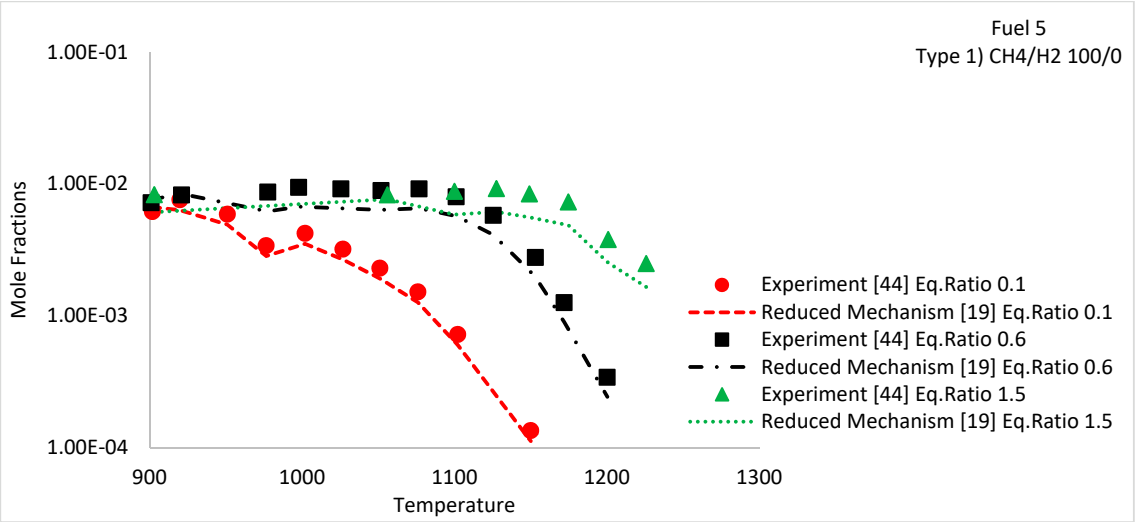


Figure 8. Comparison of the calculated CH_4 profiles by using the reduced mechanism [19] and the experimental measurements from Reference [44] for 100% methane mixture at pressure 10 bar, temperatures 900–1450 K and eq.ratios 0.1, 0.6 and 1.5.

It can be seen from the methane concentration profiles, for each equivalence ratio, that methane is reacting at different temperatures. This phenomenon is more obvious at low pressure conditions, as shown in Figure 7. At equivalence ratio 0.1, methane is reacting at temperature 1050 K, at equivalence ratio 0.6 it is reacting at 1220 K and at equivalence ratio 1.5 it is reacting at 1325 K. This phenomenon is an indicator that the equivalence ratio plays a major role on methane oxidation and is affecting the reactivity of the whole mixture. This is because at different equivalence ratios, different methane-based and hydrogen-based reactions are triggered, leading to faster or slower formation of OH species that are responsible for the increase in the temperature and the reactivity of the mixture [44,46]. Therefore, the mixture is reacting at different temperatures at different equivalence ratios.

For further investigation, the concentration profiles of H_2 and CH_4 during the combustion of CH_4/H_2 50/50% at temperature 975–1150 K, pressure 1 bar and equivalence ratios 0.1 and 0.6, have also been calculated and compared with the experimental measurements obtained from Cong et al. [44]. The results presented in Figure 9 show that the reduced mechanism accurately simulates the experimental results and clearly captures the effect of temperature on both H_2 and CH_4 concentration profiles; the higher the temperature, the lower the mole fractions of both H_2 and CH_4. By comparing the results of the methane concentration profiles for the pure methane mixture, presented in Figure 7, with the results in Figure 9, it can be seen that in the presence of hydrogen, methane was consumed more gradually. This is because different hydrogen based reactions are responsible for the initiation of mixture oxidation and the formation of OH. They trigger methane-based recombination reactions, which change the chemical stability of the combustion process.

Finally, in order to analyse the effect of H_2 on CH_4 conversion, the experimental results from Dufour et al. [45] were used, Fuel 6, Table 2. Both experimental and simulated results are presented in Figure 10 and highlight the effect of H_2 on CH_4 conversion: The higher is the initial mole fraction of H_2, the lower is the CH_4. More specifically, by increasing the initial mole fraction of H_2 from 16 to 32 vol %, the conversion rate of CH_4 is reduced from about 55 vol % to 35 vol %.

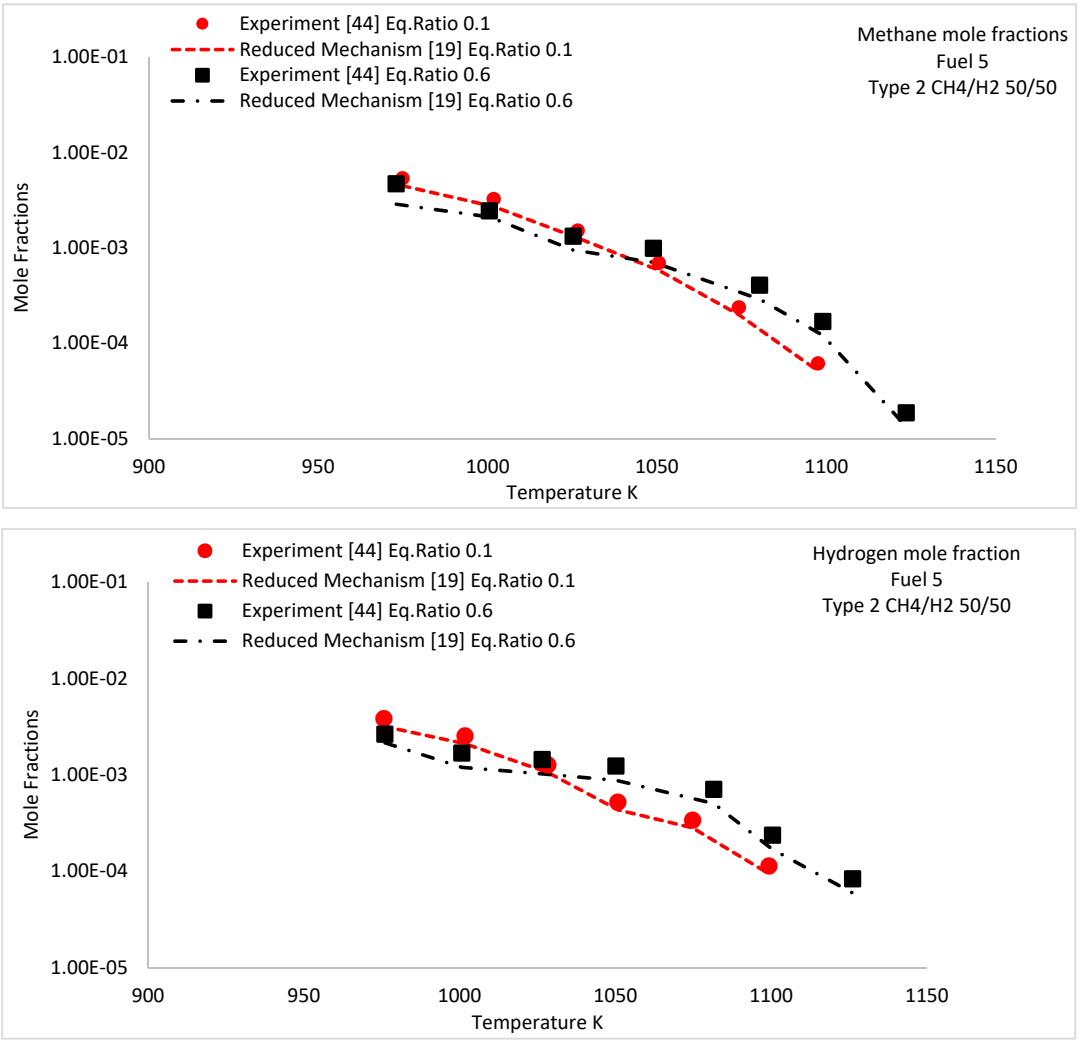


Figure 9. Comparison of the calculated CH_4 (**top**) and H_2 (**bottom**) profiles by using the reduced mechanism [19] and the experimental measurements from Reference [44] for CH_4/H_2 50/50 mixture at pressure 1 bar, temperatures 950–1125 K and eq.ratios 0.1 and 0.6.

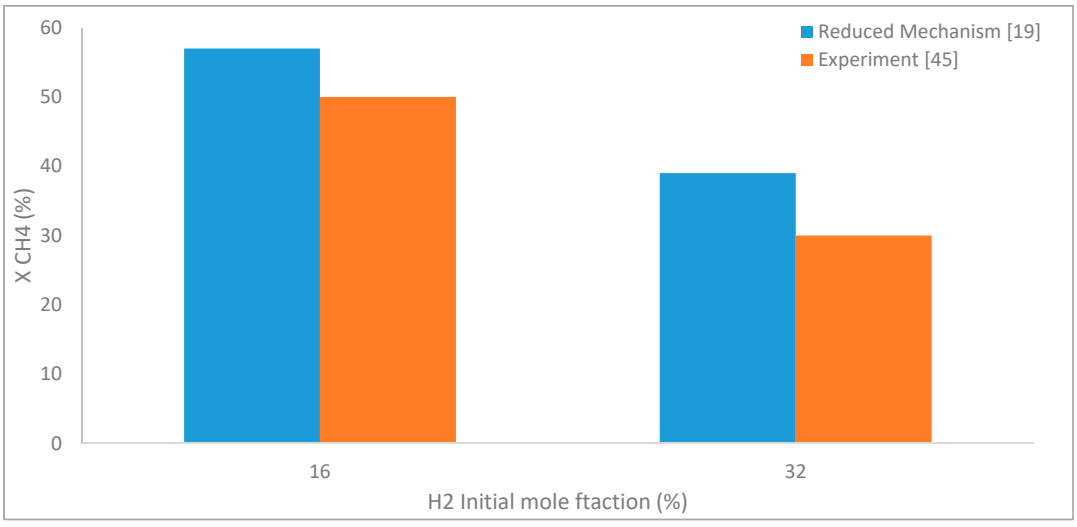


Figure 10. Effect of H_2 mole fraction on the conversion of CH_4 using the reduced mechanism [19] and the experimental data from Reference [45].

5.4. Chemical Detailed Analysis

In order to investigate in detail the reactions affecting methane oxidation during syngas and H_2/CH_4 mixture combustion, a reaction sensitivity study was conducted. This sensitivity study is separated into two parts: first, the effect of equivalence ratio on methane oxidation was investigated and important reactions were identified and analysed; second, the important reactions affecting methane-rich H_2/CH_4 and hydrogen-rich H_2/CH_4 mixture combustion were identified and analysed.

5.4.1. $H_2/CO/CH_4$ Reaction Sensitivity

For the first investigation, reaction sensitivity analysis was conducted using fuel $H_2/CO/CH_4$ 30/30/40%, at pressure 10 bar, temperature 1125 K and equivalence ratios 0.5, 1.0 and 1.5. The results for the ten most sensitive reactions are shown in Figure 11. Hydrogen and methane-based reactions are found to be the dominant reactions, driving the combustion process, more specifically, hydrogen-based reactions $H_2O_2 + M = OH + OH + M$, $H_2O_2 + H = H_2 + HO_2$, $H + O_2 = OH + O$, $H_2 + O = OH + O$, $OH + HO_2 = H_2O + O_2$ and methane-based reactions $CH_4 + O_2 = CH_3 + HO_2$, $CH_4 + HO_2 = CH_3 + H_2O_2$, $CH_4 + OH = CH_3 + H_2O$, $CH_3 + O_2 = CH_2O + OH$, $CO + OH = CO_2 + H$.

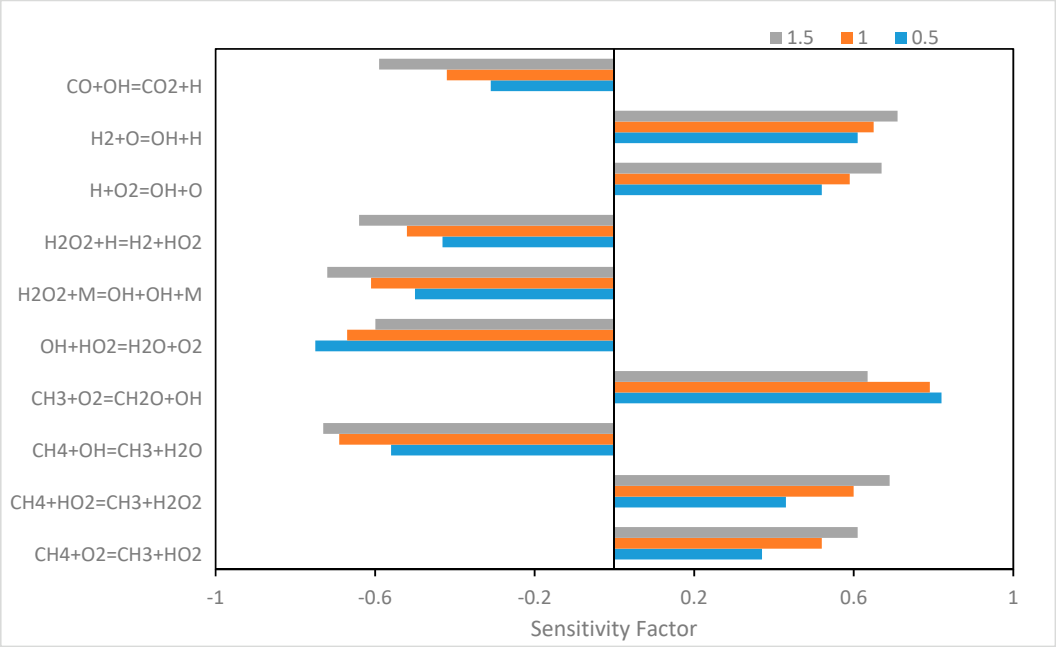


Figure 11. Ten most sensitive reactions for Fuel 6: $H_2/CO/CH_4$ 30/30/40%, at pressure 10 bar, temperature 1125 K and equivalence ratios 0.5, 1.0 and 1.5.

Hydrogen-Based Reactions

All of the hydrogen-based reactions highlighted in the sensitivity analysis are directly or indirectly related to the formation or consumption of highly reactive OH radicals. As it was already mentioned in this study, many researchers characterize OH as an indicator of the combustion occurrence due to the fact that the formation rate of OH is directly connected to the temperature and fuel reactivity variations: the higher the formation rate of OH, the faster the reactivity and the higher the intensity of the mixture and therefore the temperature.

Each hydrogen-based reaction presented in the sensitivity analysis is discussed below.

$$\text{(R19) } H_2O_2 + M = OH + OH + M$$

According to many authors [49–51] the dissociation of H_2O_2 radicals is the central kinetics feature in the operation of compression-ignition engines and has a major role on the occurrence of abnormal

combustion phenomena. R19 is one of the most important reactions affecting the decomposition of H_2O_2. By the decomposition of H_2O_2 via R19, secondary reactions that are responsible for the formation of highly reactive OH are triggered. As it can be seen from Figure 11, R19 is very sensitive to the equivalence ratio: the higher the equivalence ratio, the higher the sensitivity of the specific reaction. This is because at higher equivalence ratios, the H_2O_2/OH ratio decreased due to the faster formation of OH and therefore the faster dissociation of H_2O_2 via R19. That leads to an enhanced chain-initiation process through different hydrogen-based reactions, such as $H_2 + O_2 = OH + OH$ and $H_2 + O_2 = H + HO_2$, ensuring the occurrence of subsequent chain-branching reactions along with an increase in the OH concentration. Detailed analysis of R19 and investigation of how different reaction rates affecting the formation or dissociation of OH and therefore the H_2O_2 ratio are provided in a previous study [19].

$$(R30)\ H_2O_2 + H = H_2 + HO_2$$

R30 is one of the leading reactions under low temperature/high pressure conditions [19,27]. This reaction is responsible for the consumption of one HO_2 radical which in turn leads to the production of one H_2O_2 molecule. H_2O_2 will then be consumed via R19 for the formation of high reactive OH radicals [27]. Therefore, it can be said that R30 is indirectly affecting the reactivity of the mixture.

$$(R20)\ H + O_2 = OH + O$$

For a chemical kinetics mechanism, R20 is one of the most important reactions that has to be included. R20 is a leading controlling reaction, responsible for the control of the fuels oxidation [27]. The interaction between hydrogen and oxygen leads to the formation of OH. Especially for richer mixtures (high equivalence ratio) this reaction plays a critical role in controlling, not only the formation of OH and therefore the reactivity of the mixture but also the general oxidation process of the fuel.

$$(R21)\ H_2 + O = OH + O$$

Another reaction responsible for the control of the fuels oxidation and the production of high reactive OH radicals is R21. R21 is combined with R20, in order to control the interactions between oxygen and hydrogen. Different researchers have analysed the behaviour of R20 and R21, focusing on rich mixtures and high temperature conditions [52–54]. They showed that at rich mixture/high temperature conditions both of these reactions have high sensitivity, leading to faster consumption of oxygen and production of OH. This statement is in agreement with the results from the sensitivity analysis presented in Figure 11, in which R20 and R21 show higher sensitivity factors as the equivalence ratio increases. Moreover, the interaction between R20 and R21, triggers other controlling reactions, for example, R22 $H_2 + OH = H_2O + H$, responsible for consumption of OH and reduction of mixture reactivity.

$$(R28)\ OH + HO_2 = H_2O + O_2$$

R28 is an important reaction responsible for the consumption of OH high reactive radicals and the production of H_2O. Therefore, it can be said that this reaction decreases the reactivity of the mixture. As shown by Keromnes et al. [27], R28 is very sensitive to fuel lean flames and its sensitivity decreases as the equivalence ratio increases. This statement can be observed from the results of Figure 11 in which, the sensitivity coefficient of R28 at the equivalence ratio 0.5, is approximately −0.75, at equivalence ratio 1.0 is −0.65 and at equivalence ratio 1.5 is approximately −0.60.

Methane-Based Reactions

Five different methane-based reactions were identified as very important at all of the equivalence ratios tested; R1, R2, R3, R4 and R5. However, for each equivalence ratio, the sensitivity factor of the reactions changed significantly. For example, for a lean mixture (equivalence ratio 0.5), the sensitivity factor of R4 is approximately 0.6, while at equivalence ratio 1.0 it increases to 0.79 and at equivalence

ratio 1.5 it increases to 0.85. This is because the formation of CH_2O is much faster and has a greater effect on the reactivity of the mixture and the combustion process at lean mixtures in comparison with the rich mixture conditions [44,46].

Furthermore, at moderated combustion conditions (temperature between 900–1450 K and pressure between 1–10 bar), methane recombination reactions have been found to play a critical role in combustion control [44]. According to Cong [44], methane recombination reactions are mainly responsible for the consumption of CH_4 by metathesis with high reactive OH radicals and their sensitivity increases with equivalence ratio. This statement is confirmed from the results presented in Figure 11, which show that recombination reactions such as $CH_4 + OH = CH_3 + H_2O$, $CH_4 + O_2 = CH_3 + HO_2$ and $CH_4 + HO_2 = CH_3 + H_2O_2$, have higher sensitivity factors at richer mixture conditions (equivalence ratio 1.5) while at lower equivalence ratio 0.5 their sensitivity factor is lower. The importance of each methane-based reaction is presented in detail below.

$$(R3)\ CH_4 + OH = CH_3 + H_2O$$

R3 is one of the major recombination reactions especially at high pressure/rich mixture conditions. The oxidation of CH_4 through R3 is responsible for the slow formation of CH_3 by the consumption of CH_4 and high reactive OH and the production of more water vapor [55]. This interaction will make the fuel mixture less chemically sensitive to further concentration of H_2O but on the other hand, will increase the specific heat capacity of the product, since CH_4 is directly oxidized for the production of H_2O. This results in the fuel mixture becoming more thermally sensitive [50].

$$(R1)\ CH_4 + O_2 = CH_3 + HO_2$$

R1 is a major initiation reaction as it triggers oxidation of methane with molecular oxygen and leads to the production of HO_2 and CH_3. HO_2 then attacks CH_4 via R2, starting the main fuel oxidation path for the formation of H_2O_2. On the other hand, the produced CH_3 is reacting with molecular oxygen via R4 forming formaldehyde and high reactive OH radicals resulting in the ignition initiation of methane. Moreover, the adverse R1, $CH_3 + HO_2 = CH_4 + O_2$ is characterized as an important inhibiting reaction due to the fact that CH_3 is drastically consumed, preventing the interaction with R2 for the production of OH radicals [56].

$$(R2)\ CH_4 + HO_2 = CH_3 + H_2O_2$$

HO_2 radicals that have been produced via R1, interact with CH_4 via R2 for the formation of CH_3 and H_2O_2. The produced H_2O_2 is then consumed by hydrogen-based and methane-based reactions, for example R19, for the formation of high reactive OH radicals and the initiation of the fuel ignition. Moreover, the produced CH_3 interacts with O_2 via R4 for the production of formaldehyde and OH [56,57]. Therefore, it can be said that R2 is an intermediate reaction that affects the production of OH via the production of H_2O_2 and CH_3. Furthermore, at higher equivalence ratios, the sensitivity of R2 is also higher.

$$(R4)\ CH_3 + O_2 = CH_2O + OH$$

R4 is one of the most important reactions in the CH_4 oxidation process and is responsible for accelerating methane ignition occurrence. Different researchers [58,59] have used R4 for the accurate prediction of methane ignition delay time. The interaction between CH_3 and O_2, is a key intermediate in the combustion of multicomponent syngas mixtures and natural gas as it forms CH_2O and high reactive OH [27,29,59,60]. This reaction has a strange and complex temperature dependence especially at a temperature range between 800–1300 K and may lead to abnormal combustion phenomena. This is the reason many researchers have used various rate constants in order to express this temperature dependence and accurately predict methane auto-ignition and knocking phenomena [27,60]. For example, for the same temperature range (800–1100K) the rate constant used

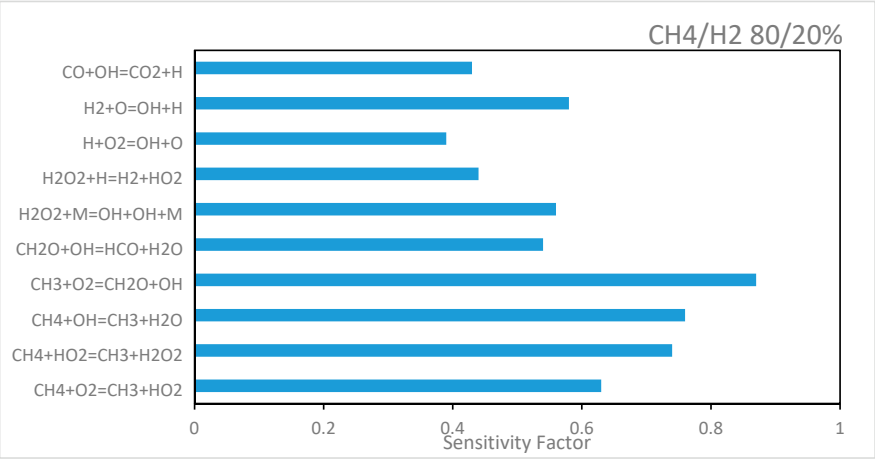
in the San Diego mechanism [61] for R4 is around 42 times higher than the rate constant used in the detailed GRI Mech. 3.0 [20]. Furthermore, R4 is very sensitive to the equivalence ratio. As it was highlighted by Cong et al. [44], at lean mixtures the production of CH_2O is faster and therefore the sensitivity of R4 at lower equivalence ratios is higher than that for rich fuel mixtures.

5.4.2. H_2/CH_4 Reaction Sensitivity

For the investigation of the important reactions affecting methane-rich H_2/CH_4 mixture combustion and hydrogen-rich H_2/CH_4 mixture combustion, a second reaction sensitivity analysis was performed. For this sensitivity analysis, two different CH_4/H_2 mixtures were used: (a) H_2/CH_4 20/80% and (b) H_2/CH_4 80/20%. For both fuel mixtures, sensitivity analysis was conducted at pressure 10 bar, equivalence ratio 0.5 and temperature 1100 K. The results are presented in Figure 12. It is very important to mention that the scope of this reaction sensitivity analysis was to compare the important reactions for methane-rich and hydrogen-rich mixtures and therefore the absolute sensitivity coefficient was used. For that reason, no negative value sensitivity coefficient is presented in Figure 12.

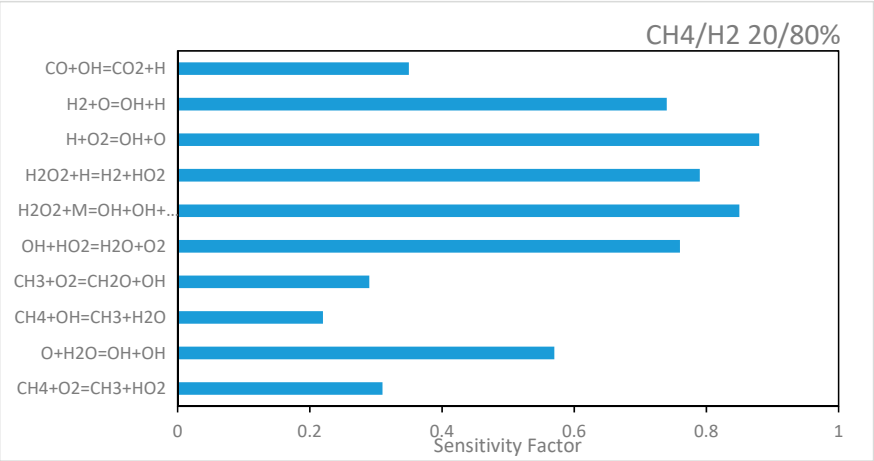
According to the results, similar reactions have been highlighted as important for both mixtures. More specifically, hydrogen-based reactions $H_2O_2 + M = OH + OH + M$, $H_2O_2 + H = H_2 + HO_2$, $H + O_2 = OH + O$, $H_2 + O = OH + O$, methane-based reactions $CH_4 + O_2 = CH_3 + HO_2$, $CH_4 + OH = CH_3 + H_2O$, $CH_3 + O_2 = CH_2O + OH$ and $CO + OH = CO_2 + H$. The main difference is that for CH_4/H_2 80/20%, (R5) $CH_2O + OH = HCO + H_2O$ and (R1) $CH_4 + HO_2 = CH_3 + H_2O_2$ are highlighted as important and have a very high sensitivity coefficients (0.55 and 0.8 respectively), while for CH_4/H_2 20/80%, (R5) and (R1) are not presented and have been replaced by (R28) $OH + HO_2 = H_2O + O_2$ and (R26) $HO_2 + H = OH + OH$. R28 is an inhibiting reaction as it decreases the reactivity of the mixture and controls the formation rate of OH radicals, while (R26) is responsible for the production of two OH radicals and increases the reactivity of the mixture. Both of these reactions have been highlighted by many researchers as being very important during the combustion of mixtures with high hydrogen content.

For mixture CH_4/H_2 80/20%, methane-based reactions have the highest sensitivity coefficient and therefore it can be said that they have more influence on the combustion process. For example, reaction $CH_3 + O_2 = CH_2O + OH$, which is responsible for the rapid initiation of methane oxidation, has the highest sensitivity factor of 0.87, followed by reactions $CH_4 + OH = CH_3 + H_2O$ with sensitivity factor of 0.76 and $CH_4 + HO_2 = CH_3 + H_2O_2$ with sensitivity factor of 0.74. On the other hand, CH_4/H_2 20/80% shows an opposite trend and hydrogen based reactions have the highest sensitivity factor and drive the combustion process. For example, reactions $H_2 + O = OH + O$ and $H_2O_2 + M = OH + OH + M$ have sensitivity factors of 0.88 and 0.85 respectively.



(**a**)

Figure 12. *Cont.*



(**b**)

Figure 12. Ten most sensitive reactions for (**a**) Fuel 7, CH_4/H_2 80/20% and (**b**) Fuel 7, CH_4/H_2 20/80%, at pressure 10 bar, temperature 1100 K and equivalence ratio 0.5.

6. Conclusions

During this study, the effects of CH_4 and H_2 concentrations on the combustion of H_2/CH_4 and multicomponent syngas mixtures have been investigated using a reduced chemical kinetics mechanism [19]. The simulated results were compared with experimental measurements collected from the literature for laminar flame speed and ignition delay time for different H_2/C_4 and $H_2/CO/CH_4$ mixtures.

For ignition delay times, the higher concentration of CH_4 worked as an inhibitor for the mixtures reactivity and resulted in a significant increase of the ignition delay time. In contrast, the ignition delay time was reduced by the higher concentration of H_2, indicating that the reactivity of the mixture increased significantly, leading to the faster auto-ignition of the mixture. For laminar flame speed, an identical trend was observed when CH_4 and H_2 were added. The reactivity of the mixture and hence the laminar flame speed reduced when mixtures with high CH_4 content were used, while in contrast the laminar flame speed increased when the amount of H_2 in the mixture increased.

For more detailed analysis, methane and hydrogen concentration profiles during the combustion of different H_2/CH_4 mixtures, have been calculated at different pressures and different equivalence ratios. The analysis shows that for high-pressure conditions, methane is consumed more gradually, enhancing the reactivity of the mixture more in comparison with low-pressure conditions, in which, methane is consumed rapidly and sharply. Additionally, it was found that at different equivalence ratios, methane is reacting at different temperatures, indicating that at each equivalence ratio, different reactions are triggered affecting the mixture oxidation. Furthermore, it was found that in the presence of hydrogen, methane is consumed more gradually.

Two reaction sensitivity analysis were conducted for the investigation of the important reactions affecting the combustion process. According to the first sensitivity analysis, hydrogen-based and methane-based reactions are found to be the dominant reactions, driving $H_2/CH_4/CO$ mixture combustion at different equivalence ratios. All of the hydrogen-based reactions identified from the sensitivity analysis were correlated with the formation or the consumption of important OH radicals indicating that OH plays a key role in the combustion process. Methane recombination reactions, responsible for the oxidation and consumption of CH_4 by metathesis with high reactive OH radicals, were found to be very important and have high sensitivity factors at all of the equivalence ratios investigated. For the second sensitivity analysis, important reactions affecting the combustion of methane-rich and hydrogen-rich H_2/CH_4 mixtures, were analysed. Hydrogen-based reactions such as $H_2O_2 + M = OH + OH + M$, $H_2O_2 + H = H_2 + HO_2$, $H + O_2 = OH + O$, $H_2 + O = OH + O$ and methane-based reactions such as $CH_4 + O_2 = CH_3 + HO_2$, $CH_4 + OH = CH_3 + H_2O$, $CH_3 + O_2 =$

CH_2O + OH were presented in the sensitivity analyses for both mixtures. However, for methane-rich mixtures, reactions $CH_2O + OH = HCO + H_2O$ and $CH_4 + HO_2 = CH_3 + H_2O_2$ were found to be more important, while for hydrogen-rich mixtures, reactions $OH + HO_2 = H_2O + O_2$ and $HO_2 + H = OH + OH$ were found to be more important. This is an indicator that by increasing methane concentration and therefore the amount of carbon atoms, the effect of hydrogen is reduced significantly.

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