Abstract: The paper describes a numerical study of the combustion of hydrogen enriched methane and biogases containing hydrogen in a Controlled Auto Ignition engine (CAI). A single cylinder CAI engine is modelled with Chemkin to predict engine performance, comparing the fuels in terms of indicated mean effective pressure, engine efficiency, and pollutant emissions. The effects of hydrogen and carbon dioxide on the combustion process are evaluated using the GRI-Mech 3.0 detailed radical chain reactions mechanism. A parametric study, performed by varying the temperature at the start of compression and the equivalence ratio, allows evaluating the temperature requirements for all fuels; moreover, the effect of hydrogen enrichment on the auto-ignition process is investigated. The results show that, at constant initial temperature, hydrogen promotes the ignition, which then occurs earlier, as a consequence of higher chemical reactivity. At a fixed indicated mean effective pressure, hydrogen presence shifts the operating range towards lower initial gas temperature and lower equivalence ratio and reduces NOx emissions. Such reduction, somewhat counter-intuitive if compared with similar studies on spark-ignition engines, is the result of operating the engine at lower initial gas temperatures.

Keywords: methane; biogas; gaseous fuels; hydrogen; combustion; internal combustion engine; controlled auto ignition; engine efficiency; NOx emissions

1. Introduction

One of the problems of today’s society regards the depletion of energy sources and their increase of cost. Just consider, e.g., that nowadays unconventional oils, i.e., oils rich in asphaltenes and waxes [1], represent the vast majority of the world oil reserves and their exploitation is technically difficult and expensive [2]. Moreover, the intensification of the energy demand and the consequent climate changes induced by carbon dioxide and other greenhouse gases suggest an increase in the use of renewable energy. An important role can be played by biofuels whose use is spreading thanks to the advantages they offer in terms of immediate energy availability and reduced environmental impact, to be correctly evaluated through a life cycle assessment, allowing, in fact, a strong reduction of CO2 emissions [3]. Moreover the use of biofuels is also becoming mandatory to fulfil the European directive on renewable energy (Directive 2009/28/EC) [4] establishing that all EU countries must ensure that at least 10% of their fuels for road vehicles come from renewable sources by 2020. The most common biofuels are bioethanol, biodiesel, and biogas.

Bioethanol is a liquid biofuel that can be used in spark ignition engines both blended with gasoline (E10, E20, etc.) or as an almost pure fuel (E85, E100), the number representing the ethanol percentage
content in the blend [5]. Bioethanol can also be used as blended with diesel oil in compression ignition engines [6], similar to biodiesel derived from the transesterification of vegetable oils, which can be used in different percentages ranging from 5% to 100% [7]. These fuels can generally be used with minor engine modifications or no modifications when present in low percentages [3].

Biogas, made of methane and carbon dioxide, is produced from the anaerobic digestion of organic matter. The most important raw materials for biogas production are municipal solid waste [8], farm waste, domestic garbage landfills [9], sewage sludge [10], agricultural products, rice paddies waste, energy crops, palm oil mill effluents [11], animal manure [12,13], and coal mining waste [14].

Despite its composition depending on the feedstock and the production process, conventional biogas is typically composed of 55–65% of methane, 30–40% carbon dioxide, and traces of hydrogen sulphide. The aerobic decomposition of the organic matter previously described produces greenhouse gases, so the use of biogas as a fuel is particularly beneficial for the environment.

The use of biogas in internal combustion engines is therefore very attractive even if in presence of an inert gas like CO$_2$ has adverse effects on combustion, reducing laminar flame speed and narrowing flammability limits [15,16]. In internal combustion engines, a slower combustion causes a larger combustion angle with a consequent negative effect on engine thermal efficiency [17]. CO$_2$ dilution also reduces combustion stability [18]. As flame speed slows down due to the presence of inert gases or excess air, combustion evolution becomes erratic and significant differences appear between consecutive indicated cycles. Such cyclic variations cannot exceed a certain threshold, expressed as the Coefficient of Variation (COV) of indicated work or of peak cylinder pressure. If such limits are overcome, engine operation becomes unacceptably irregular [19].

The addition of hydrogen to gaseous fuels may represent a possible way to increase their laminar flame speed. Ma et al. [20] experimentally investigated a lean burn engine fuelled with hydrogen-enriched natural gas and they observed a reduction in combustion angle as hydrogen content increased. The addition of hydrogen in gaseous fuels also improves combustion stability, reducing cycle-by-cycle variations. Indeed, Mariani et al. observed a reduction of COV in indicated mean effective pressure promoted by hydrogen addition to natural gas in a spark ignition engine [21].

The effect of the addition of hydrogen to a biogas was also investigated in the literature, particularly in spark ignition engines [22]. Chung et al. [23] studied the combustion performance of H$_2$/biogas in a spark ignition engine by numerical simulation; they showed that the rate of heat release increases while increasing H$_2$ content. Rakopoulos et al. [24] used a quasi-dimensional multi-zone model to study the biogas/hydrogen combustion in a single cylinder engine; they concluded that the addition of increasing amounts of H$_2$ in biogas results in a decrease of the flame development period. Park et al. studied the performance and emission characteristics of biogas mixed with hydrogen in SI engine [25,26]; they found that the presence of inert gases in the biogas can improve thermal efficiency and reduce NOx emissions; however, HC emissions and cycle variation increase. Li et al. investigated the effect of hydrogen enrichment on combustion and heat release of a biogas; they concluded that the overall reaction rate increases with H$_2$ concentration [27].

Internal combustion engines are operated very frequently at part load, especially in passenger car applications. In these operating conditions, engine efficiency is negatively affected by the combined effect of the increased relative incidence of rubbing friction, and in spark ignition engines, by intake air throttling losses [19]. An alternative to the conventional spark ignited combustion is the Controlled Auto-Ignition (CAI) combustion, allowing operation of the engine at part loads with considerable air excess, thus eliminating the need for throttling. CAI combustion is triggered by auto ignition instead of by spark ignition and subsequent flame front propagation [28]. Thanks to its characteristics, CAI combustion attracted some attention in the literature [29–32]. It is characterized by the absence of a flame front propagation and by an extremely rapid evolution. This allows an efficiency improvement, limited however by the constraint that cylinder pressure rise rate cannot exceed certain values in order to prevent unacceptable mechanical and thermal loads [29]. Biogases were also used to fuel CAI engines and the influence of the amount of combustion products recycled on combustion timing and
angular duration was investigated [30]; Jamsaran et al. [33] investigated the auto-ignition reactivity of natural gas with regard to the effects of intake air temperature and equivalence ratio; Nishi et al. [34] studied the effects of EGR ratio and engine speed on HCCI combustion; and Ibrahim et al. [35] improved the performance and extended the load range of hydrogen fuelled homogeneous charge compression ignition (HCCI) engine through charge temperature regulation and the addition of carbon dioxide in order to control the combustion phasing.

Biogas, when used in spark ignition internal combustion engines, induces an unavoidable power reduction, due to the presence of inert gases. The authors here numerically investigate biogas suitability for fuelling Controlled Auto Ignition (CAI) engines that are operated in lean conditions. If CAI engines are fuelled with a biogas, a possible change of the equivalence ratio may allow for the avoiding of engine power reduction, which is always experienced in spark ignition engines. Similarly, the effect of the presence of hydrogen in the biogas fuelled to a CAI engine is here numerically investigated for the first time in the literature. The authors compare engine performance and exhaust emissions varying fuel composition. Six different fuel compositions are selected: First, the authors focus on natural gases eventually enriched with hydrogen that are in order: Pure methane, methane with 10% of hydrogen, methane with 20% of hydrogen, successively three different biogases are considered: A biogas made of methane and carbon dioxide, two innovative biogases containing hydrogen, and thus made of methane, hydrogen, and carbon dioxide with a ratio $H_2/CH_4$ equal to 1/9 and 2/8, respectively.

The detailed chemical kinetics is taken into account with ANSYS Chemkin 17.0 that allows modelling a single cylinder CAI engine to predict engine performance in terms of Indicated Mean Effective Pressure (imep), engine efficiency, and pollutant emissions. Initial temperature and equivalence ratio are optimized for each fuel, and by comparing the results it is possible to understand the effect of hydrogen addition on the combustion process in CAI engines.

A parametric study, performed varying the temperature at the start of compression and the equivalence ratio, allowed to evaluate the temperature requirements for all fuels and the effect of hydrogen addition on the auto-ignition process. The results show that, at constant initial temperature, hydrogen promotes the ignition, which then occurs earlier, as a consequence of higher chemical reactivity. At a fixed indicated mean effective pressure, hydrogen presence shifts the operating range towards lower initial gas temperature and lower equivalence ratio and reduces the NOx emissions. Such reduction, somewhat counter-intuitive if compared with similar studies on spark-ignition engines, is the result of operating the engine at lower initial gas temperatures thanks to the presence of hydrogen.

2. Methods

2.1. CAI Engine

Controlled Auto-Ignition combustion has the potential of combining together the advantages of spark ignition and compression ignition engines. They are characterized by a combustion triggered by the auto ignition of the charge. The process is characterized by an extremely rapid evolution with high thermal efficiency, however cylinder pressure rise rate cannot exceed certain limits in order to prevent unacceptable mechanical and thermal loads and unacceptable noise.

With the absence of flame front propagation, the CAI combustion process is dominated by chemical kinetics. Implementation of a detailed reaction mechanism is therefore necessary for CAI combustion analysis.

In this paper, the complex gas-phase chemical kinetics is solved with Chemkin 17.0 [36] and the detailed radical chain reactions mechanism is the GRI-Mech 3.0 [37], which is designed for methane combustion. It is composed by 325 elementary chemical reactions and 53 species, including those to predict NOx formation; all kinetic constants are provided. The mechanism is available in the literature [37], and for the sake of brevity, the authors prefer not to report it here. GRI-Mech 3.0 mechanism includes all the reactions required to accurately describe hydrogen combustion and it is thus appropriate to also study the combustion of mixtures of methane, hydrogen, and carbon dioxide,
as those investigated in this paper. All the thermodynamics and transport parameters of the species of the reaction mechanisms are available in Chemkin libraries.

The combustion process of a CAI engine, fed with different gaseous fuels, is studied in this paper using the Package HCCI of Chemkin 17.0 that allows simulating the engine cycle, except the gas exchange process. The CAI model simulates the combustion in an internal combustion engine under auto-ignition conditions. The implemented single-zone CAI combustion model permits detailed description of the chemical kinetics by assuming homogeneous gas properties in the combustion chamber. The single-zone model can adequately predict ignition. However, because it does not account for low-temperature regions within the thermal boundary layers and crevices, the model underestimates carbon monoxide and unburned hydrocarbon emissions. For this reason NOx emissions only are here considered.

The Internal Combustion Engine CAI model has the feature of defining a convective heat loss from the gas to the solid walls. The heat losses are calculated according to:

\[ Q_{\text{wall}} = h \cdot A \cdot (T - T_{\text{wall}}) \]  

where \( A \) is the surface involved in the heat transfer process, \( h \) is the heat transfer coefficient, \( T \) the gas temperature, and \( T_{\text{wall}} \) the cylinder wall temperature set at 400 K. The heat transfer coefficient is obtained from the generalized heat transfer correlation, Equation (2):

\[ Nu_h = a \cdot Re^b \cdot Pr^c \]  

where \( Nu_h \) is the Nusselt number defined as: \( h \cdot \text{Bore}/(\text{Thermal conductivity}) \), \( Re \) is the Reynolds number, defined in an engine as \( Re = \left[ \text{Stroke} \cdot (\text{Engine Speed} \cdot \text{Bore}) / [30 \cdot \nu(T)] \right] \), and \( Pr = \nu/\alpha \) is the Prandtl number, where \( T \) is the cycle mean temperature, \( \nu \) is the gas kinematic viscosity, and \( \alpha \) the thermal diffusivity, \( a \), \( b \), and \( c \) are constants with values 0.37, 0.75, and 0.4 respectively.

The main characteristics of the engine selected for the simulations are reported in Table 1. This type of engine is used for stationary applications, i.e., power generation at constant engine speed (usually 1500 rpm). The investigated engine is supercharged, as a consequence cylinder pressure at start of compression is above ambient pressure. Temperature at the start of compression can be controlled by varying the amount of residual gases in the cylinder using, e.g., an EGR system [30–32]. The presence of residual gases has an impact on the combustion process as the burning mixture composition consequently changes. In this analysis, the authors did not consider the presence of residual gases and set the initial gas temperature as an independent parameter and thus no EGR is accounted for.

### Table 1. Engine parameters and operating conditions.

| Engine type             | 4-stroke |
|-------------------------|----------|
| Compression ratio       | 16.7:1   |
| Bore [mm]               | 135      |
| Stroke [mm]             | 170      |
| Engine speed [rpm]      | 1500     |
| Initial gas pressure (BDC) [bar] | 2       |

2.2. Fuels

The authors here focus on biogas, typically obtained from the dark anaerobic digestion of organic matter and mainly composed of methane and carbon dioxide. The molar ratio \( \text{CH}_4/\text{CO}_2 \) in a biogas can be predicted with Buswell equation for the anaerobic digestion of organic matter [38]:

\[
C_nH_{4a}O_{b}N_{d} + \left( n - \frac{a}{4} - \frac{b}{2} + \frac{3d}{4} \right) \text{H}_2\text{O}
\Rightarrow \left( \frac{n}{2} + \frac{a}{8} - \frac{b}{4} - \frac{3d}{8} \right) \text{CH}_4 + \left( \frac{n}{2} - \frac{a}{8} + \frac{b}{4} + \frac{3d}{8} \right) \text{CO}_2 + d\text{NH}_3
\]
Equation (3) predicts a CH$_4$/CO$_2$ ratio ranging from 1, for simple carbohydrates like starch (C$_6$H$_{10}$O$_5$)$_n$, or proteins (C$_5$H$_7$NO$_2$) to 2.35, for the conversion of lipids, e.g., C$_{57}$H$_{104}$O$_6$. It is experimentally found that for the fermentation of water buffalo manure the CH$_4$/CO$_2$ ratio is about 2 [39,40]. Being 2 is an intermediate value among the possible ones, we keep the CH$_4$/CO$_2$ ratio constant and equal to 2 in all the biogases investigated in our simulations.

Innovative digestion processes are developing where H$_2$ yield is maximized [41] so to produce a biogas mainly made of CH$_4$, H$_2$ and CO$_2$. Since H$_2$ enrichment of natural gas proved to have positive effects on the combustion in internal combustion engine, we here investigate the use of innovative biogases, which already contain hydrogen, in CAI engines. Water buffalo manure naturally contains the eubacteria responsible of the hydrogen production [42] and indeed it is a promising substrate to produce the innovative biogas [43]. It is experimentally shown that in the innovative biogas from water buffalo manure, the final H$_2$/CO$_2$ molar ratio is about 1 with a H$_2$/CH$_4$ molar ratio reaching a maximum of 0.25 [44]. The authors thus decided to keep H$_2$/CO$_2$ molar ratio value constant and equal to 1 in the innovative biogases studied and to investigate two different H$_2$/CH$_4$ ratios equal to 1/9 and 2/8, respectively.

To better highlight the effect of the presence of hydrogen in CAI engine combustion we also investigated the use of pure methane, i.e., of a natural gas, and of two mixtures of methane and hydrogen with molar ratio equal to those found in the innovative biogas.

The authors then investigate the behaviour of a CAI engine fuelled with six different gas blends whose compositions are summarized in Table 2 and Figure 1.

**Table 2. Fuels composition.**

| Fuel        | CH$_4$ Molar Fraction | H$_2$ Molar Fraction | CO$_2$ Molar Fraction |
|-------------|------------------------|-----------------------|------------------------|
| CH4         | 1.00                   | 0                     | 0                      |
| CH4H$_2$ _1 | 0.90                   | 0.10                  | 0                      |
| CH4H$_2$ _2 | 0.80                   | 0.20                  | 0                      |
| Biogas 1    | 0.67                   | 0                     | 0.33                   |
| Biogas 2    | 0.580                  | 0.065                 | 0.355                  |
| Biogas 3    | 0.500                  | 0.125                 | 0.375                  |

**Figure 1.** Fuels composition.

Hydrogen is a gas of very low density with a critical temperature of −239.91 °C. On a volume basis, it requires less air than methane for a stoichiometric combustion, whereas it is the opposite on mass basis, Table 3. The effect of the low hydrogen density is also important on the heating value. When the
mass based lower heating value is considered, hydrogen shows a very high energy content per kg of gas, much higher than methane, conversely on volumetric base, the opposite holds. Hydrogen has a higher auto-ignition temperature, thermal conductivity, and Octane Number than methane. In spark ignition engines, important properties are also its fast flame speed and wide flammability limits.

| Table 3. Methane and hydrogen properties [45]. |
|-----------------------------------------------|
| CH<sub>4</sub> | H<sub>2</sub> |
| Density [kg/Nm<sup>3</sup>] | 0.7064 | 0.0888 |
| Stoich AFR [mass air/mass fuel] | 17.2 | 34.3 |
| Stoich AFR [vol air/vol fuel] | 9.54 | 2.39 |
| Lower Heating Value [MJ/kg] | 50 | 119.9 |
| Lower Heating Value vol. [MJ/Nm<sup>3</sup>] | 35.32 | 10.64 |
| Auto-ignition temperature [°C] | 813 | 858 |
| Thermal conductivity at 300 K [W/(m K)] | 0.034 | 0.182 |
| Octane Number | >120 | >130 |
| Laminar flame speed at stoich. conditions [m/s] | 0.38 ÷ 0.40 | 2 ÷ 2.2 |
| Flammability limits in air [%vol.] | 5.3–15 | 4–75 |

2.3. Engine Operating Parameters

Equivalence ratio (ER) is defined as the ratio between the actual and the stoichiometric fuel-to-air mass ratio:

\[ ER = \left( \frac{m_f}{m_a} \right)_{actual} / \left( \frac{m_f}{m_a} \right)_{stoic} \] (4)

CAI’s operate with lean air-fuel mixtures (ER < 1) in order to have a better control of pressure gradient in the cylinder. For this reason, the analysis is carried out considering ER = 0.4 as a reference value for methane [30].

Indicated Mean Effective Pressure (imep) is an engine performance index independent from engine size, obtained dividing the indicated work per cycle by the displacement, \(V_d\):

\[ imep = \frac{\int pdV}{V_d} \] (5)

Engine indicated efficiency is defined as:

\[ \eta_i = \frac{P_i}{m_f \cdot LHV} \] (6)

where \(P_i\) is the indicated power, \(m_f\) is the fuel mass flow, LHV the lower heating value of the fuel.

3. Results and Discussion

3.1. Methane and Methane-Hydrogen Blends

Combustion in CAI engines strongly depends on the initial gas temperature, as reported in Figure 2 for methane. At 458 K the charge does not burn, while increasing the temperature combustion start angle moves towards the top dead center because in-cylinder gases reach earlier the thermodynamic conditions for auto-ignition. Engine indicated efficiency consequently changes: If the auto-ignition occurs too late, peak cylinder pressure is positioned later in the expansion stroke and is reduced in magnitude with negative effects on imep; if it is too advanced, peak cylinder pressure occurs
too early so increasing the compression work [19]. Figure 3 shows this trend: The best combustion phasing for methane is obtained at 468 K initial temperature, where the indicated efficiency attains its maximum value, with the engine delivering 8.4 bar imep with 47.6% efficiency.

![Pressure traces versus crank angle at different initial gas temperatures (methane)](image)

**Figure 2.** Pressure traces versus crank angle at different initial gas temperatures (methane). The thicker line shows the best operating conditions.

![Indicated efficiency and imep (methane and methane-hydrogen blends)](image)

**Figure 3.** Effect of initial gas temperature on indicated efficiency and imep (methane and methane-hydrogen blends). The best operating conditions are circled.

Adding hydrogen to methane causes the ignition to happen earlier (closer to the top dead center) for a constant initial temperature, as depicted in Figure 4.

Peak cylinder pressure with hydrogen blends is higher than that obtained using methane, but this does imply neither higher engine efficiency, nor higher imep, as shown in Figure 3. Indeed, the combustion for CH$_4$/$H_2$ blends at 468 K starts too early, and as discussed above, this reduces both imep and efficiency. However, since hydrogen has a wider flammability, which limits its addition and
extends the CAI operational range allowing the engine to run with lower initial gas temperatures. The best operative conditions can be found maximizing both imep and efficiency and it can be observed from Figure 3 that if the engine is operated at temperature between 443 K and 463 K, it would deliver a higher imep with engine efficiency slightly higher than methane.

**Figure 4.** Pressure traces versus crank angle (methane and methane-hydrogen blends).

Using methane-hydrogen blends, ER is adjusted to get 8.4 bar as maximum imep, the same value as for methane. While the maximum imep for methane is attained at 468 K, the initial gas temperature requirement for CH4H2_1 drops to 448 K with an ER of 0.38, Figure 5. It is worthwhile noting that by varying the ER, the efficiency remains practically constant and CH4H2_1 showed an efficiency at the optimal operative conditions similar to that of methane, Figure 5.

**Figure 5.** Effect of initial gas temperature on indicated efficiency and imep (methane and CH4H2_1). The best operating conditions are circled.
Results are similar with CH4H2_2 blend and also in this case the equivalence ratio is adjusted to keep the maximum imep equal to that of methane. In this case, the optimal initial temperature is 443 K so that engine delivers a maximum imep of 8.6 bar with ER = 0.38, Figure 6. Additionally, in this case the maximum indicated efficiency does not change significantly. The increase of hydrogen content induced a further reduction of the initial temperature.

Figure 6. Effect of initial gas temperature on indicated efficiency and imep (methane and CH4H2_2). The best operating conditions are circled.

Figure 7 shows the pressure traces for methane and methane-hydrogen blends at the optimal operating conditions determined above. It can be observed that the maximum pressure values and peak pressure positions are similar for the considered fuels.

Figure 7. Pressure traces versus crank angle (methane and methane hydrogen blends).
3.2. Biogas and Innovative Biogases

Due to the presence of carbon dioxide in the biogas, more energy is required to ignite the combustion. Consequently, the initial temperature of CAI engine must be higher with biogas 1, made of methane and carbon dioxide, than with pure methane, Figure 8, and the temperature range assuring auto-ignition reduces. In these conditions, imep is smaller than that obtained fuelling the engine with pure methane at the same equivalence ratio. However, the engine fuelled with biogas 1 can be adjusted to obtain the same imep as that reached with pure methane with ER = 0.4, by varying the equivalence ratio. It is found that with ER = 0.42, with an initial temperature of 478 K, the CAI engine fuelled with biogas 1 delivers the same maximum imep as that with methane, Figure 8, and the associated indicated engine efficiency results of 47.1%.

As for pure methane, adding hydrogen to biogas makes the air-fuel mixture more reactive, and consequently, auto-ignition starts at lower temperatures. In biogas 2, a mole of hydrogen is produced together with 9 moles of methane, and carbon dioxide will accordingly increase, remembering that in the digestion process, the CO₂/H₂ ratio is 1, while CO₂/CH₄ is 2. Thus, in biogas 2, two opposite effects on the auto-ignition face, the decrease of the required initial gas temperature induced by hydrogen and its increase induced by carbon dioxide. We find that CAI engine fuelled with the innovative biogas 2 can be phased to obtain the same maximum imep, as with pure methane, keeping ER equal to 0.4, by simply reducing the initial gas temperature to 457 K, Figure 9. The same can be done by increasing the hydrogen content to obtain a CH₄/H₂ ratio equal to 8:2 in biogas 3, and the maximum imep value is reached with an initial gas temperature of 453 K and ER = 0.4. Thus, the effect of hydrogen on the auto-ignition prevails on that of carbon dioxide in the two innovative biogases considered; consequently, as already observed for methane-hydrogen blends, hydrogen in the biogas has the potential of shifting the initial temperature to lower values, and the more hydrogen, the lower the initial temperature.

As for the case of pure methane, the indicated efficiency of the CAI engine fuelled with biogases is almost constant when the optimal operational conditions are found, and for the sake of brevity, we do not report its graph.

![Figure 8. Effect of initial gas temperature on imep (methane and Biogas 1). The best operating conditions are circled.](image-url)
Figure 9. Effect of initial gas temperature on imep. Biogas 1 made of CH$_4$ and CO$_2$; Biogas 2 with CH$_4$/H$_2$ = 9:1; and Biogas 3 with CH$_4$/H$_2$ = 8:2 (see Table 2). The best operating conditions are circled.

Figure 10 shows the pressure traces for all biogases at optimal operating conditions. It can be observed that the maximum pressure values and peak pressure positions are similar for the considered fuels. The higher the hydrogen content, the lower the initial gas temperature required for auto-ignition. A lower equivalence ratio is required for the target imep when the engine is fuelled with innovative biogases that are mixtures of methane, hydrogen, and carbon dioxide, with hydrogen produced together with methane in the digestion process.

3.3. NOx Emissions

This section evaluates the potential of improving the emission behaviour of the engine when adopting hydrogen-enriched fuels in CAI combustion systems. We compare NOx in terms of specific emissions in order to consider the effect of exhaust mass flow variation on the emitted NOx mass.
Figure 11 show NOx emissions as a function of the initial gas temperature for methane, CH4H2_1, CH4H2_2 and for biogases, respectively. NOx emissions increase with the initial gas temperature, essentially because of a higher peak temperature attained in the combustion chamber. Initial gas temperature has a direct influence on both the in-cylinder peak temperature and the combustion ignition. An increase of initial temperature shifts auto-ignition towards top dead centre. The results of Figure 11 also show that, at a fixed initial temperature, the more the hydrogen in the fuel, the higher the NOx emissions. However, as previously explained, hydrogen addition increases fuels reactivity and influences the combustion phasing. NOx emissions, obtained at the optimal operating conditions, set in order to maximize imep, are shown in Figure 12. It is interesting to observe that hydrogen enrichment always allows a reduction of NOx emissions. This implies that the reduction of the initial gas temperature prevails over the increase of the peak temperature induced by hydrogen. It is also interesting to underline that at the optimal operating conditions, found to obtain the same maximum imep, the indicated efficiency remains the same by changing fuel, from pure methane to methane enriched with hydrogen, from conventional biogas to innovative ones.

![Figure 11](image1.png)

**Figure 11.** NOx [g/kWh] emissions as a function of the initial temperature, for methane and methane hydrogen blends. The best operating conditions are circled.

![Figure 12](image2.png)

**Figure 12.** NOx emissions and engine efficiency at optimal initial gas temperature.
The best operating conditions of each fuel considered in this paper, with the relative imep, indicated efficiency and NOx emissions are summarised in Table 4.

Table 4. ER, initial gas temperature and NOx emissions in optimal conditions.

| Fuel          | ER [-] | T_{in} [K] | imep [bar] | ηi [%] | NOx [g/kWh] |
|---------------|--------|------------|------------|--------|-------------|
| CH4           | 0.40   | 468        | 8.4        | 47.6   | 0.0249      |
| CH4H2_1       | 0.38   | 448        | 8.5        | 48.0   | 0.0120      |
| CH4H2_2       | 0.38   | 443        | 8.6        | 48.1   | 0.0113      |
| Biogas 1      | 0.42   | 478        | 8.4        | 47.1   | 0.0275      |
| Biogas 2      | 0.4    | 457        | 8.4        | 47.5   | 0.0112      |
| Biogas 3      | 0.4    | 453        | 8.4        | 47.3   | 0.0089      |

Table 4 summarizes the results for conventional and hydrogen enriched fuels at optimal initial gas temperature.

4. Conclusions

The paper describes a numerical study on the combustion of several methane-based fuels in a Controlled Auto Ignition engine. The authors studied pure methane and methane enriched with hydrogen at 10% and 20% of H₂, and for the first time, we also focused on three biogases. The biogases investigated are a conventional one with 66% of methane and 33% of carbon dioxide, and two innovative ones obtainable from digestion processes where the hydrogen yield is maximized. The latters are mixtures of methane, hydrogen, and carbon dioxide with methane/hydrogen ratio equal to 9:1 and 8:2, respectively. Due to the stoichiometry of the digestion process, the larger is the amount of hydrogen in the innovative biogas, the smaller will be the ratio Fuel/CO₂. Being Chemkin, the modelling environment, a single cylinder CAI engine was modelled to predict engine performance, comparing the fuels in terms of indicated mean effective pressure, engine efficiency, and NOx emissions. For the sake of simplicity, we used a single-zone model for CAI engines that is known to underestimate CO and HC emissions, whose analysis is here consequently neglected. The authors adopted the GRI-Mech 3.0 detailed radical chain reactions mechanism that, though derived for the combustion of a natural gas, it is appropriate to also study the combustion of all fuels investigated in this paper. In fact, all the elementary equations required to model the combustion of hydrogen are already present in the mechanism, as well as those involving CO₂. The comparison among the different fuels is performed by adjusting the CAI engine to obtain a constant maximum Indicated Mean Effective Pressure, imep, which is limited, in the CAI engine, by mechanical and thermal loads. The parameters were the initial gas temperature and the equivalence ratio.

We can summarise main results as follows:

- Methane-hydrogen mixtures require lower equivalence ratio (ER = 0.38) than methane (ER = 0.4) to deliver the same imep;
- Hydrogen addition to methane reduces the initial gas temperature requirement: In the optimal operating conditions with methane the initial gas temperature must be 468 K and drops to 448 K with the addition of 10% of hydrogen in CH4H2_1 blend and to 443 K with the addition of 20% of hydrogen in CH4H2_2 blend;
- Biogas 1 made of 66% methane and 33% carbon dioxide requires higher equivalence ratio (ER = 0.42) than methane (ER = 0.4) to deliver the reference imep due to the presence of CO₂ in the fuel. The initial gas temperature requirement also increases to 478 K;
- For the innovative biogas 2, with a CH₄/H₂ ratio equal to 9:1, the required initial temperature decreases to 457 K with an ER = 0.4;
• For the innovative biogas 3, with a CH$_4$/H$_2$ ratio equal to 8:2, the required initial temperature further decreases to 448 K with an ER = 0.4;
• Hydrogen enrichment of methane reduces NOx emissions due to a lower initial gas temperature requirement in comparison with pure methane. The higher the hydrogen molar fraction, the smaller the NOx emissions.
• For the innovative biogases NOx emissions decrease by increasing the amount of H$_2$ in the biogas. Additionally, in this case, this is due to a lower initial gas temperature requirement in comparison with both pure methane and the conventional biogas.
• Though the initial temperature is higher, the innovative biogases show slightly lower NOx emissions than those of the equivalent blends of methane and hydrogen.

The obtained results are encouraging and opposite to what is known to happen with a spark-ignited engine. When hydrogen is added to methane in a SI engine an increase of NOx emissions is always predicted because of the increase of peak temperature. On the contrary, with CAI engine the addition of hydrogen induces a reduction of the initial gas temperature that prevails over the increase of the in-cylinder peak temperature with the consequent beneficial reduction of NOx emissions. More relevant are the results obtained with the use of biogases. If a conventional biogas is fed to a SI engine a power reduction is unavoidable because of the inert charge carried by the fuel. On the contrary, with CAI engines, which typically operate under lean conditions, it is enough to slightly increase the equivalence ratio to regain the same imep obtained with pure methane. The initial gas temperature must be increased to ignite the biogas, but despite this, the NOx emissions remain almost unvaried with respect to pure methane. With the innovative biogases containing hydrogen, keeping the imep constant, not only the equivalence ratio can be kept unvaried with respect to pure methane, but NOx emissions significantly reduce with respect to both conventional biogas and pure methane. They slightly reduce with respect to the equivalent hydrogen-methane mixture even if the initial gas temperature of biogases is higher than those of H$_2$-CH$_4$ blends.

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