

Modelling and analyzing the impact of hydrogen enriched natural gas on domestic gas boilers in a decarbonization perspective



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HIGHLIGHTS

- An insight is given on the future of gaseous fuels within a sustainable energy system.
- A model for calculating the most relevant parameters of the hydrogen/methane blends combustion is presented.
- Advantages and criticalities of utilizing hydrogen/methane blends in domestic heating are analyzed.
- A case study is conducted on a today's condensing boiler. Design guidelines are provided for the main components.
- The maximum amount of hydrogen allowing a safe and efficient operation on a today's domestic boiler is identified.

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ABSTRACT

Decarbonization of energy economy is nowadays a topical theme, and several pathways are under discussion. Gaseous fuels have a fundamental role for this transition, and the production of low carbon-impact fuels is necessary to deal with this challenge. The generation of renewable hydrogen is a trusted solution since this energy vector can be promptly produced from electricity and injected into the existing natural gas infrastructure, granting storage capacity and easy transportation. This scenario will lead, in the near future, to hydrogen enrichment of natural gas, whose impact on the infrastructures is being actively studied. The effect on end-user devices such as domestic gas boilers, instead, is still little analyzed and tested, but is fundamental to be assessed. The aim of this research is to generate knowledge on the effect of hydrogen enrichment on the widely used premixed boilers: the investigations include pollutant emissions, efficiency, flashback and explosion hazard, control system and materials selection. A model for calculating several parameters related to combustion of hydrogen enriched natural gas is presented. Guidelines for the design of new components are provided, and an insight is given on the maximum hydrogen blending bearable by the current boilers.

1. Introduction

Energy systems are evolving to reduce their environmental impact and face the challenges related to climate change, pollution, depletion of resources and growing global population. The future energy system is expected to be based on clean and renewable sources (RES), able to provide energy with a low carbon dioxide (CO₂) emission. In Europe, local and worldwide agreements pushed the States through low-carbon technologies: the Kyoto protocol signed in 1997 and enforced in 2005 by imposing all members to decrease the greenhouse gases emissions, the Climate and Energy Package signed in 2007, the COP21 agreement concluded in Paris in 2015. The European decarbonization strategy targets the 75% of final energy consumption from renewables in 2050. Decarbonization involves electricity supply, thermal energy supply to

buildings and industries, and transports. It is known that RES production is less constant and predictable than fossil-based, and that an environmentally friendly system based on electricity implies significant challenges in the electric grid management and leads to price volatility. Thus, there is a need for novel technologies allowing energy storage and grid balancing, involving an energy carrier with low shipment losses, easy transportation and easy storage.

A promising technology is power-to-gas (P2G), allowing to transform electricity into hydrogen (H₂) – that is a very flexible energy vector – or into other fuels. P2G is a technological chain whose primary step is water electrolysis process taking place in electrolytic cells, having a fast response time. The hydrogen produced can be injected directly in the natural gas grid, or used to produce methane by means of methanation process [1]. When the energy input of the P2G process

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comes from renewable energy, the fuel produced is theoretically zero carbon, and in this case hydrogen is often referred as “green hydrogen” [2].

Another decarbonisation pathway is the transformation of fossil hydrocarbons coupled with carbon capture and sequestration (CCS) technologies. Transformation of hydrocarbons allows to continue the exploitation of existing methane reservoirs, potentially with zero carbon impact. In fact, fossil methane can be transformed (for example, by steam methane reforming, or thermal dissociation) into H₂ and CO₂, and the coupling with CCS technologies avoid the release of this last component in the atmosphere [3]. The hydrogen produced in this way is usually referred as “blue hydrogen”.

Whichever would be the prevailing decarbonisation pathway, depending also on the evolution of technological and economic aspects [1,3], the future of natural gas will involve the usage of mixed H₂ and methane, also reported in literature as Hydrogen Enriched Natural Gas (HENG). The compatibility of HENG with the current production-to-consumption infrastructures is being studied and assessed with a consistent effort; in this context, the residential utilization of gas deserves special attention, both for the entity of the consumption and for the technological challenges [4,5].

The final energy consumption of residential sector in Europe is projected to keep its share up to 2050, consisting almost the 30% of the total European energy consumption. The most significant part of residential consumption (65% in 2010, projected to be still 58% in 2050) is employed for heating purposes; the share of gaseous fuels in the residential consumption is also not expected to vary significantly up to 2050 [5–7]. Gaseous fuels are used to provide water heating, space heating, and cooking; clearly, the demand varies depending on climate, building size and construction technology. Strategies for decarbonization of residential building energy services must involve the adoption of more energy efficient appliances, the improvement of thermal properties of buildings, the change of energy consumer behaviour and, indeed, the use of more environmentally sustainable fuels. The need for these changes is even more crucial when considering developing countries beyond Europe, whose building energy consumption is expected to reach soon those of developed nations. Building energy request in China is projected to double within this century, while for India the projected increase is fivefold [4]. Therefore, any serious action targeting the mitigation of climate change has to include decarbonization of the fuels used in residential sector.

The utilization of hydrogen enriched natural gas by the final consumers, by the way, requires to overcome technical challenges that are currently not extensively studied and fully understood, especially about the widely used premixed combustion appliances (e.g. domestic condensing boilers) [8,9]. This fact, together with the relevant impact of domestic heating on final energy consumption, has driven the Authors to perform this study exploiting their experience on gas fired appliances [5,10–13].

The aim of the research is to identify the potentialities and challenges related to the combustion of HENG in domestic gas boilers, by means of theoretical modelling and examination of case studies based on real applications. The impact of hydrogen enrichment is evaluated on the main components of a domestic methane fired boiler, and guidelines for the design review are provided. Finally, the maximum admissible hydrogen enrichment allowing to keep the structure of today's devices is suggested.

The rest of the paper is organised as follows: in Section 2 modelling and regulatory insights are presented, in Section 3 the results are presented and discussed, and finally in Section 4 Conclusion remarks are given.

Table 1
Properties of methane and hydrogen [14].

Property	Methane	Hydrogen
Density [kg/m ³]	0.68	0.09
Flammable range [%vol]	4.4–17.0	4.0–75.0
Laminar burning velocity [m/s]	0.4	3.1
Minimum spark ignition energy [mJ]	0.210	0.016
Autoignition temperature [°C]	600	560
Higher Heating Value [MJ/m ³]	39.8	12.7
Lower Heating Value [MJ/m ³]	35.8	10.8

2. HENG mixtures: characterization, modelling, regulatory aspects

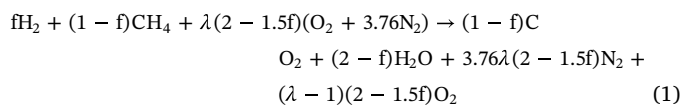
2.1. Properties of hydrogen and methane

Table 1 reports the main characteristics of H₂ and CH₄ fuels, constituting the base elements for the HENG mixtures.

Relevant differences are detectable in the properties of the fuels, and the effects are discussed in the following paragraphs.

2.2. Modelling of HENG mixtures properties and combustion

Modelling of HENG mixture properties and combustion reaction has been implemented, based on chemical reactions and on equations for gaseous mixtures properties. Eq. (1) describes the reaction in the hypothesis of complete combustion of a generic methane/hydrogen mixture. Volumetric hydrogen percentage is indicated with f , while λ is defined as the ratio between the actual air–fuel ratio and the stoichiometric air–fuel ratio (also referred in literature as air–fuel equivalence ratio).



The composition of the combustion products is very important for the evaluation of carbon impact. Equally important for the subsequent evaluations is the calculation, for given f and λ , of stoichiometric and actual fuel and air volumes. For any f and λ , Eq. (2) defines the ratio between air volume and fuel volume (AFR).

$$\text{AFR} = 4.76\lambda(2 - 1.5f) \quad (2)$$

The well-known stoichiometric air–fuel ratio of pure methane combustion (equal to 9.52) can be easily recognized in the Eq. (2) when giving to lambda a unitary value and to f a null value.

CO₂ and O₂ contents are usually measured in the flue gases during experimental tests [10], to detect the actual air–fuel ratio (or, in other terms, the excess air) for a known value of f . The calculation of volumetric exhaust composition is usually referred to the dry conditions, thus considering water completely condensed: under this hypothesis, CO₂ calculation is expressed in (3), derived from (1), and furtherly simplified in (4).

$$\text{CO}_2[\% \text{vol}] = \frac{(1 - f)}{(1 - f) + 3.76\lambda(2 - 1.5f) + (\lambda - 1)(2 - 1.5f)} \quad (3)$$

$$\text{CO}_2[\% \text{vol}] = \frac{(1 - f)}{9.52\lambda + 0.5f - 7.14\lambda f - 1} \quad (4)$$

Similarly, the oxygen concentration in the exhaust is calculated in (5), simplified in (6).

$$\text{O}_2[\% \text{vol}] = \frac{(\lambda - 1)(2 - 1.5f)}{(1 - f) + 3.76\lambda(2 - 1.5f) + (\lambda - 1)(2 - 1.5f)} \quad (5)$$

$$\text{O}_2[\% \text{vol}] = \frac{(\lambda - 1)(2 - 1.5f)}{9.52\lambda + 0.5f - 7.14\lambda f - 1} \quad (6)$$

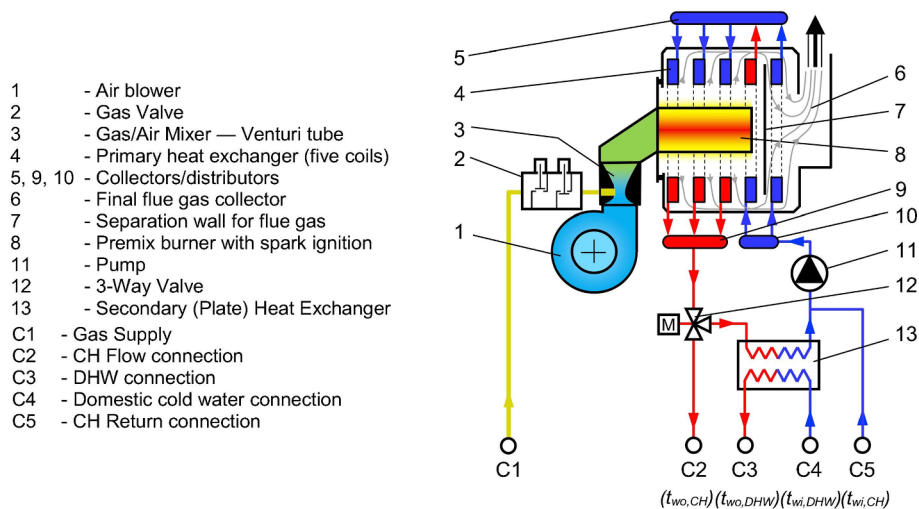


Fig. 1. Schematic of a condensing boiler system [35].

The lower heating value (LHV) of the fuel mixture is calculated by Eq. (7).

$$\text{LHV}_{\text{mix}} = f\text{LHV}_{\text{H}_2} + (1 - f)\text{LHV}_{\text{CH}_4} \quad (7)$$

Similarly, density of the mixture is calculated by Eq. (8).

$$\rho_{\text{mix}} = f\rho_{\text{H}_2} + (1 - f)\rho_{\text{CH}_4} \quad (8)$$

Given that the heat input (in terms of fuel power intake) is one of the parameters commercially characterizing a real application [9], Eq. (9) is given to calculate the fuel flow V_f based on the heat input Q .

$$V_f = \frac{Q}{\text{LHV}} \quad (9)$$

Once the fuel flow V_f is known, the air flow is calculated based on Eqs. (1) and (2).

Being decarbonization one of the main drivers for the introduction of HENG, an equation for the calculation of carbon dioxide volume (V_{CO_2}) emission per unit energy (E_f) of the HENG mixture has been developed (10). The calculation regards only the carbon emission related to the combustion of the fuel.

$$\frac{V_{\text{CO}_2}}{E_f} = \frac{1 - f}{f\text{LHV}_{\text{H}_2} + (1 - f)\text{LHV}_{\text{CH}_4}} \quad (10)$$

From (10), an equation for calculating the carbon dioxide mass (m_{CO_2}) per unit energy (E_f) of the HENG fuel is derived (11), where d_{CO_2} represents the density of CO_2 .

$$\frac{m_{\text{CO}_2}}{E_f} = \frac{d_{\text{CO}_2}(1 - f)}{f\text{LHV}_{\text{H}_2} + (1 - f)\text{LHV}_{\text{CH}_4}} \quad (11)$$

Finally, the mass flow of water contained in the combustion products ($\dot{m}_{\text{H}_2\text{O}}$) is calculated, based on the model, in the form of Eq. (12), where $d_{\text{H}_2\text{O}}$ represents the density of water vapour, for the convenience of the subsequent calculations.

$$\dot{m}_{\text{H}_2\text{O}} = V_f (2 - f) d_{\text{H}_2\text{O}} \quad (12)$$

2.3. Reference concept for domestic premixed device

The Authors analysed numerous domestic premixed boilers, both by consulting technical documents from manufacturers and by examining real devices, with the aim to identify a typical structure to be adopted as state of the art for the analysis. Notwithstanding several minor differences and peculiarities due to design options, the structure shown in Fig. 1 can be taken as a reasonable reference for the components and

the operating principle of a domestic condensing boiler.

This structure constitutes the base for the investigations explained in Section 3, where for the main components the effect of hydrogen addition to the fuel is studied, keeping the characteristics of current boilers as state of the art.

2.4. Regulatory context for gas fired boilers

The current European regulation [15] for gas boilers provides mixtures of methane and hydrogen, up to 23% H_2 , as limit gases for devices nominally working with pure methane (thus, within the second family fuel gases, known as “natural gas” family). Higher H_2 percentages, up to 59%, are provided for the first family fuel gases (covering manufactured gas, or “town gas”). Table 2 reports relevant characteristics for these standardised mixtures.

In view of firing methane boilers with HENG, the G222 gas ensures that the boilers certified with this limit gas are able to run safely at least up to 23% H_2 content. The first family gases, as G110 and G112, give an interesting insight on the possibility to set up a safe operation with high hydrogen percentages, but the consistent amount of N_2 in these blends does not allow to draw a parallel with HENG mixtures. Clearly, safe operation with limit gas is an important point but is just a part of the landscape, that should include also efficiency and reliability of the device.

3. Results and discussion

3.1. Calculation of fuel mixture properties and combustion stoichiometry

Table 3 reports the calculation of fuel mixture properties, based on Eqs. (1) and (8), for different H_2 percentage. Fig. 2 shows the trends of stoichiometric CO_2 , AFR, and LHV as function of hydrogen fraction. Volumes in this paper are always referred to pressure 1013 mbar and temperature 0 °C.

While the H_2 fraction increases, density of the fuel and volumetric heating values decrease, meaning that a higher volume of fuel is needed to get the same energy. In parallel, the stoichiometric AFR gets reduced, meaning that a lower volume of air is needed to burn the same volume of fuel. Relative Wobbe index, calculated with the model, corresponds to the values found in [16].

The implications of the findings applied to a real case-study are described in paragraph 3.3.

Table 2
Standardised fuel mixtures containing hydrogen [15].

Gas family	Designation	Purpose	Composition [%vol]	LHV [MJ/m ³]
First	G110	Reference gas	26% CH ₄ , 50% H ₂ , 24% N ₂	13.95
First	G112	Light back limit gas	17% CH ₄ , 59% H ₂ , 24% N ₂	11.81
Second	G20	Reference gas	100% CH ₄	34.02
Second	G222	Light back limit gas	77% CH ₄ , 23% H ₂	28.53

3.2. Calculation of decarbonisation potentiality

Fig. 3 reports the CO₂ produced by combustion per unit energy of different fuels, based on Eq. (10) and (11). All the data regarding HENG have been calculated, while data for other fuels are taken from [17]. The emission calculated for natural gas (NG) with the model presented in this paper is in line with the emission value given in literature [17].

The graph clearly shows how the addition of hydrogen to natural gas decreases the CO₂ emission per unit energy of the fuel. The relation between hydrogen fraction and CO₂ emission reduction is non-linear due to the effect of varying heating value of the mixtures and to the general chemistry of the reaction, as described in paragraph 2.2.

3.3. Effect on fuel and air volumetric flows

In this section, the effect of hydrogen enrichment on fuel and air flows is investigated. A case-study is reported in Table 4, for a thermal load of 25 kW (referred to LHV) and an equivalence ratio of 1.25 (typical values for domestic boilers [5,12]). Fuel, air and total mixture flow have been calculated for different H₂ fractions.

The data of Table 4 show that to achieve the same thermal load (25 kW), a higher volume of fuel is needed when increasing the H₂ content of the HENG mixture.

The increase in volumetric fuel flow is significant, as visible in Fig. 4, due to the decrease in volumetric LHV: 3.3 times flow for pure H₂ fuel than for pure CH₄. Parallely, when increasing the H₂ content of the HENG mixture the air flow keeps decreasing to achieve the same thermal load with the same λ value: 0.8 times for pure H₂ fuel than for pure CH₄, due to the stoichiometry of reaction (1). As an overall result, the total reactants flow does not vary significantly (less than 4% variation between pure H₂ fuel than for pure CH₄).

Referring to the boiler model of Fig. 1, and considering only the pressure drop related to the fluid flows, a dimensional resizing is potentially needed for the fuel side components, such as the gas valve, the gas piping and the gas/air mixer, when the H₂ fraction is high. Referring to the data of Table 4, for example, a 40% hydrogen enrichment grade involves a 38% fuel flow increase, requiring already a check on the suitability of the components designed for methane. For the considered constant lambda value, instead, the components such as the blower, the manifold connecting the blower to the burner, and the flue gas collector can be kept dimensionally equal whatever the H₂ fraction is, since the fluid flow is varying slightly. The lambda value adopted in the case study (λ = 1.25) does not substantially affect the observations above.

A dedicated analysis, that cannot be limited to the bare pressure

Table 3
Calculations of fuel mixture properties for different H₂ fraction (f).

	f = 0%	f = 20%	f = 40%	f = 60%	f = 80%	f = 100%
f _{H₂} [-]	0,0	0,2	0,4	0,6	0,8	1,0
ρ mix [kg/m ³]	0,718	0,592	0,466	0,341	0,215	0,090
HHV [MJ/m ³]	35,88	30,86	25,84	20,82	15,80	10,78
LHV [MJ/m ³]	39,82	34,40	28,99	23,57	18,16	12,75
Relative Wobbe index [%]	100	94,7	89,3	84,2	80,4	84,9
Stoichiometric CO ₂ [%vol]	11,73	11,12	10,23	8,81	6,23	0,00
Stoichiometric AFR [-]	9,52	8,09	6,66	5,24	3,81	2,38

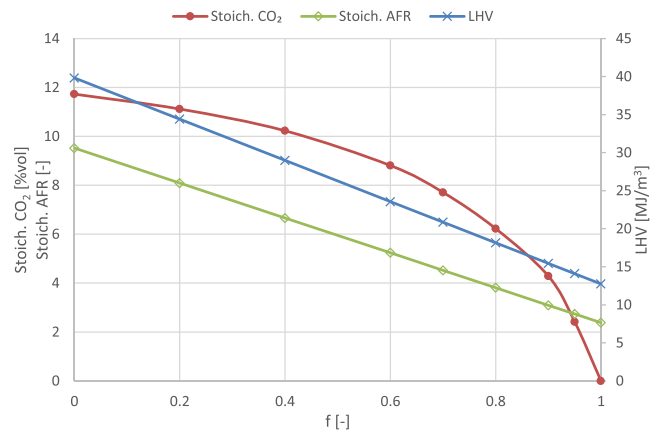


Fig. 2. Stoichiometric CO₂, AFR, and LHV as function of hydrogen fraction.

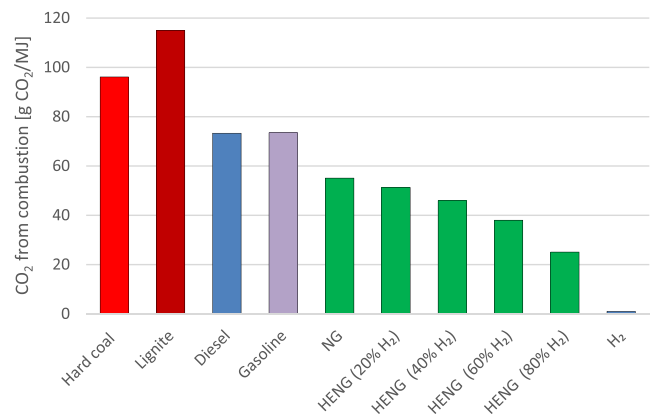


Fig. 3. CO₂ emission for the combustion of one energy unit of fuel.

drop evaluation, has to be conducted for all the components whose functionality is strictly connected with the reactions occurring, such as the burner or the flame control systems.

3.4. Effect on water condensate production

The impact of H₂ addition on the maximum amount of condensable water – and in parallel on the values of the Higher and Lower Heating values – is evaluated in this paragraph. Maximum condensed water flow is calculated by Eq. (12), for the same conditions analysed in

Table 4
Calculations for different H₂ fractions (f), referred to 25 kW thermal load and λ = 1.25.

	f = 0%	f = 20%	f = 40%	f = 60%	f = 80%	f = 100%
Fuel flow [m ³ /h]	2.51	2.92	3.48	4.32	5.70	8.35
Air flow [m ³ /h]	29.86	29.51	29.02	28.30	27.12	24.84
Total reactants flow [m ³ /h]	32.37	32.42	32.50	32.62	32.81	33.19
CO ₂ exhaust [%]	9.17	8.68	7.96	6.84	4.81	0.00
O ₂ exhaust [%]	4.59	4.61	4.65	4.70	4.81	5.05
LHV [MJ/m ³]	35.8	30.8	25.8	20.8	15.8	10.8

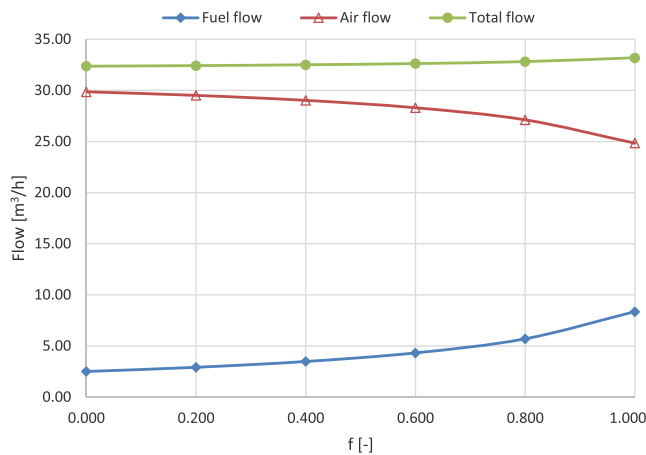


Fig. 4. Reactants flows for a heat input of 25 kW with λ = 1.25, as function of hydrogen fraction.

Table 4, while heating values are calculated based on Eq. (7). Results are reported in Table 5.

It can be noticed from the HHV/LHV ratio that the larger the H₂ percentage is, the larger is the maximum recoverable condensation heat. This fact, coupled to the amount of fuel needed, leads to an increase of the condensable water mass for a fixed thermal load (about +70% for pure H₂ than for pure CH₄).

The graph of Fig. 5 shows the water vapour mass flow for a fixed heat input (25 kW) and the water mass per unit volume of fuel. Reminding the boiler concept of Fig. 1, for high H₂ blending the heat exchanger design may need to be re-assessed to reach maximum efficiency, given that the amount of water to be condensated is significantly higher than for pure CH₄. Also, the condensate discharge ducting may need to be designed for a higher nominal water flow, even if the ducts used in the methane fired boilers examined seem to be oversized for the nominal volume flow, so there is the possibility they are still appropriate for HENG fuels.

3.5. Effect on flashback and reactants ignition

As highlighted by Table 1, H₂ has higher burning velocity, wider flammability range and lower ignition energy than methane. These aspects are transferred, even if not linearly, to the hydrogen enriched natural gas, thus a deepening on the potential effects is needed. Flashback phenomena and unwanted ignitions of reactants must be

Table 5
Calculations for different H₂ fractions (f), referred to 25 kW thermal load and λ = 1.25.

	f = 0%	f = 20%	f = 40%	f = 60%	f = 80%	f = 100%
Fuel flow [m ³ /h]	2.51	2.92	3.48	4.32	5.70	8.35
LHV [MJ/m ³]	35.8	30.8	25.8	20.8	15.8	10.8
HHV/LHV [-]	1.10	1.11	1.12	1.13	1.15	1.18
Water vapour flow [m ³ /h]	5.02	5.25	5.57	6.05	6.83	8.35
Condensable water [kg/h]	3.76	3.93	4.17	4.53	5.12	6.25

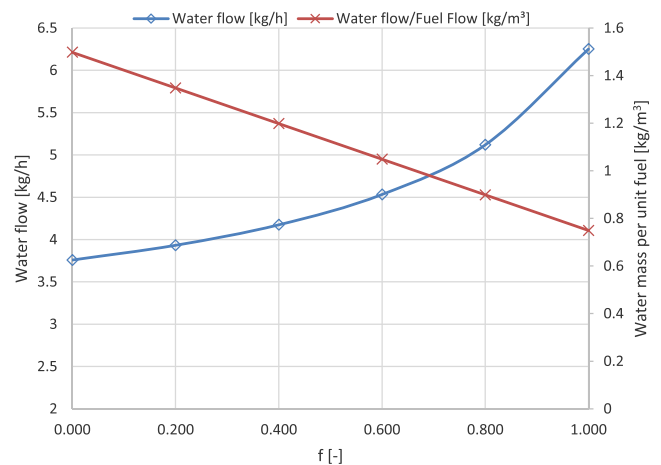


Fig. 5. Water flow rate for variable hydrogen fractions and 25 kW thermal load.

avoided to grant safety and reliability of the boiler. The mixture ignition due to the flame speed exceeding the unburnt mixture speed (leading to the flame propagation upstream into the burner) has to be managed mainly by a proper burner design, ensuring the speed balance to be adequate in every location and operating condition. Premixed flame stabilization is a complex matter [10] involving heat transfer, fluid dynamics and chemical equilibrium, and the flashback threshold cannot be simply correlated to the average mixture exit speed; nevertheless, a higher unburnt speed would generally help flashback avoidance [12]. A premixed burner designed for hydrogen enriched natural gas, thus, would require a lower open area than a methane burner, to increase the average unburnt speed, and a lower diameter of the flow channels, to enhance quenching phenomena. It is known that the value of λ is very impacting on flashback, so a safety margin must be taken by increasing the lambda value; the implications on the air flow increase have to be evaluated in the terms of paragraph 3.3. In addition to the flashback mechanism described above, attention has to be paid to the low ignition energy of hydrogen, which makes the reactants more susceptible to be ignited by unwanted energy sources [18], such as mechanical friction, high temperatures or electrical fields. Literature studies [14] suggest that the risk of ignition by electrostatic discharges significantly increases in methane mixtures containing more than 25% H₂, due to the fact that the ignition energy goes below 0.1 mJ, typical threshold for corona discharges. Fig. 6 gives an insight about the effect of hydrogen fraction on this aspect: data from an experimental study [19] are plotted, showing the relation between minimum ignition

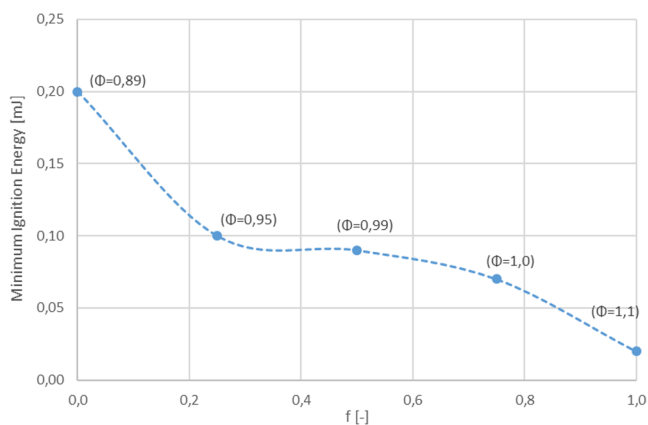


Fig. 6. Minimum Ignition Energy versus hydrogen fraction, and equivalence ratio Φ at which minimum energy occurred (data interpolated from [20]).

energy and the fuel mixture composition, together with the equivalence ratio Φ at which minimum ignition energy occurred.

A practical idea on the difference between hydrogen and methane, in terms of tendency to ignite, is given in [20]: this study states that the load applied on a steel surface with a rubbing tool is at least an order of magnitude lower to ignite hydrogen than methane. Very little is available in literature about flashback on premixed devices fed with HENG, but looking to the data in Table 2 it can be concluded that at least up to 23% H_2 , the current methane fired devices are able to operate without safety issues. With reference to the concept of Fig. 1, the implication of the findings exposed in this paragraph are involving all the components in contact with flammable mixture or in its proximity, i.e. the burner, the manifold connecting air/gas mixer to burner, the air/gas mixer itself and the blower. Although there is a gap in knowledge and a need for experiments on these topics, and despite the probabilistic nature of the ignition process [19], guidelines for these components are possible to be provided, and include the reduction of thermal ignition sources (e.g. friction, vibration, resonance, shock waves in the flow [18]) and electrical ignition sources (e.g. static electricity, sparks and arcs). The effects of unwanted ignition of the flammable mixture are discussed in the following paragraph 3.6.

3.6. Effect on explosion hazard

One aspect linked to safety of a combustion appliance is potential explosion. Even if it can be considered unlikely in methane fired systems, a proper evaluation has to be done, especially when considering different fuels. A gas explosion process is defined as a process where the combustion of a premixed gas cloud (like fuel/air) is causing a rapid pressure increase. Gas explosions can occur inside buildings, inside closed pipes, recipients or other equipments, in partially open volumes, or even in unconfined areas [21].

The pressure peak and pressure rise rate depend on how fast the flame propagates, and on the possibility of pressure release. In turn, these aspects are depending on many different factors, comprising chemical composition of the explosive gas cloud, initial conditions, properties of the confinement. Especially this last property has a significant role and has to be evaluated for each specific case study. The ignition of the flammable air/gas mixture contained in a premixed application is to be considered in the category of “partly confined gas

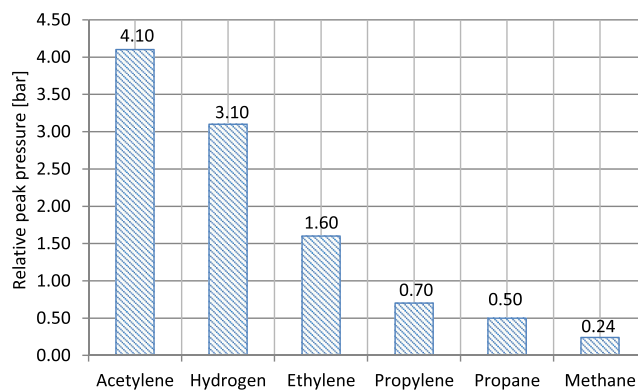


Fig. 7. Values for stoichiometric explosion peak relative pressure in a 1 m radial vessel with blockage ratio 0,5 [25].

explosions”: generally, the walls of the appliance will confine the explosion and the pressure can be relieved through the open areas, unless a rupture is achieved at a certain overpressure level.

Multiple experimental studies [22,23] have shown that different fuels can be, at least qualitatively, ranked in terms of explosion hazard. Table 6 reports results from experiments [24] comparing peak pressure for explosions of different air/fuel stoichiometric mixtures, using a fixed test system (a 1 m radial vessel, blockage ratio 0.5), while in Fig. 7 a graphical representation of the same data is given.

The peak pressure for stoichiometric hydrogen/air explosion is about 13 times the one of methane/air in the same conditions. An analogous ranking between fuels can be derived from [21], where peak pressures are measured in a different test system (a 10 m wedge-shaped vessel).

Peak pressure is not the only significant parameter to be considered: in general, the fundamental parameters for the quantitative characterization of explosion risk and severity are the flammability limits, maximum explosion pressure, and maximum rate of pressure rise [25]. Studies on the explosions generated by hydrogen/methane/air mixtures state that hydrogen addition acts on all these parameters, enlarging the flammability range, shortening the combustion time, and accelerating the pressure rise in confined spaces [26]. The pressure rise rate (dp/dt) prominently grows up with hydrogen content, due to the increase of laminar flame speed.

There are indications that the hazard is not likely to increase with respect to methane for low hydrogen blending, in practical situations [14], but for higher blending the risk increases significantly.

There are certainly knowledge gaps relating to explosion and fire hazards of HENG; despite this, the analysis performed by the Authors suggests some advisable prevention measures to be adopted in the design of hydrogen fired boilers. Firstly, the volume of cavities containing flammable mixture should be kept as low as possible, in order to reduce the energy stored in the unburnt. Secondly, a duly studied rupture disk or relief valve, placed in a proper position depending on the specific device, can reduce the risks related to the explosion. Finally, the algorithms managing the boiler operation (including pre-and post-purge, ignition, power modulation phases) should be designed in order to ensure a sufficient cooling of the components and dilution of the reactants, with a wide margin of safety.

In conclusion, hydrogen blending of methane could enhance the explosion risk and consequences [25], and the risk has to be carefully evaluated with specific studies involving the systems of interest.

Table 6

Values for stoichiometric explosion peak relative pressure in a 1 m radial vessel with blockage ratio 0,5 [24].

Fuel	Acetylene	Hydrogen	Ethylene	Propylene	Propane	Methane
Peak pressure [bar]	4.1	3.1	1.6	0.7	0.5	0.24

3.7. Effect on energy efficiency and pollutant emissions

Boilers, and more in general premixed devices, use heat exchangers to transfer energy from the fuel combustion to the heat transfer fluid (e.g. water, hot air). The physical principle remains valid if instead of methane another gaseous fuel (like hydrogen) is burned, but the performances may be not optimal. Certainly, flame shape and length are different when changing fuel, emission spectra of the flame changes, dew point and heat transfer coefficients change. Generally speaking, a re-development of the exchanger must be done to optimize the performance [27], even if existing studies state that the efficiency of methane boilers burning HENG mixtures with 25% H₂ is about the same, or higher, than the original [15,28].

Detailed studies on pollutant emissions of premixed boilers burning HENG are missing, while deep investigations are available in the field of internal combustion engines [29]: compared to methane engine, hydrogen enrichment could reduce unburnt hydrocarbons, CO₂ and CO emissions, but may lead to higher NO_x emissions. A direct parallel between boilers and engines is of course not possible, but some combustion principles are shared when handling different fuels. Literature studies focused on boilers mention potentialities for CO and NO_x reduction [8,16,28]. Regarding CO production, it is reasonable to expect a decrease with the H₂ percentage increase – at least until a certain threshold level – because of several aspects: faster chemistry, reduction of flame quenching distance, extension of flammability range, increase in OH radicals (promoting the oxidation of CO to CO₂ [30]) and, naturally, decrease of total carbon in the reactants. A cornerstone about CO production with hydrogen enrichment is the fact that current gas fired devices, nominally working with methane, are already required to safely work with limit gases containing H₂ (see Table 2): this is an indication that a safe operation in terms of CO emission can be achieved with H₂ content up to 23%, even in today's boilers.

Coming to NO_x formation, H₂ enrichment leads to higher quantities of OH, H and O radicals (promoting the thermal NO formation [29]) and higher combustion temperatures (triggering higher NO_x production), but also allows a stable combustion with higher λ values than methane (so, higher excess air and lower combustion temperatures). This last effect could be managed in order to prevail, resulting in an overall lower NO_x production.

3.8. Effect on flame detection and controls

Flame detection and combustion control systems are a complex and evolving technology, thus dedicated studies are needed to assess their suitability to be used in HENG fired systems. One of the most used systems in domestic boilers is based on ionization current, exploiting the electrical conductivity of the flame, indirectly measured by means of an electrode [14]. Experimental studies [15,31] concluded that the detected ionization current is weakened when H₂ is added to methane. Reasonable causes for the decrease in the detected signal are a lower quantities of CH and H₃O⁺ radicals and a shift in the flame location, with respect to pure CH₄ combustion. Since these control devices have been designed for hydrocarbons, the utilization with HENG gases has to be assessed and may need a tuning. Experimental research [28] determined that boilers equipped with ionization-based combustion control systems can operate safely, and with lower emissions, with gases containing up to 30% hydrogen, but the control system does not work as exactly as for fuels without hydrogen enrichment.

Other common flame detection devices are based on temperature measurement, by means of thermocouples measuring indirectly the flame temperature. These devices are, in principle, suitable for monitoring the combustion of HENG, but the position of the sensor and the threshold values could need to be adapted. Further technologies for the flame detection [13,16], usable for methane as well as for HENG mixtures with the due adaptations, are based on light emission from the flame (e.g. IR and UV sensors), and on sensors examining the exhaust

composition (e.g. O₂ sensors).

Finally, flame visibility for the user of a combustion appliance is considered a very important safety aspect: frequently, spyholes are present for the visualization of the flame. There is a consistent literature stating that Hydrogen combustion is not visible (e.g. [13,18]), even if dedicated researches [32] highlighted that visible light emissions from hydrogen flames are significantly weaker than those from hydrocarbon flames, but indeed still visible at reduced light levels. Nevertheless, there is a clear evidence that visual flame detection is a critical point for hydrogen combustion with respect to methane.

In conclusion, the most used technologies for flame detection could remain still valid at least for low hydrogen enrichment, but the functionality and necessity of re-tuning has to be verified. High hydrogen enrichment would involve the necessity to develop and introduce new technologies for flame detection and combustion control.

3.9. Materials selection and durability

With regard to the boiler concept of Fig. 1, the impact of H₂ addition to NG has to be considered on all the components in contact with fuel, fuel/air mixture, and combustion products. There is published evidence [14,27,18] suggesting that materials in contact to hydrogen enriched natural gas mixtures can degrade, by means of specific damage mechanisms as hydrogen attack, embrittlement, cracking. The susceptibility to these phenomena varies depending on the material properties and dimensions. By the way, most of the available specific studies are related to high pressure operation (magnitude of tenth of bars, versus the usual tenth of millibars involved in domestic applications), high pressure cycling (e.g. hydrogen tank refuelling), or hydrogen presence during welding or metal forming operations, thus the potential concern has to be assessed with an analysis dedicated to premixed domestic applications.

Metallic materials as austenitic stainless steel, aluminium alloys, copper and copper alloys are generally deemed satisfactory for hydrogen service [18].

In addition to the damaging mechanisms described above, it has to be considered that components in contact with combustion processes (e.g. burner, heat exchanger, insulation materials) could be subjected to different temperature conditions when shifting from methane to HENG, due to different flame temperature, flame shape and heat exchange mechanism. The effect of different temperature levels and gradients has to be verified and is depending not only on the material, but also on the geometric characteristic of each component.

Beyond mechanical degradation, the permeability of materials to the different fuels must be taken into account, since H₂ molecule is smaller and more diffusive than methane. Referring, by way of example, to some of the currently used materials, polyethylene PE-100 is 4.6 times more permeable to H₂ than to methane, and nylon PA-12 is 40 to 50 times more permeable to H₂ than to methane [33]. Polymer PA-11 is considered an interesting solution for H₂ transportation [34].

Finally, hydrogen has a greater tendency to leak through small apertures than methane, and this has an implication also on the design of mechanical joints and interface between different materials of the parts in contact with the fuel. Flanged and screwed connections should be avoided, in favour of welded joints, when possible. On the other side, the properties of weldings and the necessity to make the application accessible to servicing have to be taken in consideration.

In conclusion, the material selection has to be performed considering together physical and chemical properties, and has to be experimentally validated with lifetime tests.

4. Conclusions

This study is focused on the assessment of hydrogen enriched natural gas on end-user appliances. Premixed boilers, in particular, constitute a fundamental point to be studied for their wide diffusion, their

design complexity and safety implications. A model for calculating several parameters related to HENG combustion is presented in this study, a reference structure for the analysis of premixed boilers is identified, and a series of evaluations is performed on case studies.

The need for component re-design was found to be strongly dependent on the hydrogen blending percentage, and is particularly impacting for high H₂ addition. To reach the same thermal load, the fuel flow with hydrogen blending is up to 3.3 times than with pure methane, and this has an implication on the design of the fuel-side components (e.g. fuel/air mixer, gas valve). The total flammable mixture flow, instead, is less dependent on the enrichment grade so components such as the heat exchanger could still be adequate, even if an optimization may be useful to maximize the performances for high hydrogen blending. Further studies emerged to be necessary about the impact of hydrogen on pollutant emissions and on boiler efficiency, even if the expectation for premixed devices inclines to be positive.

Another relevant point is the consistent increase in the maximum condensable water flow, calculated to be up to +70% when comparing pure hydrogen to methane; this requires a proper dimensioning of the condensate discharge system.

Components in contact with the HENG mixture need a special design for high hydrogen enrichment, considering the increased tendency to unwanted ignition and flashing back. Especially on this last point, the burner needs to be re-designed to adapt to the new reaction chemistry; guidelines have been provided on this aspect. An evaluation has been made on the effects of a potential explosion involving HENG, and an increase of the hazard has been found, giving one more reason to deepen the knowledge on this field.

The flame detection systems and combustion controls developed for methane remain still valid for low hydrogen enrichment (up to about 20–30%), but a re-tuning has to be performed. High hydrogen enrichment, instead, involve the necessity to introduce new control technologies.

Finally, suggestions for the material selection – to be carefully conducted and supported by endurance testing – are given keeping into account the peculiarities of HENG mixtures and the degradation mechanisms involved.

The modelling and analyses presented in this study allowed to determine that a moderate hydrogen enrichment of natural gas, cautiously up to about 20%, could be sustained by the current methane premixed boilers without substantial re-design necessities, even if minor adjustments and verifications are indeed needed. Higher hydrogen enrichment grades have a growing impact on the boiler design, and major actions are required; guidelines for the re-design have been suggested based both on the modelling results and on a review of available literature.

This research paves the way for future deepening, including a more detailed system modelling, focusing on critical boiler components, and experimental campaigns on real applications.

CRedit authorship contribution statement

Fabio Schiro: Writing - original draft, Conceptualization, Investigation, Writing - review & editing, Data curation, Formal analysis. **Anna Stoppato:** Investigation, Writing - review & editing, Data curation, Formal analysis. **Alberto Benato:** Investigation, Writing - review & editing, Data curation, Formal analysis.

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