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## An overview on safety issues related to hydrogen and methane blend applications in domestic and industrial use

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### Abstract

The share of electrical energy hailing from renewable sources in the European electricity mix is increasing. The match between renewable power supply and demand has become the greatest challenge to cope with. Gas infrastructure can accommodate large volumes of electricity converted into gas whenever this supply of renewable power is larger than the grid capacity or than the electricity demand. The Power-to-Gas (P2G) process chain could play a significant role in the future energy system. Renewable electric energy can be transformed into storable hydrogen via electrolysis and subsequent methanation.

The aim of this paper is to provide an overview of the required technical adaptations of the most common devices for end users such as heating plants, CHP systems, home gas furnaces and cooking surfaces, wherever these are fuelled with methane and hydrogen blends in variable percentages by volume. Special attention will be given to issues related to essential safety standards, firstly comparing existing Italian and European regulations in this regard, and secondly highlighting the potential need for legislation to regulate the suitability of hydrogen methane blends. Finally, a list of foreseeable technical solutions will be provided and discussed thoroughly.

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## 1. Introduction

Hydrogen is being pursued as a sustainable energy carrier for fuel cell electric vehicles (FCEVs) and as a means for storing renewable energy at utility scale. Hydrogen can also be used as an eco-fuel in stationary fuel cell systems for buildings, backup power, or distributed generation. Furthermore, blending hydrogen into the existing natural gas pipeline network has been proposed as a means of increasing the output of renewable energy systems such as large wind farms. If implemented with relatively low concentrations, ranging in 5%-30% of hydrogen by volume, this storage strategy and delivering renewable energy to markets appears to be viable without significantly increasing risks associated to the blended gas utilization in end-users devices (e.g. household appliances) [1]. Additionally, all public safety features, as well as the existing natural gas pipeline network durability and integrity are not strongly affected by the hydrogen enrichment. However, the appropriate blend concentration may vary significantly due to NG composition within pipelines and the end-user typology, which is the reason it must be assessed on a case-by-case basis. Blending hydrogen into natural gas pipeline networks has also been proposed as a means of delivering pure hydrogen to markets, using separation and purification technologies downstream to extract it close to the point of delivery. In such a way, blending can defray the building costs of dedicated hydrogen facilities or other costly delivery infrastructure during the early market development phase. This paper deals with key issues related to the hydrogen mixtures uses, which are described briefly in the following sections: an overview of benefits of blending, the impact on end-use systems in terms of modification in different set-up, furthermore a great attention was paid to all of safety issues related to the most common and user devices as well as their material durability and integrity management [2].

## 2. Chemical-physical properties of hydrogen

Hydrogen is characterized by a wide range of flammability and by a high speed of flame propagation. Indeed, in the case of combustions with air, the flame's laminar propagation speed is equal to 270 cm/s, compared to 37 cm/s in methane/air flames. The consequence can be severe control issues in addition to the risk of the insurgence in premixed flames of the backfiring phenomenon, which involves the propagation of the flame front in the direction opposite to that of the premixed reagent source, leading to the potential risk of explosions or other serious damage to the burner. Another unique characteristic is the high adiabatic flame temperature (2380 K compared to 2222 K in methane combustion with air), which implies problems with materials and, in general, makes dilution necessary before exhaust gas inlet in burners of several devices such as gas turbines internal combustion engines and boilers.

The preheating temperature influences the flame front propagation speed, which increases it significantly. This is why it is possible to stabilize hydrogen flames even at high efflux speeds (160 m/s).

Another important aspect can be the emergence of thermo-acoustic instability. This kind of instability can lead to self-sustaining oscillations with amplification of the pressure fluctuations within the combustor. The consequence would then be considerable vibrations that could cause serious structural damage.

A solution to all these problems is offered by new, more advanced combustion technologies characterized by the absence of drastic temperature gradients and by high levels of control over the kinetic-chemical process. Applying these technologies implies the general redesign of the combustion system (burner-combustion chamber) and the development of adequate methods of design and controls.

To this end, this paper reviews the impact of the use of hydrogen blended with natural gas on the performance of engines as well as the most common appliances, and on emissions with reference to research activities in this field. It must be noted that the percentage of hydrogen that can be used in thermal engines has a maximum threshold strictly dependent on the knock limit, which is a function of the compression ratio; this is normally quite high in thermal engines. Consequently, that threshold must always be kept in mind, along with the methane number (MN), which indicates the gas quality and, more specifically, its capacity to resist auto-ignition. That parameter was defined as the percentage by volume of methane blended with hydrogen that exactly matches the knock intensity of the unknown gas mixture under specified operating conditions in a knock testing engine. For the range beyond 100 MN, methane-carbon dioxide mixtures were used as reference mixtures. In accordance with the definition, the MN is 100 plus the percent CO<sub>2</sub> by volume in the reference methane carbon dioxide mixtures. Malenshek et al. [3] have

provided also the methane number as an empirical correlation between MN values and the compression ratio of the engine being considered after testing the engine with various fuels. This correlation is linear and reads as follows:

$$MN = 11.438 r_{\text{compress}} - 61.652 \quad R^2 = 0.9766 \quad (1)$$

All the pertinent coefficients related to the Equation 1 are calculated based on the composition of the test gas listed in the table:

Table 1. Sample gases composition for determining the correlation between MN and engines compression ratio.

	%CH	%H <sub>2</sub>	%N <sub>2</sub>	%CO	%CO <sub>2</sub>
Natural gas	39.7	47.7	0.8	0.9	11.9
Carbon gas	-	24.8	16.3	58	1
Wood gas	10	40	3	24	23
Wood gas	1	31	35	18	15
Landfill gas	60	-	-	-	40
Natural gas	1.2	30.8	49	15.6	3.4
Carbon gas	7	44	-	43	6

Thanks to these values it is possible to derive the critical value of the compression ratio for methane as 14.4 [4]. This is a fundamental parameter in order to define the characteristics of the engine used. In any case, the MN method has a defect in that it does not give enough weight to the fact modern engines tend to operate on lean consumption, i.e. with an air/gas blend that is low in gas and with different temperature/pressure conditions for the gas at the end of its compression, whereas the MN method is calculated based on the engine functioning stoichiometric conditions. The literature [5] has proposed various alternative methods to assess the detonation limit. Normally the technical guide for every commercial CHP engine lists the minimum required MN value. This means that, in order to avoid any detonation problem the methane number for the gas blend must be greater than the minimum required MN.

For instance, a normal CHP engine available on the market has a MN figure of 80 for the use of natural gas and 65 for biogas, respectively. By adding hydrogen to natural gas the blend's MN value decreases and the required MN value determines the maximum quantity of hydrogen in the blend accepted by the engine. Furthermore, when hydrogen was added, the dew point temperature increased as well as the theoretical recoverable energy by water condensing out [6]. From literature, it emerged a leverage effect on carbon reduction due to the enhancement of engine mechanical performance.

For instance, cooling the exhaust gases up to 35 °C, with NG the condensation efficiency is equal to 81%, while with H<sub>2</sub>NG @ 30% it is 83%. These values correspond to the heat recovery efficiency gains of a CHP equal to 8.55% and 9.45%, respectively. When the CHP was fuelled with H<sub>2</sub>NG @ 15% vol. the hydrogen addition generated an electrical efficiency increase globally. In detail the maximum measured gain was equal to 2.276% at 3.5 kW<sub>el</sub> of power output [6].

Instead, when H<sub>2</sub>NG is used, it reduces the total thermal power due to the heat exchangers derating and the heat recovery efficiency as well. At the same time, the energy from water condensation offsets partially this power reduction owing to its higher contribution to the overall recovered thermal power (i.e. up to 1% compared to NG).

The most important thermo-physical properties (density in normal conditions, lower heating power, percentage of air in the fuel in stoichiometric conditions, etc.) can be estimated by using a linear combination of the individual properties of hydrogen and methane, albeit this calculation is only an approximation.

Even though hydrogen is characterized by a lower heating power per mass unit that is considerably greater than the lower heating power of methane (i.e. 121,000 KJ/Kg compared to 50,000 KJ/Kg for methane), when this is expressed volume units the associated thermal energy is considerably reduced. This is mainly due to the fact that hydrogen has a density approximately 1/10 lower than that of methane.

Table 2. Thermo-physical properties of the hydro-methane blends as the hydrogen percentage varies

%H <sub>2</sub>	ρ <sub>n</sub> [kg/Nm <sup>3</sup> ]	LHV [kJ/kg]	LHV' [kJ/Nm <sup>3</sup> ]	α <sub>st</sub> [kg/kg]	α' <sub>st</sub> [Nm <sup>3</sup> /Nm <sup>3</sup> ]	[CO <sub>2</sub> ] <sub>th</sub> [%vol.]
0%	0.713	50.000	35.691	17.391	9.569	11.669
5%	0.682	50.467	34.449	17.506	9.210	11.535
10%	0.651	50.979	33.206	17.656	8.851	11.390
15%	0.620	51.543	31.964	17.766	8.492	11.231
20%	0.589	52.166	30.721	17.918	7.234	11.058

Table 2 recaps in a systemic overview the main H<sub>2</sub>NG (Hydrogen enriched natural gas blends) thermo-physical properties as the percentage of H<sub>2</sub> varies in the blend and the theoretical mole fraction of CO<sub>2</sub> present in dry exhaust gases. It also gives the values of the lower heating values by mass for the various blends with a varied percentage of hydrogen, due to the lower density of hydrogen compared to methane [4].

The energy flow in terms of the various gas blends feeding a device is characterized by a parameter called Wobbe Index. As reported in German Technical Regulation DIN 51857, the following expression defines the Wobbe Index as W:

$$W = \frac{H_{Vol}}{\sqrt{d}} \quad d = \frac{\rho_{gas}}{\rho_{air}}$$

Where:

W is the Wobbe Index abbreviation [MJ/Nm<sup>3</sup>];

H<sub>vol</sub> is the volumetric heating value [MJ/Nm<sup>3</sup>];

d is the so-called gas relative density;

ρ<sub>gas</sub> is the gas density in the reference conditions [kg/Nm<sup>3</sup>];

ρ<sub>air</sub> is the air density in the reference conditions [kg/Nm<sup>3</sup>].

If two different gas blends have the same Wobbe Index it means that at the speed of sound and at a given pressure the flow through the nozzle provides the engines/burners with the same quantity of energy. The Wobbe Index is shown in the following Figure 1 built by one of the authors, along with the percentage mass and the percentage reduction of the natural gas blend enriched with hydrogen, compared to the quantity of hydrogen per volume. It can be seen that the Wobbe index decreases as the percentage of hydrogen in the blend increases linearly [5].

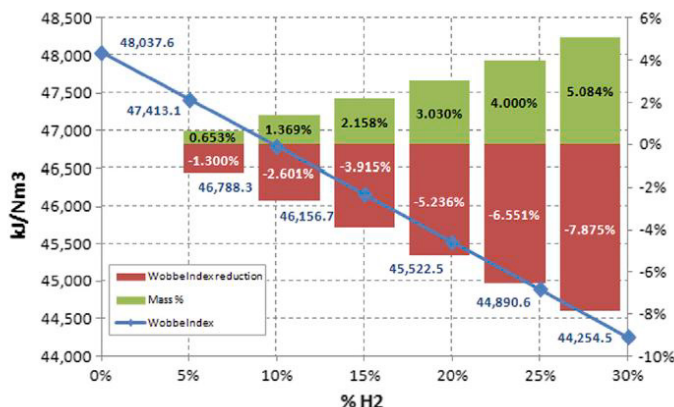


Fig 1. Wobbe Index, mass percentage, Wobbe Index percentage reduction vs %H<sub>2</sub> vol. Source: ref [5]

Currently, that parameter is kept under control by NG distributors and utilities in small range, i.e.  $\pm 5\%$  in order to assure the right operating conditions of devices. As a consequence, it is possible to state that H<sub>2</sub>NG blend at 20% vol. is already suitable and shows no risks for the appliances given that it belongs to the aforementioned span.

### 3. “MILD” combustion

Current technologies involve the combustion of a gaseous fuel with air or oxygen taking place in three basic modes such as diffusive combustion, premixed combustion and flameless catalytic combustion.

In diffusive combustion the two reagents, initially separated, blend together in a combustion chamber, diffusing one in another, and burning as the flammability limits are reached if a cause is present that leads to ignition (spark plug, pilot light, etc). Diffusive combustion is characterized by high stability in a broad range of the equivalence ratio and by a high temperature specific to the flame front, to which high NO<sub>x</sub> emissions are associated. Over 95% of combustion devices of an industrial end-user operate based on this principle [7].

In premixed combustion, the reagents enter the combustion chamber already blended and they are able to burn immediately, as long as they are in relative concentrations that respect the aforementioned flammability limits.

This is the most efficient way to burn a fuel with a broad ability to control the combustion (emissions) by adjusting the equivalence ratio. In particular, if that decreases (combustible excess), with the blend becoming considerably diluted, the average temperature of the combustion products decreases considerably and thus the nitrous oxide emissions decrease significantly as well.

Negative aspects of this kind of “burning” include the reduced stability range (significantly less than that of diffusive flames) along with the possibility of flash-backs (propagation of the flame front in a direction that is opposite that of the pre-mixed reagents), with a risk of potential explosions.

In the case of hydrogen, it must be highlighted that, in air, its laminar flame speed is approximately 7.3 times higher than that of methane, while in oxygen it is in excess of 31 times higher. The efficient exploitation of an energy process implicitly requires effective control over it. In this respect, MILD (Moderate and Intense Low oxygen dilution) combustion has thus far been considered in applications for high-temperature processes industry (industrial furnaces for the thermal treatment of steel, smelting metals and glass, reforming and gasification of fossil fuels) thanks to its specific characteristics of high efficiency and low emission of pollutants [8].

Indeed, the uniformity of the temperature field involves a thermal flow that is, on average, higher and this makes the process easier to control. In order to enter into the operational conditions of “MILD Combustion” the reagents must be at a temperature higher than the blend auto-ignition threshold and they must be diluted with inert compounds and/or exhaust gas that are low in oxygen, so that its concentration in the fuel is lower than the level in air. To this end, MILD systems foresee a thermal recovery section in which the air is preheated through with the exhausts (recovery or regeneration exchange) and the internal and external recirculation of the exhaust itself in the combustion chamber. The technological solutions that achieve “flameless” combustion have so far been studied and some have been tested on a pilot scale only for traditional fuels (natural gas, GPL and coal). In general, the characteristics of diluted combustion are advantageous in the field of gas turbine and more generally in power generation, thanks to the following reasons: reduction of the nitrous oxides mentioned earlier; operation stability, while eliminating problems linked to vibrations and a broad margin of variability in the air-to-fuel ratio; damping of temperature spikes that could damage the liner (internal casing) of the combustion chamber or the first stage of the blades of the fan assembly, and the absence of thermal stress in the gas injection points thanks to the delocalization of the reaction zone.

### 4. The hobs case

The new regulation UNI 7129:2015 regarding hobs states that appliances without flame supervision devices cannot be installed in the following cases:

- new installations;
- installation of appliances in existing systems;

- substitution of appliances;
- transformation or systems refurbishment.

It should be recalled that flame supervision (also called thermocouple) is a device that interrupts the flow of gas when the flame is absent, which may happen, for example, when the flame is accidentally extinguished or when the gas is opened inadvertently without lighting at the same time [9].

There are 4 different aeration systems for spaces where cooking surfaces are installed: natural draught cowl, electrical forced draught cowl, electrical Fan and direct aeration.

The updated version of Italian standard UNI 7129 enhanced the thermal power limit up to 15kW (instead of 11.7 kW as in the previous version) beyond which the direct space aeration it is not permitted. Notwithstanding, the new standard UNI 7129 call for using mandatory the electrical forced draught cowl also for cooking surface of rated thermal power output higher than 15 kW [10].

Domestic hobs are usually below the level of 15 kW and thus it should always be possible to aerate an enclosed space via the direct kind. Nonetheless, the best ventilation system is still, without a doubt, the electrical forced draught cowl (extractor fan), which in the new version of the regulations must have an air capacity of 2 m<sup>3</sup>/hour per kW of installed power (no longer 1.72 m<sup>3</sup>/hour as in the previous UNI 7129:2008). For example, an electrical forced draught cowl for a cooking surface of 10 kW must have minimum air power of 20 m<sup>3</sup>/h [11].

It should also be remembered that the direct type of aeration foresees an opening near the ceiling at least 1.80 m above the floor, with a section of at least 100 cm<sup>2</sup> (hole diameter 12 cm) and a bottom opening with a lower ventilation edge of 30 cm at most from the floor, equal to a section of at least 100 cm<sup>2</sup> [12].

## 5. Sustainable mobility

As far as alternative and sustainable mobility is concerned, in Italy the Official Gazette no.10 dated 13-1-2017 published Legislative Decree 16 December 2016, no. 257, implementing EU Directive 2014/94/EU (DAFI) as concerns the building of infrastructure for alternative fuels, including hydrogen, approved by the Council of Ministers. The European directive requires each member to send a national strategic framework illustrating its plan to create incentives for the extension of infrastructure. One goal is to create an adequate number of refueling stations by the end of 2025, and this includes revising Interior Ministry Decree no. 213 dated 31 August 2006, which lays out technical rules that limit the delivery of hydrogen to 350 bar, changing it to allow for up to 700 bar. This was to guarantee compatibility with modern hydrogen vehicles, including the Toyota Mirai. The updating of this decree is to take place by the end of 2017, namely in time for the arrival in Italy of the first hydrogen automobiles next year. Currently there are only three hydrogen fueling stations – in Milan, Bolzano and Collesalveti (Tuscany) – and it is clear that the new directive will lead to a notable increase in the number of these stations in coming months.

Document IGC 15/96/E, Gaseous Hydrogen Stations [13], constitutes the so-called “Code of Practice” prepared as a guideline for gaseous hydrogen fueling station designers and operators, and it lays out the rules for the safe operation following the best industrial practices available. The document addresses certain specific issues related to the normal activities that take place at a hydrogen fuelling station, such as compression, purification, filling of containers and storage at the user's site. However, it does not deal with production, transport or final distribution, nor with safety aspects for the use of gas in technical or chemical processes [14].

Hydrogen systems must never be located under high tension aerial lines or near the pipelines or storage of other flammable gases or liquids or other substances that could put the wellbeing of the installation at risk. If there are other dangerous installations nearby involving the risk of fire and/or explosion, suitable safeguarding measures must be taken, such as, for instance, increasing the minimum safety distances required. As a matter of fact, gaseous hydrogen systems must be surrounded by Hazard Zones, which are identified by safety distances starting from the points calculated in the plan view where, during operation, there could be hydrogen leaks; in particular, when systems are installed in buildings, these distances are measured starting from the openings present in the external walls, such as doors and/or windows. Pipes with valves, flanges or removable connections must be considered potential sources of emission, though only at their connection points [15].

It is important to note that the IGC explicitly requires all electrical devices within buildings that involve a risk of hydrogen leaks and those installed within safety distances to be of the kind approved by national electrical codes

and, as such, they must not be considered potential sources of ignition; to this end, all the well-known methods of protection can be used, such as immersion in oil or intrinsic safety, that are normally used to prevent the formation of sparks, electrical anomalies or excessive temperatures. The exact type of devices will also depend on the classification of the surrounding area. Outside of the Hazard Zone, in comparison, conventional electrical devices can be used. Thus, Hazard Zones are in and of themselves electrical classification areas that other documents identify as Zones or Divisions; the other points are mainly only safety distances.

## 6. ATEX Regulations

ATEX (atmosphere explosions) regulations is the name commonly given to a grouping of two European Union directives. One is 94/9/EC regulating devices for use in areas at risk of explosion. The directive is aimed at manufacturers of devices that will be used in areas with potentially explosive atmospheres; these products must, as a result, be certified. [16]

Directive 99/92/EC regards the safety and health of workers in explosive atmospheric environments and is applied to workplaces that are at risk of explosion, where systems and certified devices are in operation and users are consequently exposed to them. The directive relate to the minimum provisions for improving the maintenance of the safety and health of these workers. Explosive risks are defined as the blending with air in atmospheric conditions of flammable substances in gaseous, vaporous or powdered states in which, once lit, combustion can propagate with the unburned mixture. The directive was ratified in Italy via Legislative Decree 233/03 and the subsequent Legislative Decree dated 9 April 2008 no.81 (title XI). [17]

The employer must subdivide the areas in which explosive atmospheres may form into zones. To determine the type of zone, its dimensions and its features – where flammable gases are or could be present – EN regulations apply. The technical specifications are therefore compulsory. In ATEX regulations, the classification of areas, in general terms, can be broken down into the following steps:

- identifying the sources of emission (SE);
- attributing a grade to the emission sources;
- determining the dimensions of the fluid emission being considered (gas, vapour, low-boiling liquid or high-boiling liquid);
- calculating the hypothetical volume of the potentially explosive atmosphere ( $V_z$ ) around each SE;
- calculating the average volume concentration ( $X_m\%$ );
- estimating the amount of time the worker is present;
- determining the type of zone identified;
- determining the shape of the danger zone;
- determining the surface dimensions of the danger zone;
- determining the envelope of the various danger zones identified. [18]

It should be noted that as far as hydrogen-methane blends are concerned, of the last 6 values on which the ATEX assessment is based, only the first value, relating to the calculation of the average concentration, actually influences the assessment itself when hydrogen is present in the methane. Assessing the amount of time the worker is present involves shorter times, given the high level of volatility of hydrogen and of its vertical propagation, i.e. without fraying.

## Conclusions

In this brief overview of the use of hydrogen-methane blends in distribution networks, an analysis has been offered of the adjustments that need to be made to devices if using these blends. It is reasonable to think that, even though a range from 5% to 30% of hydrogen in methane has been considered, the limit of 20% considered for combustion engines in order to avoid the risk of detonation will be the maximum limit to be used in existing distribution networks. For these engines, new technologies such as Mild Combustion can offer further solutions to improve the yield of engines fuelled with hydro-methane. As regards everyday technologies, by using the Wobbe

Index the flow from the nozzles of cooking surfaces or small domestic boilers can easily be calculated in order to maintain analogous flame flows without special adaptations being necessary. Finally, in regard to fuelling stations for vehicles using hydrogen-methane blends, the physical characteristics of hydrogen make it possible to have stations with safety systems and distances that are not unlike those of normal methane or LPG fuelling stations. In particular, the considerable volatility of hydrogen along with its upward and frayless dispersion in case of leaks means that safety distances can be similar to or at least not any greater than those of normal LPG fuelling stations; in the latter case, consideration must be given to the horizontal propagation of LPG over the ground in case of leaks. In this sense, ATEX regulations, which are rather strict when it comes to the storage of pure hydrogen in pressure tanks, could easily remain the same in the case of blends with low percentages of hydrogen in methane.

### Nomenclature

FCEVs	fuel cell electric vehicles	Xm%	Volumetric concentration
CHP	Combined Heat and Power	A/F	Stoichiometric Air to Fuel ratio
EGR	Exhaust Gas Recirculation	$c_{p,l}$	Specific Heat at constant pressure (kJ/molK)
H <sub>2</sub> NG	Hydrogen enriched Natural Gas blend	$H$	Specific enthalpy (kJ/mol)
ICE	Internal Combustion Engine	P2F	Power to Fuel
P2H	Power to Heat	ATEX	Atmosphere Exposable
P2G	Power to Gas	LPG	Liquefied Petroleum Gas

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