

Admissible Hydrogen Concentrations in Natural Gas Systems

Klaus Altfeld and Dave Pinchbeck

1. Summary and conclusions

There are proposals to inject hydrogen (H₂) from renewable sources in the natural gas network. This measure would allow the very large transport and storage capacities of the existing infrastructure, particularly underground storage facilities and high-pressure pipelines, to be used for indirect electricity transport and storage.

The results of this study show that an admixture of up to 10 % by volume of hydrogen to natural gas is possible in some parts of the natural gas system. However there are still some important areas where issues remain:

- underground porous rock storage: hydrogen is a good substrate for sulphate-reducing and sulphur-reducing bacteria. As a result, there are risks associated with: bacterial growth in underground gas storage facilities leading to the formation of H₂S; the consumption of H₂, and the plugging of reservoir rock. A limit value for the maximum acceptable hydrogen concentration in natural gas cannot be defined at the moment. (H₂-related aspects concerning wells have not been part of this project);
- steel tanks in natural gas vehicles: specification UN ECE R 110 stipulates a limit value for hydrogen of 2 vol%;
- gas turbines: most of the currently installed gas turbines were specified for a H₂ fraction in natural gas of 1 vol% or even lower. 5 % may be attainable with minor modification or tuning measures. Some new or upgraded types will be able to cope with concentrations up to 15 vol%;
- gas engines: it is recommended to restrict the hydrogen concentration to 2 vol%. Higher concentrations up to 10 vol% may be possible for dedicated gas engines with sophisticated control systems if the methane number of the natural gas/hydrogen mixture is well above the specified minimum value;
- many process gas chromatographs will not be capable of analysing hydrogen.

Investigations have been conducted to evaluate the impact of hydrogen as related to the above topics. At present it is not possible to specify a limiting hydrogen value which would generally be valid for all parts of the European gas infrastructure and, as a consequence, we strongly recommend a case by case analysis. Some practical recommendations are given at the end of the paper.

2. Introduction

In certain parts of Europe we have the situation already where the generation of 'renewable' electricity from wind and solar energy has led, from time to time, to production plants being shut down because the electricity generated exceeds local requirements and the transportation or storage capacities are inadequate. It's a problem that will become even more severe in the future because construction of new electricity lines and high-capacity pumped storage power plants is a costly and very lengthy process. Projects are therefore being discussed in which the surplus electricity is used to power electrolyzers that will split water into its component parts, with the hydrogen being directly injected into natural gas pipelines for both storage and transportation. The concept has become known as "Power to Gas" or P2G.

It is becoming more widely accepted that hydrogen could become an important energy carrier in the energy mix in the quest for sustainability, because it offers several benefits related particularly to the potential for energy storage. Indeed it's possible that, with the existing infrastructure, hydrogen/natural gas mixtures could be transported, stored and converted into electricity where required. However, if the addition

of small quantities of hydrogen, up to 10 %, to natural gas pipelines is to be accepted, it must guarantee a technically feasible, economically viable and, crucially, safe system of storage, transportation and use.

It's clear that the European natural gas pipeline network has the potential to offer such a solution and several studies, including the EC-supported NaturalHy [1] project, have examined the feasibility of using it as a means of widespread hydrogen storage and transportation. However a number of crucial aspects were not sufficiently addressed in earlier studies and work remains to examine these bottlenecks in the interaction between hydrogen and the wider European natural gas network, including aspects of utilisation.

The volume of hydrogen that may be added to natural gas is limited. There are already some very low 'ad hoc' limits in place, but studies [1] have shown that, with certain restrictions, admixture up to 10 % is not critical in most cases. However, there are bottlenecks which this project sets out to identify, proposing, where possible, solutions so that the natural gas infrastructure can be developed sufficiently to support the storage and transport of hydrogen-natural gas mixtures in a move towards a low carbon economy. This will, of course, cause natural gas and electricity networks to become even more interdependent, as shown in Figure 1, and the project highlights the R&D that will be necessary to achieve a robust solution based on the existing natural gas grid and its various constituent components.

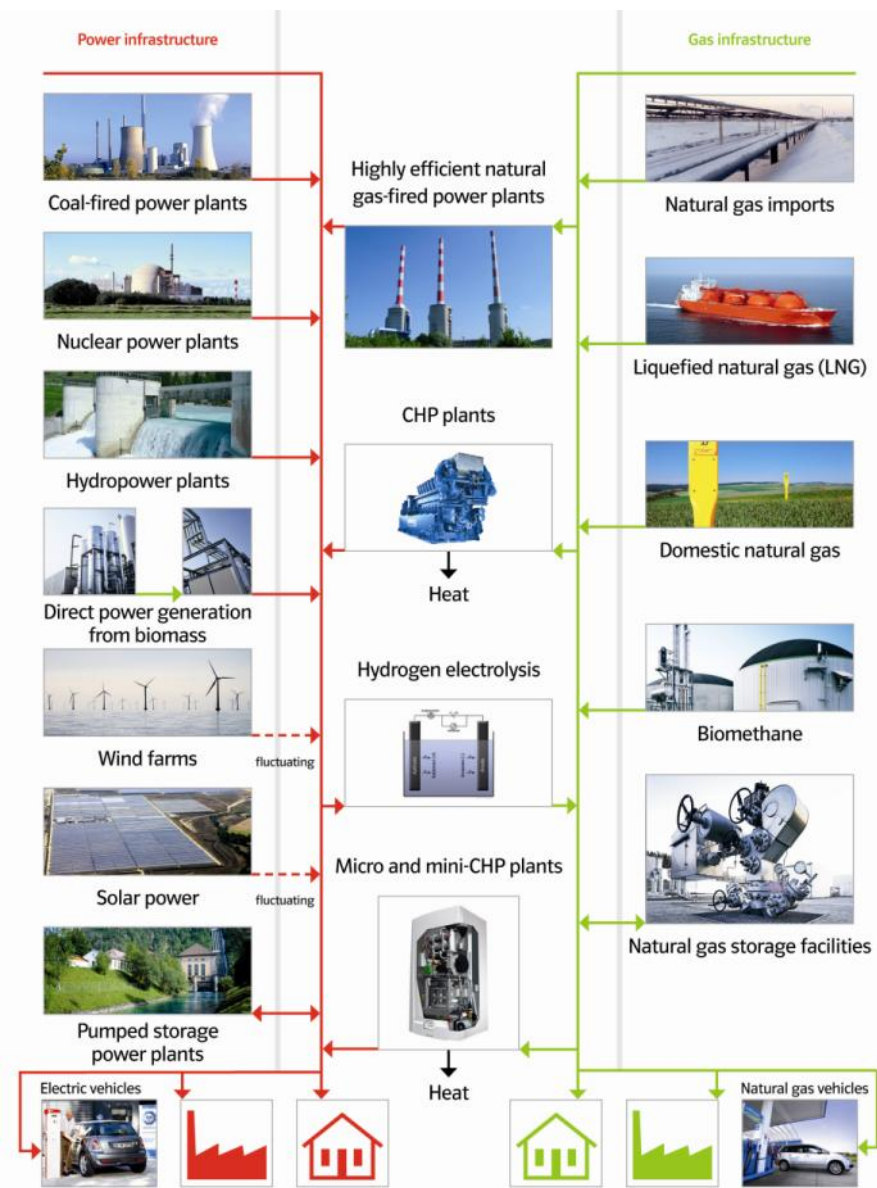


Figure 1: Convergence of power and gas infrastructures

The project was initiated by E.ON New Build and Technology GmbH, under the auspices of GERG, the European Gas Research Group, and has been conducted on behalf of a consortium of interested parties from a range of relevant industry sectors, including; gas industry; energy transmission, power generation, equipment manufacturers, institutes, etc. (See annex 1). Most of the work, which has consisted of reviews of existing work and literature searches, was carried out by a few, specially selected 'active' partners. No experimental work was involved but the collated, existing information has been substantially augmented by in-house knowledge from both 'active' and project partners.

3. Combustion of different gases: General remarks

The most important combustion parameters are Wobbe index, methane number and laminar flame speed. H-gases only are considered in this study.

3.1. Wobbe index

The Wobbe index (W) is an indicator of the interchangeability of different fuel gases. Regardless of calorific value, gases with the same W produce the same heat load in a gas burner. Therefore W is by far the most important combustion parameter for gas appliances (except engines) and is specified in all countries. Admixture of hydrogen slightly decreases W (10 % hydrogen lowers W by some 3 %). Figure 2 illustrates the W of pure methane, biomethane (simplified analysis: C1=methane: 96 %; CO₂: 4 %) and a "medium rich" LNG (C1: 92 %; C2: 5 %; C3: 2 %; C4: 1 %). (N.B.: % always means vol% in this paper).

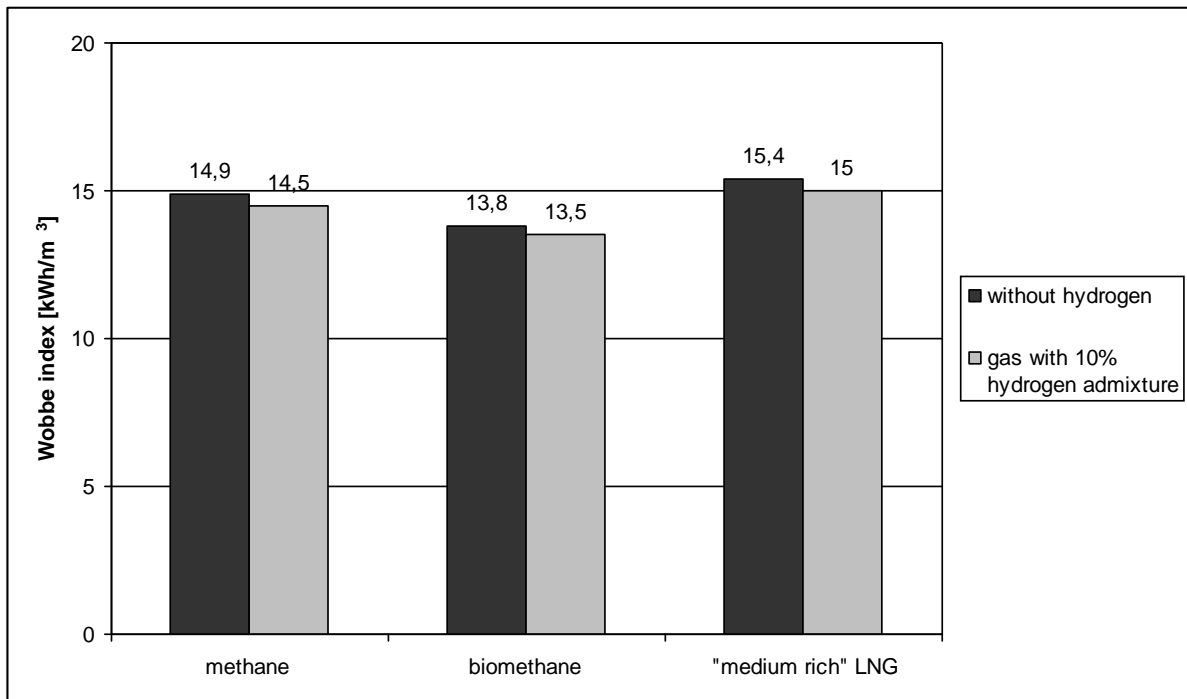


Figure 2: Wobbe index of different gases without / with 10% hydrogen admixture

The W range is 13.8 kWh/m³-15.4 kWh/m³ for the gases without hydrogen admixture and 13.5-15.0 kWh/m³ if 10 % hydrogen is admixed (Wobbe index reference temperatures: 0 °C (volume), 25 °C (combustion), 1.02325 bar). It is obvious that the variations caused by the different gases are significantly higher than the effects caused by 10 % hydrogen. However, if biomethane is considered, local Wobbe specifications can prevent hydrogen injection because biomethane has already a low Wobbe index (H-gases only are considered in this study).

3.2. Methane number

The methane number (MN) describes the knock behaviour of fuel gases in internal combustion engines and strongly depends on the specific gas composition and especially the amounts of higher hydrocarbons (C3, C4, C5) and hydrogen in the fuel gas. The MN of pure methane is 100, for pure hydrogen it's 0 and for rich LNG: 65-70, according to the AVL method [2].

Figure 3 shows the MN of the gases described in chapter 3.1 without/with 10 % hydrogen admixture.

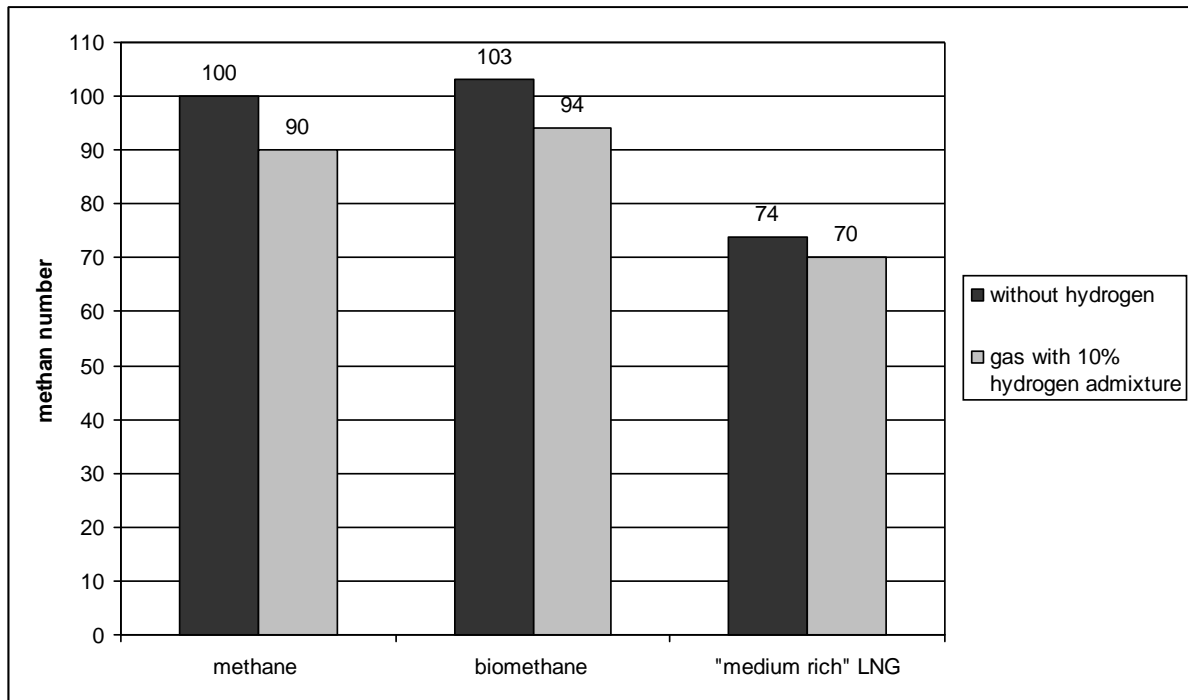


Figure 3: Methane number of different gases without / with 10% hydrogen admixture

Again it can be concluded that the MN of different gases without H₂ show a greater variation (from 100 to e.g. 74) than the effect of 10 % hydrogen (reduction by 10). However, if the natural gas already has a low MN (e.g. rich LNG) the admixture of 10 % hydrogen can result in an unacceptably low MN from a gas engine operator's perspective (combined heat and power plants, dedicated natural gas vehicles).

Although the MN is an important parameter for gas engines it has not been specified in most of the EU member states. This may be changed as a result of the CEN TC 234 activities in developing a European gas quality standard which includes the methane number.

3.3. Laminar flame speed

Flame speed is a complex combustion parameter related to flash back and flame stability. Both laminar and turbulent flame speeds may be defined but, unfortunately, they are difficult to measure and are not, therefore, specified in technical rules and standards.

Figure 4 illustrates that the experimental data for laminar flame speed, from different authors [3, 4, 5, 6, 7, 8], have significant deviations but there is a trend to increasing flame speed with increasing hydrogen addition. There is typically a ~5 % increase of the laminar flame speed for hydrogen admixture of 10 %. This increasing trend is also true for different air ratios and combustion conditions. However, depending on the device, the addition of hydrogen to natural gas can also change the fuel-air ratio, which may change the flame speed significantly, as shown in figure 5 (Chapter 5.5).

With regard to gas turbines, turbulent flame speed is an important parameter. However, relevant information is limited, but calculations [9] suggest that hydrogen has a stronger influence on turbulent flame speed. Hydrogen admixture of 10 % may result in a ~10 % increase in turbulent flame speed.

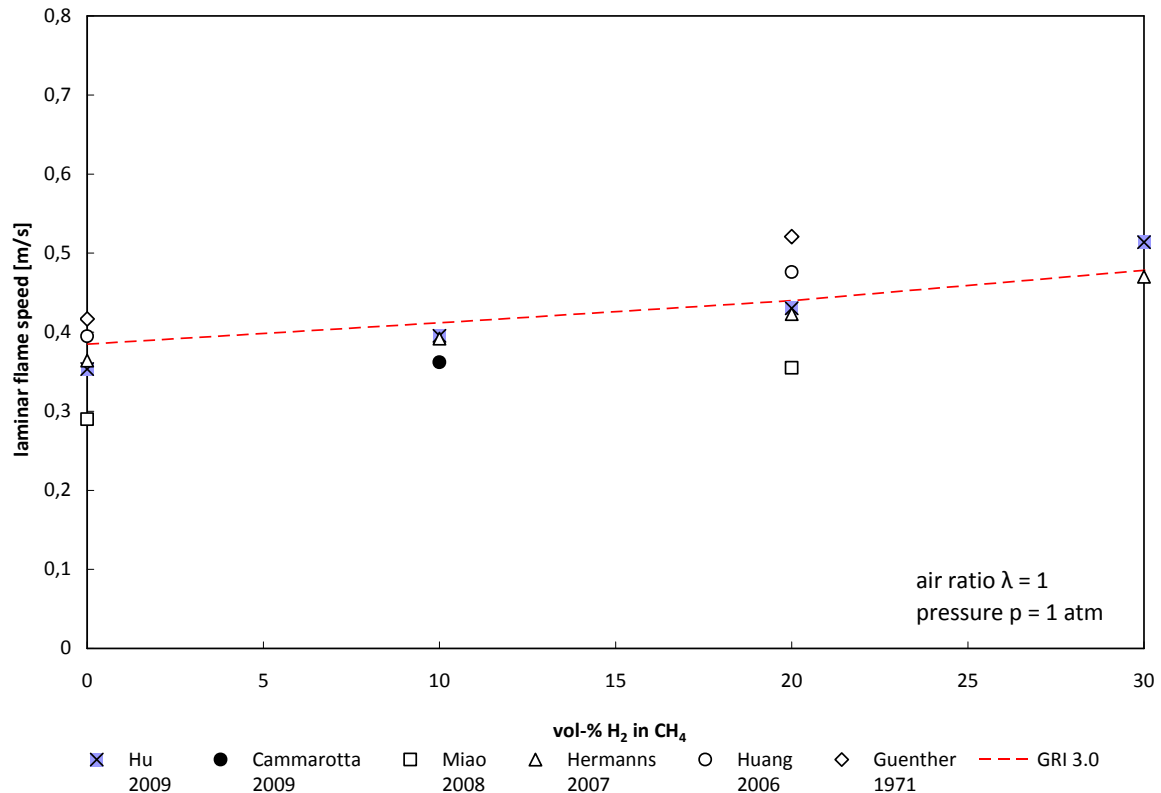


Figure 4: Laminar flame speed versus hydrogen fraction in methane

4. Non-critical aspects

Various studies have shown that most parts of the natural gas system can cope well with hydrogen addition of up to 10 %, with no adverse effects and, as a result, they do not feature prominently in this paper. However, the whole system has been analysed and, for completeness, the components or particular aspects which should cause no problems are listed below:

- natural gas transmission pipelines and compressors, despite concerns about hydrogen embrittlement;
- gas distribution pipework systems, including metering and billing equipment, seals, etc., where leakage was shown to be negligible;
- in-house pipework systems, with no problems reported at all;
- industrial applications, where no specific problems are anticipated if the Wobbe index of the gas mixture is well within the specified range. (See chapter 7);
- safety parameters (e.g. flammability limits, ignition energy, flame speed) affected only marginally; the increase of risk is very small. However special attention must be given to gas detection devices. (See chapter 5.7). A re-assessment of the ATEX Zoning may be required, depending on the methods used;
- some standards recommend a maximum content of hydrogen and other components of 5 % (ISO 6976).

More details are available in the full report¹, although this is confidential to the project members.

¹ Copies are available to the general public from GERG at a cost of €500 (€200 for universities)

5. Sensitive components

It's useful here to define what is meant by "sensitive components" and it's simply those elements of the gas system which are affected, or in the longer term, could deteriorate or could cause adverse effects in the presence of hydrogen admixtures up to 10 % in natural gas. As such, they are considered as limiting factors to the introduction of hydrogen into the natural gas system and require some investigation if they are to be understood and resolved. The specific effects vary depending on the component and may relate to the way processes operate, accuracy, susceptibility to corrosion effects, etc. As far as possible, all of the components known to be sensitive have been considered and are detailed below.

5.1. Underground storage

Gas storage is a key component in the natural gas chain and, in a future scenario, its various facilities could come into contact with natural gas/hydrogen mixtures. Little consideration has been given to this prospect until very recently, and experts have been reluctant to suggest a limit value for hydrogen addition because of the difficulty of identifying and quantifying the relevant processes among all possible reactions in underground storage facilities.

There are three aspects to underground storage: inner reservoir phenomena, phenomena linked to the well and the phenomena of interactions between well and reservoir. This review focuses only on inner reservoir phenomena and excludes well phenomena and phenomena of interactions between well and reservoir. Wells, which link reservoirs to the surface, were excluded from the study but they are the subject of a parallel exercise²[10].

Approximately twenty reservoir phenomena have been identified, all of which could impact reservoir exploitation. They have been ranked in importance, based on data found in the literature and from user experience, and, as a result, the review has been focused on four major types of storage or reservoirs, namely: aquifers, oil and gas depleted fields, salt caverns and lined rock caverns.

The most serious issue, or potential issue, identified, particularly in aquifers and oil/gas depleted fields, is the potential for bacterial growth [11]. The associated issues are principally loss of gas volume and disappearance of injected hydrogen, whether partial or total. There is also potential for damage to the cavity itself, and production of H₂S.

No problems were identified with salt cavern storage, so they could possibly be used for storage of hydrogen and natural gas mixtures, if necessary. However, it's important to note the potential for leaks from steel-lined rock caverns and we await results from the above-mentioned project. [10]

It's clear then that the effect of bacteria is the main concern for underground storage of hydrogen and natural gas mixtures, specifically in aquifers and depleted fields, as the interaction phenomena are not well understood, nor is it easy to identify specific bacterial species and to know, or measure, their quantities *in situ*.

In summary, it's not possible at the moment to define a limit value for the maximum acceptable hydrogen admixture for natural gas stored underground. Clearly more work is required on a number of aspects. (See chapter 6.1)

5.2. CNG steel tanks, metallic and elastomer seals

Addition of even small quantities of hydrogen to natural gas networks is currently a show-stopper with regard to steel CNG vehicle tanks. The potential for harmful interaction between hydrogen and steel has been known for many years and severe restrictions have long been in place. According to UNECE³ Regulation 110 for CNG vehicles, the H₂ content in CNG is limited to 2 vol %, if the tank cylinders are manufactured from steel with an ultimate tensile strength exceeding 950 MPa. This limit stems from the risk of hydrogen embrittlement which is known to cause accelerated crack propagation in steel and is, therefore, a critical safety issue. It's worth mentioning that the same 2 % limit is echoed in the corresponding ISO standard 11439 [12] and under DIN 51624, the German national standard for natural gas as a motor fuel.

In Europe, quenched and tempered steel 34CrMo4 is employed exclusively for CNG tanks and is compatible with hydrogen, provided that the tensile strength of the steel is less than 950 MPa, and that the inner surfaces of the cylinder have been inspected for allowable defects. However, existing steel CNG tanks are made predominantly of steel grades with a tensile strength greater than 950 MPa,

² DGMK - Deutsche Wissenschaftliche Gesellschaft für Erdöl, Erdgas und Kohle e.V.

³ United Nations Economic Commission for Europe

because these materials allow smaller wall thicknesses and thus reduced weight of the cylinders, which is preferred for vehicle use. In addition, CNG tanks are not inspected for surface defects (simply since there is no need for it.)

A key aspect here is that, under UNECE rules, car manufacturers are held responsible for the suitability of car components, including CNG tanks. This inevitably means that CNG vehicles will only be fuelled with natural gases containing more than 2% hydrogen when substantial tests have proved that it's safe and the existing regulations have been amended accordingly.

A complete screening of the existing tank population will be complex, as tests must prove that the storage tanks are safe under daily conditions, from -40 to +85 °C, including exposure to frequent cyclic loads induced by the fueling process and consumption and, finally, a lifetime of 20 years. So, clearly this will be a long-term process where, at the moment, final success cannot be guaranteed.

In addition to the well-known embrittlement difficulties with hydrogen, there are concerns regarding leak tightness of seals, both metallic and polymer. All gas carrying components inside the vehicle are currently designed and tested for a maximum 2 % H₂. As a result, all such components are potentially critical and their ability to cope with higher H₂ fractions remains to be tested.

5.3. Gas engines

Despite the limited availability of published information in this area, the physics of combustion, supported by experimental evidence from real engines, shows that the increase in flame speed and reactivity caused by hydrogen addition to natural gas typically increases in-cylinder peak pressures. As described in chapter 3.2 the methane number decreases if the proportion of hydrogen (or higher hydrocarbons) is increased.

This can result in:

- increased combustion and end-gas temperature, which leads directly to enhanced sensitivity for engine knock and increased NO_x emissions;
- improved engine efficiency, but with increased engine wear and increased (non-compliant) NO_x emissions;
- reduced power output or tripping, for engines with knock control;
- an adverse effect on lambda sensors which can cause an inaccurate (low) measurement of oxygen in the exhaust gas. (This will cause the control system to change the air:fuel ratio, resulting in a leaner mixture than intended, thus influencing performance and increasing both emission levels, especially NO_x, and the possibility of misfiring.

That even low fractions of hydrogen can precipitate engine knock, compared to the natural gas to which it has been added, directly implies one limitation on hydrogen fraction: if the knock resistance of the fuel is at the lowest value acceptable for an engine or population of engines and no adaption of engine operation is possible, then no hydrogen can be added to this gas.

For natural gases with a relatively high knock resistance, such that the engines that use it have a substantial knock “reserve”, the question of maximum hydrogen addition is complicated by other performance issues, partially related to the large diversity of engine types and field adjustments of the installed base. At the least, installed base engines are not expected to have controls to adapt engine conditions for (fluctuating fractions of) hydrogen addition.

One of these performance issues regards NO_x emissions; many gas engines that are not capable of adapting their operating conditions for hydrogen addition (air-fuel ratio, timing), and are at the permitting limit for NO_x, can also admit no hydrogen. A more complex issue regards the consequences of the higher cylinder pressure for engine/component lifetime, reliability and maintenance requirements, which are more difficult to quantify. However, these issues are not hydrogen specific; for example, the admixture of LPG leads to similar effects.

There are recommendations that 2 - 5 % hydrogen addition should be acceptable for engines, depending on the source of the gas. However, given the large and unknown variation in operating conditions of the installed base of engines, and the dependence of knock and NO_x emissions on the gas composition supplied to any given engine, it is strongly recommended that a case by case approach be used to determine the maximum allowable hydrogen fraction. (See chapter 7).

Most of the above has been derived from experience with stationary engines. Of course, the physical effects are the same for engines used in the transportation sector and, hence, the conclusions made here remain valid.

5.4. Gas turbines

It is widely understood that there are strict limitations to the degree to which hydrogen may be added to gas turbine fuel. It is normal for customers to specify a particular fuel, often depending on what is available locally, sometimes even process gas, so that the gas turbine combustion system could be carefully specified and tuned for optimum operation.

Current fuel specifications for many gas turbines place a limit on hydrogen volume fraction in natural gas below 5 %. Exceptions are dedicated (syngas) gas turbines that can accept very high hydrogen fractions (> 50 %) and some specific gas turbines which are capable of burning natural gas containing 10 % hydrogen and even more.

A large amount of literature exists on new gas turbine developments for gases containing high and mostly fixed fractions of hydrogen. However, literature relevant to hydrogen admixture in natural gas for the installed gas turbines is very rare.

From an end-user point of view, Abbott *et al* [13] conclude that fuel composition variation can have an adverse impact on gas turbine operation, despite being within the range allowed in the grid and manufacturers' specifications. The indication is, therefore, that for some gas turbines there is little or no margin for additional variations in fuel quality which reinforces the view that addition of even very low fractions of hydrogen to natural gas is likely to increase such issues for the installed gas turbine fleet.

It seems clear that, for the installed base gas turbines, 1 % must be considered as the general limit for hydrogen admixture to natural gas in a first step. Again, a case by case approach is required with special attention given to early or highly optimised DLN⁴ burners. After tuning and/or modifications much of the installed base may be capable of tolerating 5 % to 10 % volume hydrogen admixture.

Clearly, further work will be necessary to modify this situation.

As with gas engines, admixture of hydrogen to natural gas fuels that are towards the extremes of current acceptability will prove more problematic than admixture to "mid-range" fuels. The development of criteria that limit the amount of hydrogen addition to extreme fuels while allowing more addition to mid-range fuels may aid the introduction of hydrogen to the natural gas network.

5.5. Specific gas burners in the domestic sector

The risk when mixing 10 % H₂ with natural gas depends on the combination of two factors: the primary air excess and the initial Wobbe index. Therefore, atmospheric burners used with low-Wobbe gas are more sensitive to H₂, if they have been adjusted with G20 (methane).

The addition has a direct and indirect effect on the flame speed in burners used in domestic appliances:

- it slightly increases the flame speed, as shown in figure 5, below;
- it increases the air ratio if rich premix burners are considered (unless there is a systems that controls it) and so indirectly changes the flame speed.

Figure 5 shows that, for rich premixed combustion, the addition of H₂ will result in both direct and indirect increase of the flame speed. For lean premix combustion, there will be an increase because of H₂ and an indirect decrease because of the air ratio. So a larger H₂ impact is expected with rich premixed combustion (atmospheric burners).

⁴ Dry low NOx

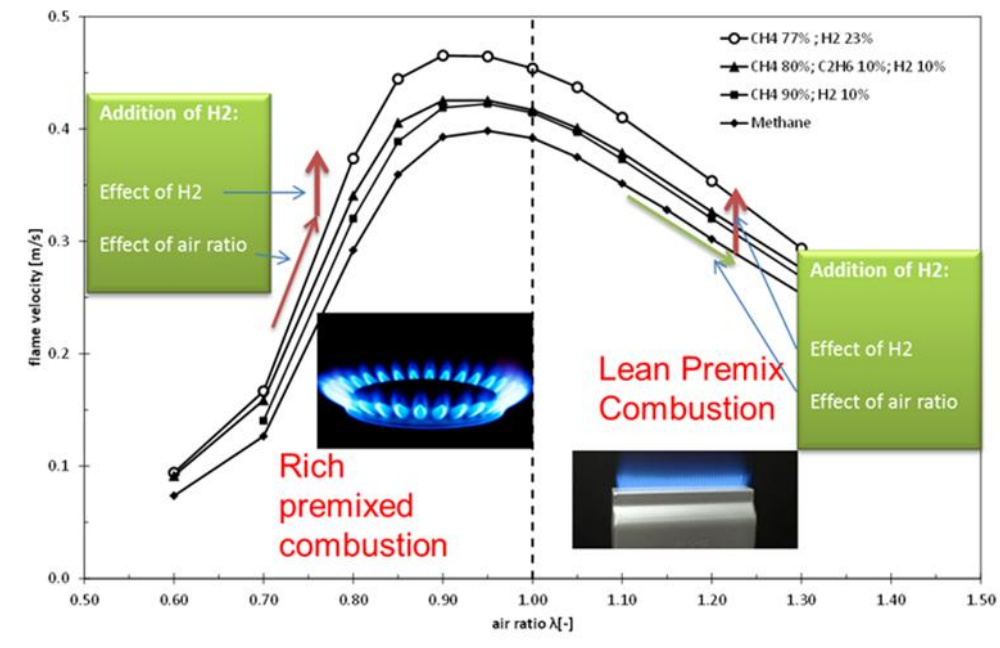


Figure 5: Flame speed and air ratio for different gases

All GAD⁵ appliances (i.e. since the beginning of the 90's) have been routinely tested with test gas G222, which is a mixture of 23 % H₂/77 % CH₄, and this gives a strong indication that such a high H₂ content in natural gas is acceptable, at least in the short-term. There are however, some limitations to that conclusion among which are:

- the possible long term impacts, which are not known;
- the fact that some countries may have gases in which the Wobbe index can be lower than that of the G222 test gas.

| | | | Theory | CE approval (1) | Long term effects | Testing |
|-----------------------------|--|-------------------|-------------|-----------------------------|-------------------|---------|
| BOILERS with full premix | | | Green | Green | Grey | Green |
| BOILERS without full premix | | | Grey | Green | Grey | Green |
| COOKERS and OVEN | | | Grey | Green | Grey | Green |
| WATER HEATERS | | | Grey | Green | Grey | Green |
| SPACE HEATERS | | | Grey | Green | Grey | Green |
| NEW TECHNOLOGIES | | | Grey | Green | Grey | Green |
| PRE-GAD APPLIANCES | | | Grey | Grey | Grey | Grey |
| | | (1) for W > 48 MJ | | | | |
| | | | Green | No impact | | |
| | | | Light Green | No impact but lack of tests | | |
| | | | Grey | Not known | | |
| | | | Red | Impact | | |

Table 1. Overall sensitivity from different sources by appliance type for 10% hydrogen in the natural gas

⁵ Gas Appliances Directive (Directive 2009/142/EC on appliances burning gaseous fuels)

The table summarises the current overall situation and it's clear that some uncertainties remain. (N.B. The results are valid for gas grids with a Wobbe number exceeding 14 kWh/m³ (equivalent to 48 MJ/m³ at a reference temperature of 15 °C/15 °C), 1.01325 bar).

On this basis, injection of 10 % of H₂ in natural gas grids (H gas) seems to be a reasonable future prospect for the domestic and commercial appliances considered. A “safety margin” should be taken into account. (See chapter 7).

However, the uncertainties need to be clarified, and in that regard, it would be beneficial to initiate some additional tests to acquire more data, as detailed in 6.5.

5.6. Gas chromatographs

There is a problem with the current generation of process gas chromatographs (PGC) which use helium as the carrier gas and, as a result, are unable to detect hydrogen because of the relative proximity of their thermal conductivities (helium = 151 W/m²*K; hydrogen = 180 W/m²*K.).

It's possible to solve this by retrofitting an additional separating column of argon as a carrier gas for hydrogen detection or by using new process gas chromatographs licensed for the metering of hydrogen. Another possibility might be to use PGCs with two single separating columns and two types of carrier gas. Some manufacturers have already developed new gas chromatographs ready for a hydrogen content up to 10 %.

5.7. Leak Detection

Gas detection devices designed for natural gas may not be accurate for mixtures of natural gas and H₂. Some gas detection devices will be more sensitive for H₂ than for natural gas while others are not sensitive at all to H₂ and will only react to the fact that the methane is diluted.

Semiconductor technology is suitable for detection of hydrogen/natural gas mixtures as it can identify methane as well as hydrogen. Most devices for measurement of the lower explosion limit of a gas mixture are configured for methane. Alarms are triggered upon reaching 10 % or 20 % of the lower explosion limit, i.e. 0,44 % or 0,88 % methane in air. The lower explosion limit declines slightly (4,36 %) with admixture of 10 % hydrogen. Limitations to the functionality are therefore not expected. Manufacturers generally understand how the addition of H₂ to natural gas affects the accuracy of their equipment and devices can be adjusted and calibrated for use with hydrogen.

FID devices (flame ionization detection - based on a hydrogen flame) and thermal conduction sensors have been designed for the specific detection of hydrocarbons, which means that these technologies can be applied only for low admixtures of hydrogen.

The usual safety and screening methods with gas detector devices and detectors currently used for pipeline grid inspections (by foot, by vehicle, by helicopter) are typically FID or, in the case of helicopters, DIAL (differential, infrared laser, absorption spectroscopy); neither of these technologies is capable of detecting hydrogen but would be acceptable, in terms of accuracy, in situations with hydrogen admixtures up to 5 % in natural gas, as the main component of the gas remains methane.

We must conclude therefore that the addition of H₂ to natural gas changes the accuracy of gas detectors. Some will react on the safe side and others won't. It is essential, therefore, to re-calibrate gas detection devices when H₂ could be present in natural gas to ensure that they will react on the safe side.

6. Proposals for further research

6.1. Underground storage

As bacteria are considered to cause the most severe problems, there have been attempts at eradication with disinfectants, but trials have been inconclusive to date, (froth/foam formation had caused problems). It is proposed now that more investigation is needed to overcome this problem.

An alternative solution may be to separate the hydrogen from the natural gas before injection into storage and to store the hydrogen separately, and then to mix hydrogen and natural gas before injection in the gas network. (N.B. This separation of hydrogen from the natural gas/hydrogen mixture, using specially developed membranes, was investigated in some detail in the NaturalHy [1] project and was found to be both problematic and expensive.)

There appears to be potential for estimating the impact of hydrogen addition following earlier attempts at numerical simulation by Maurer [14] and Bonnaud [15].

It may also be instructive to define a model for each kind of reservoir, to run simulations with various scenarios and to compare results with current projects such as HyUnder⁶ or Underground Sun Storage⁷.

6.2. CNG tanks, metallic and elastomer seals

For the existing fleet of CNG vehicles, with steel tanks (type 1), the hydrogen limit for admixture with natural gas is set in accordance with ECE-R110 and DIN51624 and CNG customers must be able to rely on the availability of compatible fuel.

A dedicated research program, which may help to determine a higher limit for the existing fleet would be of limited suitability as it cannot replace the certification procedure covering the complete set of relevant specifications. So, a backdated fleet approval for higher hydrogen contents on the basis of a test program cannot be expected.

Amendment of the existing regulations would imply that all CNG vehicle components in the field must be thoroughly investigated under all operation conditions, including all relevant parameters of durability such as hydrogen partial pressure, assembly temperature between -40 and +85 °C, relative humidity etc., in order to be approved for higher hydrogen contents. The enormity of this task suggests that it will probably never happen.

It may be useful also to analyse the theory and assumptions that led to the current 2% limit.

In the future it may be possible to introduce CNG vehicles which are specifically designed to tolerate higher hydrogen content. As this is linked to higher expenditure, it will be implemented only when the introduction of higher hydrogen fractions in natural gas becomes a realistic prospect.

If we assume increasing market penetration of such advanced CNG cars and the normal, progressive phase out of older models, a gradual transition to the acceptance of higher hydrogen levels in CNG would appear feasible. It is worth mentioning that this will be a long-term process as, for example, CNG vehicle tanks have a life-time guarantee of 20 years.

6.3. Gas engines

To allow higher fractions of hydrogen, engine configuration/adjustment/controls must be adapted to remove the physical cause of the issues:

- for engine knock, NO_x and engine wear, the peak pressures and temperatures must be lowered to those that will negate the effects of hydrogen. However, it's clear that unless the hydrogen fraction, and the natural gas composition to which it is added, can be constant, adaptations will have to accommodate fluctuating amounts of hydrogen;
- modern controls for air-fuel ratio and/or ignition timing that make use of exhaust NO_x sensors, temperature sensors or pressure sensors in the combustion chamber may compensate for fluctuating hydrogen fractions in the fuel. However, the adequacy of such solutions and the adaptability to the various engine types must be examined.

So, to enable the fluctuating hydrogen content in natural gas to be increased, further work is required to resolve a number of issues:

- effect of hydrogen on knock resistance and pre-ignition - a better method of accounting for the effects of hydrogen addition to the knock resistance of natural gas is required;
- the way in which engine control systems handle the effect of hydrogen on NO_x emissions and combustion pressures must be examined. The installed base has a diversity of control systems with various components. Their response to, and the ways they handle, hydrogen admixture vary. Different engine types with different control hardware and software may require different adaptations;
- risk of occurrence of explosions in intake, crankcase and exhaust will increase with hydrogen admixture. The effects and measures that should be taken must be identified.

⁶ www.hyunder.eu

⁷ www.undergroundsunstorage.at (operational October 2013)

6.4. Gas turbines

Tests on gas turbines are required with specific attention being paid to starting, flame stability (pulsations and flashback) and emission issues. Two possible approaches are to build experience:

- with new turbines and expand conclusions to the installed base;
- from pilot hydrogen projects that inject hydrogen in the natural gas grid.

For turbines and many other industrial processes it's important also to know the range and rate of change of the hydrogen content in natural gas. Consequently, this question has to be addressed before considering widespread injection of hydrogen in the gas network. (See chapter 7).

The development of criteria that limit the amount of hydrogen addition to extreme fuels while allowing more addition to mid-range fuels may be beneficial. Consideration should be given as to whether common criteria may be applicable to gas turbines, gas engines and other combustion processes.

6.5. Specific gas burners

With regard to domestic applications, uncertainties remain which need to be clarified so it would be useful to acquire more data from additional series of tests on:

- atmospheric burners, as the majority of the technologies on the market use these burners and the available test results do not sufficiently cover all segments of appliances;
- new technologies, especially those with features not previously present in the tests;
- pre-GAD appliances, for which we don't have a documented safety margin, such as CE approval.

Further investigations are recommended:

- on potential long-term effects of hydrogen addition to natural gas, such as overheating of burners and heat exchangers;
- to clarify the impact for Wobbe numbers below 14 kWh/m^3 (under which CE approval results cannot be used).

Finally, it is strongly recommended that, in EN 437, there should be a definition of new test gases and test procedures for approval of appliances that operate with hydrogen/natural gas mixtures; this would seem to be a fundamental requirement for preparing the future market.

6.6. Leak detection

Special attention must be given to gas detection devices because some are not sensitive to hydrogen. As a result, they see only the diluting effect of addition of H_2 to natural gas and will therefore give an inaccurate response.

For measuring systems which are not able to detect hydrogen explicitly, such as FID and DIAL, modification or replacement is recommended for admixtures of hydrogen of more than 10 vol.%. This statement is a first recommendation and certainly needs further investigation.

7. Practical recommendations for hydrogen injection

In general, a case by case analysis is necessary before injecting hydrogen in the natural gas network.

For the time being, porous rock underground gas storage is a "show stopper".

Most gas chromatographs will require modification.

It is recommended that manufacturers' specifications should always be followed, particularly when gas turbines or gas engines are connected to the network.

However, on the basis that much of the natural gas system can tolerate admixture of up to 10 % by volume of hydrogen, depending on the specific local situation, the following maximum hydrogen concentrations are recommended:

- 2 % - if a CNG filling station is connected;
- 5 % - if no filling station, no gas turbines and no gas engines with a hydrogen specification < 5 % are connected;
- 10 % - if no filling station, no gas turbines and no gas engines with a hydrogen specification < 10 % are connected.

N.B. For both 5 % and 10 %, care should be taken to ensure that the Wobbe index and methane number of the natural gas / hydrogen mixture are not close to the existing limit values for the network (“safety margins” for Wobbe index and methane number).

Injection of hydrogen should be carefully controlled to avoid sudden increases of the hydrogen concentration in the natural gas (e.g. speed of change < 2 % / min).

8. References

1. Florisson, O. et al.: *NaturalHy – Preparing for the hydrogen economy by using the existing natural gas system as a catalyst; An integrated project*, Final Publishable Activity Report: <http://www.naturalhy.net/>
2. Christoph, K.; Cartellieri, W.; Pfeifer, U.: *Bewertung der Klopffestigkeit von Kraftgasen mittels der Methanzahl und deren praktische Anwendung bei Gasmotoren*. MTZ 33, (1972), Nr. 10, pp. 389-429.
3. Cammarota, F.; Benedetto, A. D.; Sarli, V. D.; Salzano, E.; Russo, G.: *Combined effects of initial pressure and turbulence on explosions of hydrogen-enriched methane/air mixtures*. Journal of Loss Prevention in the Process Industries 22 (2009), Nr. 5, 607 – 613
4. Günther, R.; Janisch, G.: *Meßwerte der Flammgeschwindigkeit von Gasen und Gasgemischen*. Chemie Ingenieur Technik 43 (1971), Nr. 17, 975–978
5. Hermanns, R. T. E.: *Laminar Burning Velocities of Methane-Hydrogen-Air Mixtures*, Technische Universität Eindhoven, Diss., 2007
6. Hu, E.; Huang, Z.; He, J.; Jin, C.; Zheng, J.: *Experimental and numerical study on laminar burning characteristics of premixed methane–hydrogen–air flames*. International Journal of Hydrogen Energy 34 (2009), Nr. 11, 4876 – 4888
7. Huang, Z.; Zhang, Y.; Zeng, K.; Liu, B.; Wang, Q.; Jiang, D.: *Measurements of laminar burning velocities for natural gas–hydrogen–air mixtures*. Combustion and Flame 146 (2006), Nr. 1–2, 302 - 311
8. Miao, H.; Jiao, Q.; Huang, Z.; Jiang, D.: *Effect of initial pressure on laminar combustion characteristics of hydrogen-enriched natural gas*. International Journal of Hydrogen Energy 33 (2008), Nr. 14, 3876 - 3885
9. Brower M, Petersen E, Metcalfe W, Curran H J, Furi M, Bourque G, Aluri N, Güthe F, *Ignition delay time and laminar flame speed calculations for natural gas/hydrogen blends at elevated pressures*, ASME Paper GT2012-69310, Proceedings of ASME Turbo Expo 2012, June 11-15, 2012, Copenhagen, Denmark
10. DGMK Research Report- *Influence of hydrogen on underground gas storages*, Project 752, expected end of year 2013
11. M. Wagner, Dr. H. Ballerstedt, *Influence of Bio-methane and Hydrogen on the Microbiology of Underground Gas Storage / Einfluss von Biogas und Wasserstoff auf die Mikrobiologie in Untertagesgasspeichern*, Literature Study / Literaturstudie (DGMK-Projekt 756) / DGMK-Projekt 756, 2013, ISBN 978-3-941721-36-4⁸
12. ISO Standard 11439: *Gas cylinders - High pressure cylinders for the on-board storage of natural gas as a fuel for automotive vehicles*
13. D J Abbott , J P Bowers, and S R James, *The impact of natural gas composition variations on the operation of gas turbines for power generation*, 6th International Gas Turbine Conference, 17-18 October 2012, Brussels, Belgium
14. Maurer O., *Etude de la distribution des espèces soufrées et de la formation de l'hydrogène sulfuré dans les stockages de gaz naturel en aquifère*, ENPC thesis, décembre 1992

⁸ Available from: www.dgmk.de/upstream/agber_untertagespeichert.html

15. Bonnaud E., *Hétérogénéités compositionnelles dans les réservoirs de gaz acides. Compréhension et modélisation du rôle d'un aquifère actif*, Ph.D. Thesis, École nationale supérieure des mines de Paris - Spécialité "Hydrologie et Hydrogéologie quantitatives", June 29 2012

9. Bibliography

Recommended further reading:

1. Power to Gas
 - G. Linke, K. Steiner, M. Hoppe, H. Mlaker, E.ON Ruhrgas, *Power Storage in Smart Natural Gas Grids: Fiction or Fact?* EGATEC, Copenhagen, May 2011
 - K. Altfeld, P. Schley, E.ON Ruhrgas, *Development of natural gas qualities in Europe*, GWF international 2011
 - Judd R., Pinchbeck D., *Power to Gas Research Roadmap. Offering a solution to the energy storage problem?* Gas for Energy, Issue 2/2013
2. Underground storage
 - K. Schulze, *Hydrogen and bacteria – the big unknown*, 4th RWE Dea Research and Development Day, Hamburg 16th May 2013, Wietze Lab
 - M. Pichler, *Assessment of hydrogen-rock interactions during geological storage of CH₄-H₂ mixtures*; Master thesis, Department Mineral Resources & Petroleum Engineering Chair of Reservoir Engineering, 2013
 - J.-L. Garcia, *Les bactéries méthanogènes – The Methanogenic Archaea*, C. R. Acad. Agric. Fr. 1998, 84, 23-33
3. CNG tanks
 - UN ECE Regulation No. 110: Uniform provisions concerning the approval of:
 - (i) Specific components of motor vehicles using compressed natural gas (CNG) in their propulsion system;
 - (ii) Vehicles with regard to the installation of specific components of an approved type for the use of compressed natural gas (CNG) in their propulsion system.
 - Barthélémy, H.: *Compatibility of Metallic Materials with Hydrogen. Review of the Present Knowledge*, International Conference on Hydrogen Safety, San Sebastián, Spain, Sept. 2007
 - EU-Project "Integrated Gas Powertrain", Final report, 2012. <http://www.ingas-eu.org>
4. Gas engines
 - K. Gillingham; Stanford University Department of Management Science & Engineering, *Hydrogen Internal Combustion Engine Vehicles: A Prudent Intermediate Step or a Step in the Wrong Direction?*
 - S. Orhan Akansua; Z. Dulgerb, N. Kahramana, T. Nejat Vezirogluc; *Internal combustion engines fuelled by natural gas-hydrogen mixtures*; International Journal of Hydrogen Energy 29 (2004)
 - Klell, M., Eichsleder, H. and Sartory, M., *Mixtures of hydrogen and methane in the internal combustion engine – Synergies, potential and regulations*, International Journal of Hydrogen Energy, 37(2012)
 - DIN 51624; Kraftstoffe für Kraftfahrzeuge – Erdgas – Anforderungen und Prüfverfahren
Automotive fuels – Compressed natural gas – Requirements and test methods
5. Gas turbines
 - M. Andersson, J.Larfeldt, A. Larsson, *Co-firing with hydrogen in industrial gas turbines*, SGC Rapport, 2013
 - C. Marchmont, S. Florjancic, Alstom Baden, Switzerland, *Alstom gas turbine technology trends*, Proceedings of ASME Turbo Expo, 2012 GT2012 June 11-15, 2012, Copenhagen, Denmark

- S, J. Wu, P. Brown, I. Diakunchak, A. Gulati, Siemens Power Generation, Inc., Orlando, USA, M. Lenze, B. Koestlin, Siemens Power Generation Inc., Muelheim, Germany; *Advanced gas turbine combustion system development for high hydrogen fuels*, Proceedings of GT2007 ASME Turbo Expo 2007: Power for Land, Sea and Air; May 4-17, 2007, Montreal, Canada

6. Gas burners

- Nitschke-Kowsky, P., Wessing, W. E.ON Ruhrgas AG. *Impact of hydrogen admixture on installed gas appliances*. World Gas Conference (WGC), Kuala Lumpur, 2012
- EN 437 Test gases. Test pressures. Appliance categories
- Huang, Z., et al. *Measurements of laminar burning velocities for natural gas-hydrogen-air mixtures*, Combustion and Flame 146(2006)
- Di Sarli, V. and Di Benedetto, A., *Laminar burning velocity of hydrogen-methane-air/ premixed flames*, International Journal of Hydrogen Energy, 32(2007)
- Ayoub, M. et al., *An experimental study of mild flameless combustion of methane/hydrogen mixtures*, International Journal of Hydrogen Energy, 37(2012)
- Levinsky, H.B., *Consequences of “new” gases for the behaviour of gas utilization equipment*, 2004, International Gas Research Conference, Vancouver

7. Safety

- De Vries, H., Florisson, O. and G.C. Tiekstra, *Safe operation of natural gas appliances fuelled with hydrogen/natural gas mixtures (progress obtained in the NaturalHy-project)*, International Conference on Hydrogen Safety (ICHS 2007), San Sebastian, Spain, September
- Jurdik, E., Darneveil, H. and Levinsky, H.B., *Flashback in mixtures of molecular hydrogen and natural gas*, 2004 International Gas Research Conference, Vancouver
- Lowesmith, B.J., Hankinson, G., *Large scale high pressure jet fires involving natural gas and natural gas/hydrogen mixtures*, Process Safety and Environmental Protection, Volume 90, Issue 2, March 2012

10. Acknowledgements

The authors would like to thank GERG⁹ and the project partners, as detailed in the annex, for their support and, in particular, the following active partners for their specific contributions:

- G Müller-Syring, S Schütz, DBI-GUT, (gas distribution systems, gas metering / billing)
- J Schweitzer, M Näslund, DGC, (domestic / commercial gas applications)
- A Dijks, A D Bloemsmas, H de Vries, DNV Kema, (gas turbines / gas engines, analysis of safety relevant gas parameters)
- K Altfeld, M Hoppe, E.ON New Build & Technology GmbH, (CNG tanks / compressors, valves etc.)
- F Lebovits, L Nadau, R Batisse, Nicolas Richard, GdF Suez, (transmission pipelines / underground storage / industrial applications)
- H Rijpkema, W H Bouwman, Kiwa Technology, (in-house installations)

⁹ The European Gas Research Group (www.gerg.eu)

Annex 1: Partners

(i) Active partners

| | |
|----------------------------------|-----------------|
| DBI-GUT | Germany |
| DGC | Denmark |
| DNV Kema Nederland BV | The Netherlands |
| E.ON New Build & Technology GmbH | Germany |
| GdF Suez | France |
| Kiwa Technology | The Netherlands |

(ii) Project partners

| | |
|---|-----------------|
| Alliander N.V. | The Netherlands |
| BP Exploration Operating Company | U.K. |
| DBI-GUT | Germany |
| DGC | Denmark |
| DNV Kema Nederland BV | The Netherlands |
| DVGW e.V. | Germany |
| E.ON Gas Storage GmbH | Germany |
| E.ON New Build & Technology Ltd | U.K. |
| E.ON New Build & Technology GmbH | Germany |
| Enagas S.A. | Spain |
| Energinet | Denmark |
| Euromot | Belgium |
| EUTurbines | Belgium |
| Fluxys S.A. (ARGB) | Belgium |
| Gas Natural sdg | Spain |
| Gassco AS | Norway |
| Gasum Oy | Finland |
| GdF Suez | France |
| GL Noble Denton | U.K. |
| Infraserv GmbH & Co | Germany |
| Italgas | Italy |
| ITM Power GmbH | U.K. |
| Kiwa Technology | The Netherlands |
| National Grid plc | U.K. |
| Naturgas Energia Distribucion, Saur | Spain |
| OGE GmbH | Germany |
| ÖVGW | Austria |
| RWE Dea AG | Germany |
| Shell Global Solutions International B.V. | The Netherlands |
| Snam Rete Gas S.p.A. | Italy |
| SVGW | Switzerland |
| Volkswagen AG | Germany |
| KOGAS - Korea Gas Corporation | South Korea |