HYGRID

FLEXIBLE HYBRID SEPARATION SYSTEM FOR H2 RECOVERY FROM NG GRIDS

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WP2 – Industrial Requirements Definition

D.2.1
Industrial specifications for a system to recover hydrogen from Natural Gas grids

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PU	Public	X
PP	Restricted to other programme participants (including the Commission Services)	
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CO	Confidential, only for members of the consortium (including the Commission Services)	
CON	Confidential, only for members of the Consortium	

Content

1. EXECUTIVE SUMMARY (3 pages max. all points)

1.1. Description of the deliverable content and purpose

This document aims to collect information about the state-of-the-art of natural gas separation systems to hydrogen and identify process parameters as well as present constraints of the technology. This report also summarizes the hydrogen requirements in terms of purity and pressure and present a target cost for the hybrid system to be designed in the HyGrid project.

It should be mentioned that although within this project technical barriers to extract low amounts of hydrogen from natural gas will be overcome, it is necessary to establish a legal framework enabling the use of hydrogen to storage energy and its transport by using existing natural gas grids.

1.2. Brief description of the state of the art and the innovation brought

One of the main problems for the implementation of the hydrogen based economy is the transportation from production centres to the end user. One approach to solve this problem is to use the existing Natural Gas network for storing and distributing hydrogen.

The HyGrid technology will provide a route to:

- Increase the value of hydrogen blended into the natural gas grid, improving the economics of central hydrogen production from excess renewable energy coupled with natural gas grid injection.
- Reduce cost, and therefore increase the use of hydrogen from very dilute hydrogen streams in energy and transport applications.
- Further applications could be found in separating hydrogen from mixtures produced in chemical or biological processes, where it otherwise would be used to generate heat or even be vented.

1.3. Deviation from objectives

There are no deviations.

1.4. If relevant: corrective actions

There are no deviations.

1.5. If relevant: Intellectual property rights

2. INTRODUCTION

2.1. THE HYDROGEN POTENTIAL

The interest in hydrogen is rising because it is considered a sustainable energy carrier which allows high amounts of energy storage at a utility scale. Development of infrastructure to its transportation and storage would increase the interest in it as a fuel to be used for example in fuel cells for electric vehicles, in stationary fuel cells for buildings, backup power or distributed generation. As it is a clean fuel that produces 0 emissions of CO_2.

There are several limitations to the spreading of the use hydrogen, for example, hydrogen does not exist naturally but it has to be produced and delivered as it happens with the electricity.

One way to produce sustainable hydrogen is the Power to Gas process well known nowadays and with an innovative technology in which the excess of energy produced by renewable sources is used to electrolyze water to produce hydrogen and oxygen. This hydrogen can be used directly, to obtain methane or to upgrade biogas.

To use the hydrogen directly, it has to be transported first. Building new infrastructures to transport hydrogen is expensive and not technically feasible in most cases, however, an alternative could be to use the existing gas grid to transport and store hydrogen from the production point to the end user. This is limited by the maximum hydrogen concentration allowed in gas grids.

For the end user be able to use hydrogen it is necessary to separate hydrogen from the natural gas in a technically and economically affordable way, and to study the best technologies for achieving that, the HyGrid project was set up. No very high concentrations of hydrogen are technically permitted in natural gas grid so existing technologies should be overdesigned to separate hydrogen in low concentrations making them economically unacceptable. Development of new technologies is necessary.

3. LIMITS TO HYDROGEN INJECTION IN GAS GRID

Limits to Hydrogen concentration in gas grid are defined by technical and safety issues. Also economics has to be taken into account as the use of hydrogen as energy carrier will be realistic only when it becomes economically favourable.

3.1. TECHNICAL CONSTRAINTS

Technical constraints are referred to the maximum amount of hydrogen allowed in the grid to guarantee technical feasibility, economic viability and safety.

It is well known that the maximum hydrogen content injected into natural gas pipelines could be in the range 2 to 10 %[1] depending on the end-use elements existing in the grid, although a case by case analysis is necessary before injecting. First of all, 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 most of the natural gas systems can accept admixture of up to 10 % by volume of hydrogen, the following maximum hydrogen concentrations in natural gas based upon safety are recommended (see 1):

- Max. 2% if a CNG filling station is connected.
- Max. 5% if there aren´t any CNG filling station, gas turbines or gas engines with a hydrogen specification <5%.
- Max. 10% if there aren´t any filling station, gas turbines or gas engines with a given hydrogen specification <10%.

It is important to point out that the maximum amount of hydrogen has to comply with the requirements of the end users. This raises the question, who will be the responsible for the hydrogen separation in order to reach the desired composition? Should it be the responsibility of the gas transporter to avoid damages to the end user´s facilities or should be the end user who deals with the gas treatment? Another question which should be answered is if the separation affects the whole flow or only a part of it.

Injecting a 2% would be the best solution to prevent the difficulties described above. Although a higher percentage will carry a higher amount of hydrogen and it should be more economic,

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[1] Blending Hydrogen into Natural Gas Pipeline Networks: A review of Key Issues (2013). M.W. Melaina, O. Antonia and M.Penev. Technical Report NREL/TP-5600-51995; Admissible hydrogen concentrations in natural gas systems Klaus Altfeld and Dave Pinchbeck. Reprint gas for energy 03/2013 ISSN 2192-158 X; Injection of Hydrogen into the Natural Gas System (2014), Aksel Hauge Pedersen, DONG Energy A/S Denmark

in the end the cost of reducing the hydrogen concentration to a suitable one for the end user could involve a higher cost that could make disappear any benefit.

Safety is the next most limiting condition and pipeline material durability imposes fewer limitations.

3.1.1. Influence on combustion parameters

Although the main goal of the HyGrid project is to acquire the necessary knowledge to separate hydrogen from natural gas and the use of the blend is not considered, we will summarize the principal effects of adding hydrogen on the combustion parameters of the natural gas.

Wobbe Index

Wobbe Index is an indicator of the interchangeability of different fuel gases. It is studied that the admixture of 10% of hydrogen lowers the Wobbe Index by 3%. Therefore, hydrogen doesn´t significantly affect this parameter.

If biomethane is considered, local Wobbe specifications can prevent hydrogen injection because biomethane has already a low Wobbe Index.

Methane number (MN)

The methane number describes the knock behaviour of fuel gases in internal combustion engines and strongly depends on the specific gas composition (especially the amounts of higher hydrocarbons C3, C4 and C5) and hydrogen. The MN of pure methane is 100 and hydrogen is 0; for rich LNG is 60-70. According to these figures, an admixture of hydrogen of 10% can result in an unacceptably low MN from a gas engine operator´s perspective.

Laminar flame speed

Flame speed is a complex combustion parameter related to flash back and flame stability. There is a trend to increasing flame speed with increasing hydrogen addition. Typically, for hydrogen admixture of 10% there is a 5% increase of the laminar flame speed.

With regard to gas turbines, turbulent flame speed is an important parameter. Relevant information is limited (measurement of laminar and turbulent flame speed is very difficult) but calculations show that hydrogen has a stronger influence on flame speed; a 10% of hydrogen may result in a 10% increase in turbulent flame speed.

3.1.2. Durability of materials

The effects of hydrogen on the durability of the materials and components used in the natural gas transmission and distribution network as well as the end user devices have to be taken into account in the technical constraints to inject hydrogen in the natural gas.

Due to the fact that very little experience exists for hydrogen in modern natural gas pipelines made of steel and plastic, several companies are carrying out studies in order to determine how hydrogen can affect the lifetime of the gas grid components.

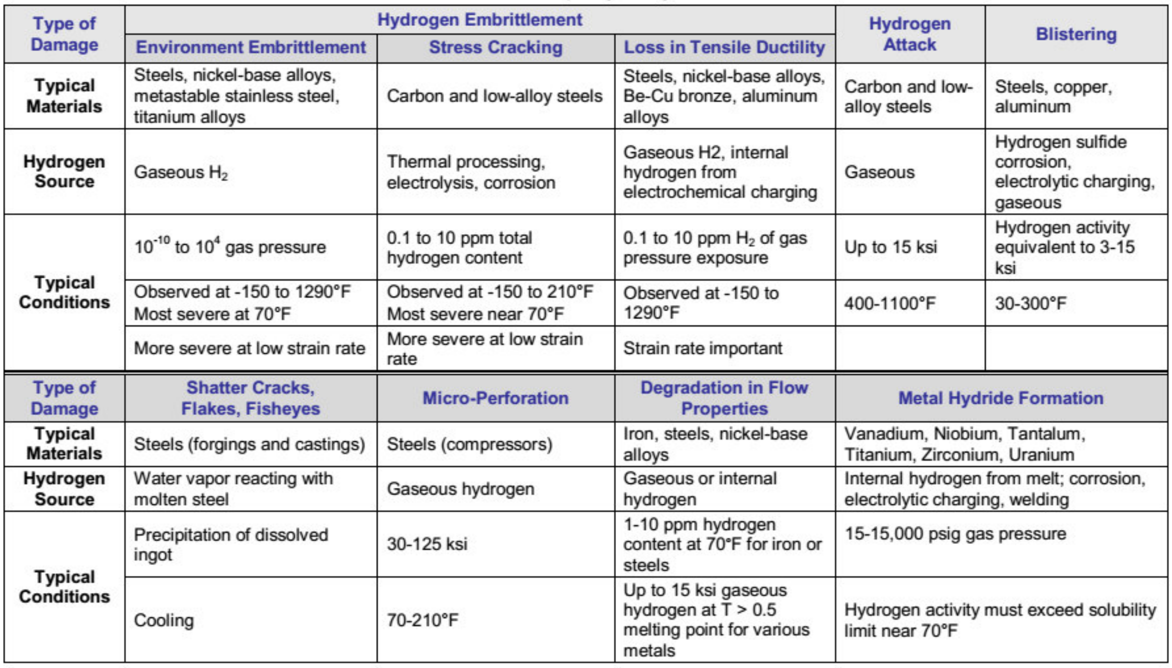
Effects of adding hydrogen in metals

Some studies show that adding up to 50% hydrogen into the natural gas transmission pipelines may not cause catastrophic failure, although the acceptable hydrogen level depends on the type of steel used for high pressure pipeline.

Hydrogen damage is the result of the combined action of hydrogen and residual or applied tensile stress. In general, hydrogen damage occurs at stress levels below those typically experienced for a particular metal in an environment without hydrogen. It is affected by hydrogen pressure, purity, temperature, stress level, strain rate, material microstructure and strength.

The table below (from ASM Handbook vol. 13A (Hydrogen Damage) includes the materials that are susceptible to hydrogen damage, the various types of hydrogen damage, the source of hydrogen and the typical conditions for the occurrence of failure.

Table I. Damages caused by hydrogen in different kind of pipes



Type of Damage	Hydrogen Embrittlement			Hydrogen Attack	Blistering
	Environment Embrittlement	Stress Cracking	Loss in Tensile Ductility		
Typical Materials	Steels, nickel-base alloys, metastable stainless steel, titanium alloys	Carbon and low-alloy steels	Steels, nickel-base alloys, Be-Cu bronze, aluminum alloys	Carbon and low-alloy steels	Steels, copper, aluminum
Hydrogen Source	Gaseous H_2	Thermal processing, electrolysis, corrosion	Gaseous H2, internal hydrogen from electrochemical charging	Gaseous	Hydrogen sulfide corrosion, electrolytic charging, gaseous
Typical Conditions	10^{-10} to 10^{4} gas pressure	0.1 to 10 ppm total hydrogen content	0.1 to 10 ppm H_2 of gas pressure exposure	Up to 15 ksi	Hydrogen activity equivalent to 3-15 ksi
	Observed at -150 to 1290°F Most severe at 70°F	Observed at -150 to 210°F Most severe near 70°F	Observed at -150 to 1290°F	400-1100°F	30-300°F
	More severe at low strain rate	More severe at low strain rate	Strain rate important		

Type of Damage	Shatter Cracks, Flakes, Fisheyes	Micro-Perforation	Degradation in Flow Properties	Metal Hydride Formation
Typical Materials	Steels (forgings and castings)	Steels (compressors)	Iron, steels, nickel-base alloys	Vanadium, Niobium, Tantalum, Titanium, Zirconium, Uranium
Hydrogen Source	Water vapor reacting with molten steel	Gaseous hydrogen	Gaseous or internal hydrogen	Internal hydrogen from melt; corrosion, electrolytic charging, welding
Typical Conditions	Precipitation of dissolved ingot	30-125 ksi	1-10 ppm hydrogen content at 70°F for iron or steels	15-15,000 psig gas pressure
	Cooling	70-210°F	Up to 15 ksi gaseous hydrogen at T > 0.5 melting point for various metals	Hydrogen activity must exceed solubility limit near 70°F

Conditions for hydrogen damage on iron or copper do not apply to natural gas distribution system. Nevertheless, hydrogen embrittlement is a potential concern for steel pipes; this effect varies with the type of steel. In general, high-strength steel are more susceptible to hydrogen induced cracking than low-strength steel which is only subjected to loss in tensile ductility.

The impacts of hydrogen on the durability of materials can be outlined in three points:

Impact of Hydrogen on the Durability of Metallic Pipes in Distribution Systems:

Studies in USA

If pipes are made of low strength steel (more common in distribution grids), the hydrogen damage consists of a loss in tensile strength or blistering which strongly depends on the hydrogen content in the environment. Under pressures of 17bar, the potential risks for this material is very low.

High-strength steels are more susceptible to hydrogen induced cracking.

For metallic pipes made of ductile iron, cast and wrought iron and copper pipes, there is no concern of hydrogen damage under usual operating conditions.

Studies in Denmark

Tests carried out in Denmark by the DGC (Danish Gastechnology Center) to steel pipes and weldings were dynamic tests equivalent of 80 years with two times the maximal pressure variations found in the Danish gas transmission system showed no defect growth and therefore no safety problems.

Impact of Hydrogen on the Durability of Plastic Pipes in Distribution Systems:

Due to the little experience in transporting hydrogen in modern natural gas pipelines made of steel and plastics, the DGC among others, began to test about 10 years ago, PE for transporting hydrogen. Other studies also included PVC. Conclusions of the tests performed were the same:

- Structure analysis accomplished to the structure indicates no interaction between hydrogen and the polymer.
- Mechanical analysis (tensile tests, elongation at break, elastic modulus, slow crack growth) show that no deterioration occurred as a result of the exposure to pressurised hydrogen during the tests (4 years)

It should be highlighted that there could be potential contaminants in hydrogen gas that may be introduced into the network that may affect material durability.

Impact of Hydrogen on the Durability of Gas Meters:

Impact depends strongly on the manufacturer. Deviations can be positive or negative when measuring hydrogen/methane mixtures although they are not important when the gas mixture contains less than 50% of hydrogen (in this case the requirement for recalibration is <4%).

3.1.3. Safety

The concepts expressed in this section are not applicable to dedicated hydrogen pipelines. In the NaturalHy project a safety assessment was developed which main conclusions are still applicable:

- Gas build up: it was found that gas build up behaviour of natural gas and hydrogen blends lower than 50% was similar to that of pure natural gas. No separation of hydrogen from the mixture was observed
- Explosions in enclosures: Blends with less than 20% hydrogen barely have an increase in severity of confined vented explosions compared with pure gas natural. However, blends with more than 50% hydrogen have a more significant increase in overpressure and, therefore the risk is higher compared with natural gas. Risk can be substantially reduced if ventilation is used or if the structural congestion causing confinement is reduced.

- Risk from transmission pipelines: Behaviour of hydrogen blends is slightly different from natural gas due to the rapid dispersion of hydrogen. The risk associated with explosion drops faster in hydrogen admixtures as distance from pipeline rises.

Inside this point, **leakage** has to be taken into account. Hydrogen is a much smaller molecule than methane, so its leakage rate through pipe walls and joints may be greater and most of the detection devices are not able to detect hydrogen losses without modifications for admixtures of hydrogen of more than 10%.

Leakage also has to be considered when an economic analysis is done because of the total gas loss. Studies about leakage were carried out by Gaz de France during the NaturalHy project. Tests were performed to PE 63, PE 80 and PE 100 at operating pressures (1-12 bar) and temperatures (5-25ºC) with hydrogen/methane mixtures. Main results were the following:

- While there is an incubation time for methane to diffuse through the pipe, the incubation time for hydrogen is close to zero.
- Permeation rate of methane and hydrogen depend on the working pressure.
- Permeation coefficient of hydrogen is 4 to 5 times greater than that of methane in mixtures, even when hydrogen partial pressure is lower than methane partial pressure by an order of magnitude.
- It seems that pipe aging has no influence on the permeation coefficients under the experimental conditions.

These studies were completed with hydrogen leakage rate from PE and PVC pipes at 200 mbar distributing 100% H_2 and the leakage rate of methane and hydrogen calculated from PE disc samples under a mixture of 80% of natural gas and 20% hydrogen at 4 bar. Calculated results are:

Table II. Hydrogen leakage rates

H_2 leakage rate in plastic pipes		H_2 leakage rate in PE discs	
PE100	5 L/km/day	**Methane**	1,1 L/km/day
PVC	13,2 L/km/day	**Hydrogen**	2,3 L/km/day

GTI (Gas Technology Institute-USA) reviewed other relevant information about hydrogen leakage in natural gas distribution system. Main conclusions are the following:

- Gas leakage from steel or ductile iron systems: leakage mainly passes through the threads or the mechanical joints being three times higher than that for the natural gas.

- Gas leakage from steel or ductile iron systems: reviewed documents show that losses calculated in the Dutch grid represent 0.0005% of the hydrogen transported, thus the hydrogen loss is considered as negligible and will not create a significant problem.
- Estimation of gas loss of US distribution network: because the differences in the materials employed in Europe and USA, a different assessment has to be done to the US grid. The majority of the plastic pipes used in US natural gas distribution systems are MDPE (medium density polyethylene), HDPE (high density polyethylene) and a small percentage of PVC. Studies done with admixtures of 20% show that at low pressure losses are not significant. The majority of gas loss is produced when pipes operate at 4.1bar or higher.

By way of summary, it can be pointed out that calculated losses in previous projects are lower than those predicted by using theoretical estimates. This may be because hydrogen activity is much lower in mixtures H_2/CH_4 than when it is pure.

3.1.3. Impact on end-use systems

In case of a high hydrogen blend level, adaptation of end-use systems is required. Studies carried out during the development of the NaturalHy project concluded that hydrogen concentrations up to 28% may be safely used with properly serviced existing domestic appliances although long term material compatibility with hydrogen and natural gas mixtures is uncertain.

Inside the group End-Use Systems sensitive devices are gathered:

- **Underground storage**: Gas storage is a key component in the natural gas chain and because of that its various facilities could come into contact with natural gas/hydrogen mixtures. Although it is very difficult to identify and quantify all the relevant processes related to underground storage phenomena, approximately twenty reservoir phenomena which could impact reservoir exploitation have been identified. The most serious issue identified in aquifers and oil/gas depleted fields is the potential for bacterial growth. Other issues are loss of gas, potential for damage to the cavity and production of H_2S. In case of salt cavern storage it was not detected any problem. However it is important to point out that it is not possible at the moment to define a limit value for the maximum acceptable hydrogen admixture for natural gas stored underground.
- **CNG steel tanks, metallic and elastomer seals**: the potential for harmful interaction between hydrogen and steel has been known for many years, the expressed limit of

2% being the maximum amount of hydrogen for CNG vehicles. This limit is echoed in ISO 11439 and DIN 51624 and it is has been determined to avoid accelerated crack propagation in steel because of hydrogen embrittlement. All gas carrying components inside the vehicle (for example, metallic or polymeric seals) are currently designed and tested for a maximum 2% H_2.

- **Gas engines**: As it was described above, the admixture of hydrogen and natural gas modifies flame speed and reactivity making them greater as hydrogen concentration rises. Likewise, the methane number decreases as hydrogen percentage increases. All of that can lead to:
    - An increased combustion and end-gas temperature, which leads directly to enhanced sensitivity for engine knock and increased NOx emissions.
    - An improved engine efficiency, but with an increased engine wear and NOx emissions (non-compliant).
    - A reduced power output for engines with knock control.
    - An adverse effect on lambda sensors which can cause an inaccurate measurement of oxygen in the exhaust gas.

  Even low fractions of hydrogen can cause engine knock. Many gas engines are not capable of adapting their operating conditions for hydrogen addition (air-fuel ratio, timing) and are at the permitting limit for NOx can also admit no hydrogen.

  Recommendations are about 2-5% of hydrogen depending on the source of the gas.

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

  For some gas turbines there is little or no margin for additional variations in fuel quality because it would have impact on gas turbine operation. The accepted limit for gas turbines is 1%, a step by step approach being necessary and for tuned or modified turbines 5-10%.

- **Specific gas burners in the domestic sector**: the addition of hydrogen leads to an increasing flame speed and a reduction in Wobbe Index. Although long term impacts are not known, the injection of 10% of H_2 in natural gas grids seems to be reasonable for the domestic and commercial appliances such as, boilers, cookers and oven, water heaters, space heaters and so on.

3.2. ECONOMIC CONSTRAINTS

A comprehensive economic analysis will be done during the HyGrid project, but estimations made points out:

- Main cost parameters are the costs of electricity, investment in electrolyser and operational costs, although possible incomes are hydrogen sale and delivery. The electrolyser is the main cost, so the price of power is an essential factor for hydrogen production. The investment costs power to gas plant is represented in next figure[2].

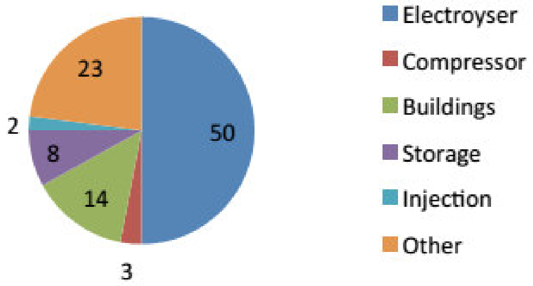


Fig. 1. Investment costs power to gas plant (5MW, 1000 m^3/h H_2)

The amount of gas loss from service lines is negligible from the economic point of view.

A further analysis is needed to valorise the cost estimate of hydrogen extraction from a Distribution Natural Gas Pipeline. NREL[3] performed a cost estimate of hydrogen extraction from a distribution natural gas pipeline employing PSA units. They used previous data to develop the extraction cost modelling.

Capital cost estimate for PSA units is based on a mature system that is functionally reliable in the field and has been produced in sufficiently high annual and cumulative quantities as to have a capital cost (and unit cost) close to its asymptotic limit. At low manufacturing volumes, capital costs are high due to relatively time-intensive manufacturing and assembly methods. As the manufacturing rate increases, more efficient production methods become economical, capital cost (per unit output) decreases, and unit cost decreases. At extremely high manufacturing rates, all possible cost improvements have been achieved, and production rates are increased only by replicating process machinery. At those levels, capital cost (per unit output) and unit cost flatten in relation to the manufacturing rate.

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[2] WOC 5.4 - Study group report – “Economic aspects".
[3] National Renewable Energy Laboratory, US Department of Energy

The N^th plant[4] assumption affects the H2A[5] cost computations in two ways. The primary effect is in the estimated value of plant capital cost. The capital cost used in the Hydrogen Analysis computation should not pertain to the initial or "one off" cost of a system, but rather to a relatively mature system produced in high volumes. Blended into the capital cost estimate are factors such as bulk discounts on material costs and low-cost manufacturing and assembly methods. These are made possible by serial production of the systems, efficient and streamlined business operations, and a lower profit margin consistent with a mature product that must be priced competitively. NREL assess only the cost of hydrogen extraction here. The other costs (injection cost, hydrogen losses along the pipeline, capital cost increase caused by underutilization during lag-in-demand seasons, analytical costs, etc.) are not accounted for here. The estimated cost of hydrogen extraction by PSA from a 300 psi pipeline is shown in Fig. 2.

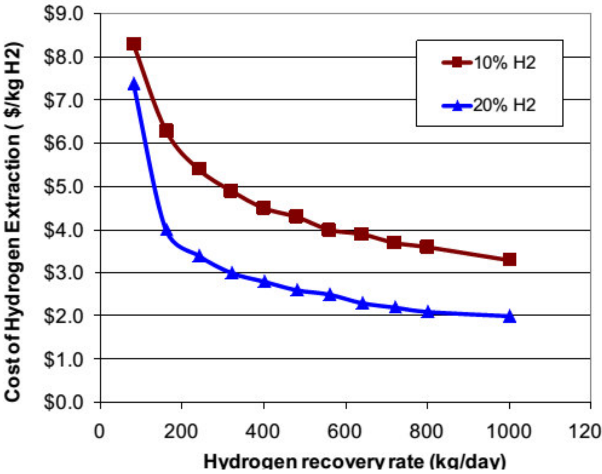

Fig. 2. Estimated cost of hydrogen extraction by PSA unit from 300 psi natural gas distribution pipeline (assumed hydrogen recovery factor is 80%)

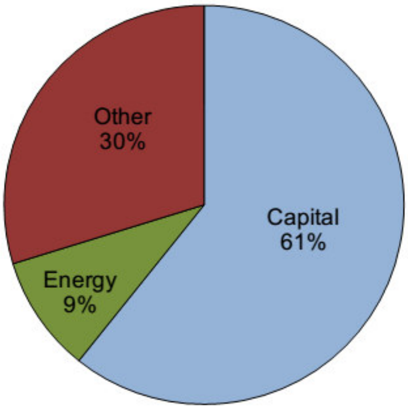

Fig. 3. Hydrogen extraction cost breakdown

Assumptions: PSA unit from 300 psi natural gas distribution pipeline with 10% added. Hydrogen recovery rate 100 kg/d, hydrogen recovery factor 80%

For the assumptions made, the extraction cost is $3.3–$8.3/kg of hydrogen extracted, depending on the scale of extraction or recovery rate in kg/day, as showed in Fig. 2. For a 20% hydrogen concentration, the extraction cost across the same scale of extraction drops to $2.0–$7.4/kg.

The high cost of hydrogen extraction from a natural gas pipeline is largely due to high capital costs. For example, for a 10% hydrogen pipeline, the capital cost contribution to the levelised cost of hydrogen extraction is 61% (Fig. 3), 66% of which is the cost of the compressor. Gas

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[4] First plant
[5] Hydrogen Analysis

pressure at the PSA exit is about 2 atm (30 psi). If hydrogen is extracted from a pipeline at 300 psi, the separated natural gas has to be recompressed back to the pipeline. Due to low concentrations of hydrogen, the amount of natural gas that has to be recompressed is high and requires a large compressor. High recompression costs can be avoided if hydrogen is extracted at a pressure-reduction facility so natural gas does not need to be recompressed.

Pressure differentials can vary between pressure-reduction facilities, but are often significant at the city gate where transmission lines feed into distribution lines. The hydrogen extraction cost for a 10% hydrogen blend under these circumstances is 6 to 11 times lower ($0.3–$1.3/kg of hydrogen extracted) depending on the scale of extraction or recovery rate in kg/day. These extraction costs were modelled for a pressure drop from 300 to 30 psi.

These figures were obtained from previous studies, so they probably will be updated during the project development.

Based on this significant cost reduction, it appears that hydrogen extraction from a natural gas distribution pipeline at a pressure-reduction facility will prove to be a lower-cost option, mostly due to the fact that natural gas exiting the PSA unit would require minimal or no recompression.

4. STANDARDS FOR INJECTING GASES IN EUROPEAN GRIDS. OPERATING CONDITIONS.

4.1. THE NETHERLANDS[6]

In this country there are three different types of natural gas, being the main difference the caloric value of the gas:

- **G-gas** or Groningen-gas: this gas comes from the Groningen region in the Netherlands. It is also known as Slochteren gas. This gas has a relatively low caloric value. Dutch central heating systems are only capable of burning G-gas.
- **H-gas**: This gas comes from the North Sea and has a higher caloric value and to be used in the distributed/regional gas grid it must be mixed with N_2 to reduce the caloric value.
- The last kind is **L-gas**, with an even lower caloric values than G-gas.

There are also different types of gas grids depending on the work pressure and owners:

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[6] Source: HyET B.V. and HYGEAR

- **HTL**: This is the main transport line. It works at high pressure (from 43 up to 66 bar, and occasionally it can reach 80 bar) transporting H-gas or high calorific gas. The owner of this grid is *Gasunie Transport Services* (TSO).
- **RTL**: This is the regional transmission line. It has an absolute working pressure between 16 and 40.5 bar and it is dedicated to G-gas. The owner of this grid is *Gasunie Transport Services* (TSO).
- **RNB-net**: gas transport network of G-gas or low calorific gas, managed by the regional operator (DSO). There are two types, the regional high pressure distribution grid and the regional low pressure distribution grid. Operational pressure of high pressure grid varies in the range 1<P<4 and 3<P<8 and operational pressure of low pressure grid goes from 40 to 100 mbar.

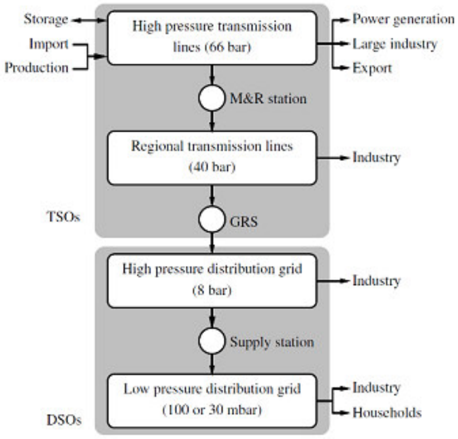


Fig. 4. Dutch gas grid supply chain

Most households, buildings and businesses in the Netherlands have a connection to use G-gas for heating and warm tap water, and approximately 80 large industrial consumer use H-gas.

The HTL grid that transports low-calorific gas delivers gas to the metering and regulating (M&R) stations, which reduce the gas pressure to approximately 40bar, and supply gas to several regional transmission lines (RTL) grids. The RTL grids transport the gas further into the country with a finer mesh of pipelines. The RTL grid delivers the gas to gas receiving stations (GRS), which reduce the gas pressure to 8 bar and supply gas to the high pressure distribution grids.

The high pressure distribution grids transport the gas over longer distances and feed the gas into the low pressure distribution grids via a supply station, which reduces the gas pressure to 100 mbar. The low pressure distribution grid supplies gas to households and smaller industry.

At the entry points to homes the gas pressure is reduced to 30mbar as most household appliances are designed to operate at approximately 30 mbar.

The map below shows the HTL transport lines, together with import and export connections.

Fig. 5. HTL transport lines and import and export connections

Key:

- Transportation lines
  - yellow=H-gas, dark-grey=G-gas, light-grey=N2
- Import and export
  - Filled grey circles: feed points of gas into the grid
  - Circles with grey triangle: export station
  - Circles with letter L: storage of LNG
- Conversion
  - Half-filled grey circles: Underground storage
  - Circles with letter N: nitrogen injection stations (conversion of H to G gas)
  - Double circles: compressor stations
  - Bold grey circles: mixing stations
  - Control station (transfer to regional network; pressure reduction and odorisation)

4.1.1. Experimental conditions for Dutch Grid

It is allowed to feed in the RNB supply networks up to 0.5 mol% hydrogen gas to enable the addition of gas from sustainable sources. Both the HTL and RTL supply networks are not resistant towards higher concentrations hydrogen and thus the limit is set to 0.02 mol% hydrogen. Because of that, in the HyGrid project the G-gas in the regional network (RNB-net) will be considered.

4.1.2. Regulations for the injection of biomethane into the Natural Gas Grid

On the first of April, a new law was approved about gas quality and limits to inject special gases to grid[7].

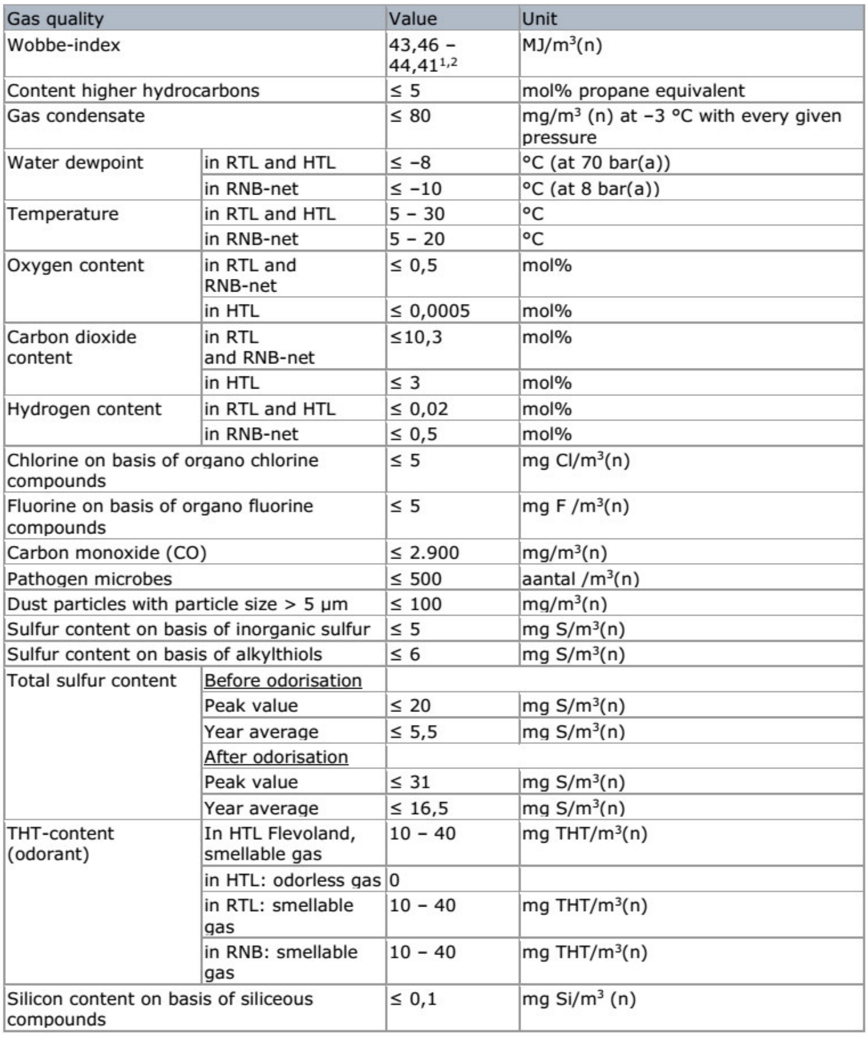
Depending on the type of gas and gas grid, the amount of hydrogen allowed is different. The permitted amounts are stated in the tables of appendices (‘*Bijlage*’).

Table III. Amount of hydrogen allowed in Dutch grid

Type of gas grid	**H-gas**	**G-gas**	**L-gas**
HTL	≤ 0.02	≤ 0.02	Not specified
RTL	≤ 0.02	≤ 0.02	Not specified
RNB-net	≤ 0.02	**≤ 0.5**	Not specified

The gas quality requirement of G-gas is listed as fixed by the Dutch Government in Table IV.

Table IV. Gas quality requirements of G-gas



Gas quality		Value	Unit
Wobbe-index		43,46 – 44,41[1,2]	MJ/m^3(n)
Content higher hydrocarbons		≤ 5	mol% propane equivalent
Gas condensate		≤ 80	mg/m^3 (n) at −3 °C with every given pressure
Water dewpoint	in RTL and HTL	≤ −8	°C (at 70 bar(a))
	in RNB-net	≤ −10	°C (at 8 bar(a))
Temperature	in RTL and HTL	5 – 30	°C
	in RNB-net	5 – 20	°C
Oxygen content	in RTL and RNB-net	≤ 0,5	mol%
	in HTL	≤ 0,0005	mol%
Carbon dioxide content	in RTL and RNB-net	≤10,3	mol%
	in HTL	≤ 3	mol%
Hydrogen content	in RTL and HTL	≤ 0,02	mol%
	in RNB-net	≤ 0,5	mol%
Chlorine on basis of organo chlorine compounds		≤ 5	mg Cl/m^3(n)
Fluorine on basis of organo fluorine compounds		≤ 5	mg F /m^3(n)
Carbon monoxide (CO)		≤ 2.900	mg/m^3(n)
Pathogen microbes		≤ 500	aantal /m^3(n)
Dust particles with particle size > 5 μm		≤ 100	mg/m^3(n)
Sulfur content on basis of inorganic sulfur		≤ 5	mg S/m^3(n)
Sulfur content on basis of alkylthiols		≤ 6	mg S/m^3(n)
Total sulfur content	Before odorisation		
	Peak value	≤ 20	mg S/m^3(n)
	Year average	≤ 5,5	mg S/m^3(n)
	After odorisation		
	Peak value	≤ 31	mg S/m^3(n)
	Year average	≤ 16,5	mg S/m^3(n)
THT-content (odorant)	In HTL Flevoland, smellable gas	10 – 40	mg THT/m^3(n)
	in HTL: odorless gas	0	
	in RTL: smellable gas	10 – 40	mg THT/m^3(n)
	in RNB: smellable gas	10 – 40	mg THT/m^3(n)
Silicon content on basis of siliceous compounds		≤ 0,1	mg Si/m^3 (n)

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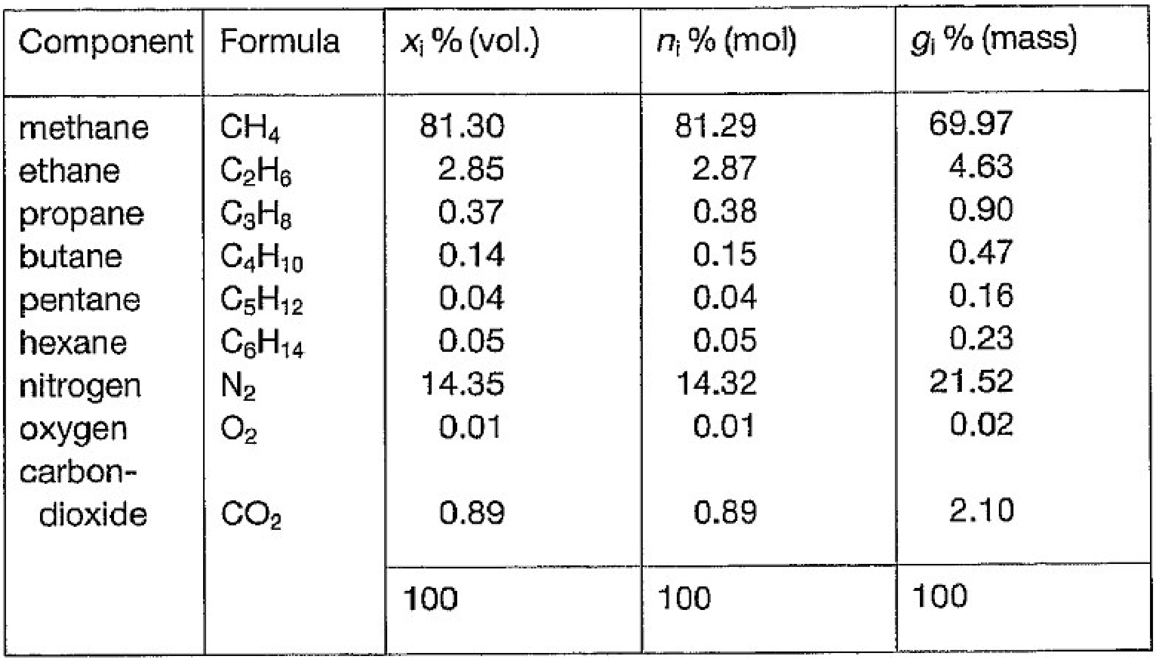
[7] Regeling gaskwaliteit - http://wetten.overheid.nl/BWBR0035367/2016-04-01

The water dew point requirements correspond to about 44 ppmv H_2O for the RTL-HTL networks, and 325 ppmv H_2O for the RNB network.

The G-gas is mainly methane (81 mol%) and nitrogen (14 mol%) being the rest 5%, hydrocarbons from C2 to C6, oxygen and CO_2. The next table shows the average composition of Groningen natural gas.

Table V. Groningen natural gas (average composition)



Component	Formula	x_i % (vol.)	n_i % (mol)	g_i % (mass)
methane	CH_4	81.30	81.29	69.97
ethane	C_2H_6	2.85	2.87	4.63
propane	C_3H_8	0.37	0.38	0.90
butane	C_4H_{10}	0.14	0.15	0.47
pentane	C_5H_{12}	0.04	0.04	0.16
hexane	C_6H_{14}	0.05	0.05	0.23
nitrogen	N_2	14.35	14.32	21.52
oxygen	O_2	0.01	0.01	0.02
carbon-dioxide	CO_2	0.89	0.89	2.10
		100	100	100

Gasunie Transport Services (GTS) allows the decentralised feeding of bio-methane (upgraded biogas) firstly in the lowest pressure level network (at 8, 4 or even lower bar) near to the production installation, although they also can inject it into the transmission grid (40<P<80 bar). Injection of biogas into a distribution grid has lower costs:

- **Lower CAPEX costs**:
    - The distribution grid is located as close to the production facility as possible (to reduce the length of the pipeline connecting this facility to the distribution grid and hence the costs).
    - Different pipeline connection specifications: transmission grid operator's requirements regarding the pipelines materials, diameter, length etc. which necessitate a larger investment in comparison to the requirements of the distribution grid operators.
    - Less stringent pressure demands on compressor.
- **Lower OPEX costs**:

- These are fully borne by the producer in the Netherlands (costs of compression from 0 to max. 8 bar for the distribution grid are significantly lower in this case, compared to compression from 0 to 40 bar for the transmission grid).

The manager of distribution grid is the Local Distribution Company (LCD). GTS also explains on its website[8] that feeding into the GTS network may be appropriate. That is the case if the demand in the LDC network is too low for the quantity of bio-methane produced at certain times in the year. This may be the case when the weather is warm and particularly at night, when there are no, or very low, sales to households. Because bio-methane is mainly produced in rural areas and sales are limited there in comparison to urban areas, this situation occurs regularly. It is of essential importance that the potential for feeding gas into the natural gas network is considered at an early stage when making a decision about the place of operation.

An incentive scheme for sustainable energy exists. In order to apply for that subside (SDE+-subsidy) it is necessary to be able to submit a feasibility study (without cost) put together by the network operator concerned. Then, the “feeder” will receive an indication of the price and technical feasibility and a global delivery time for the connection.

In April 2013, 21 production locations for green gas also called biomethane were operating in the Netherlands, with an overall production capacity of 11900 Nm^3/hour; annual production approximately 90 million Nm^3/year. The map below shows the main biomethane production sites in the Netherlands.

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[8] https://www.gasunietransportservices.nl/en/connected-party/system-operators/become-a-bio-methane-feeder

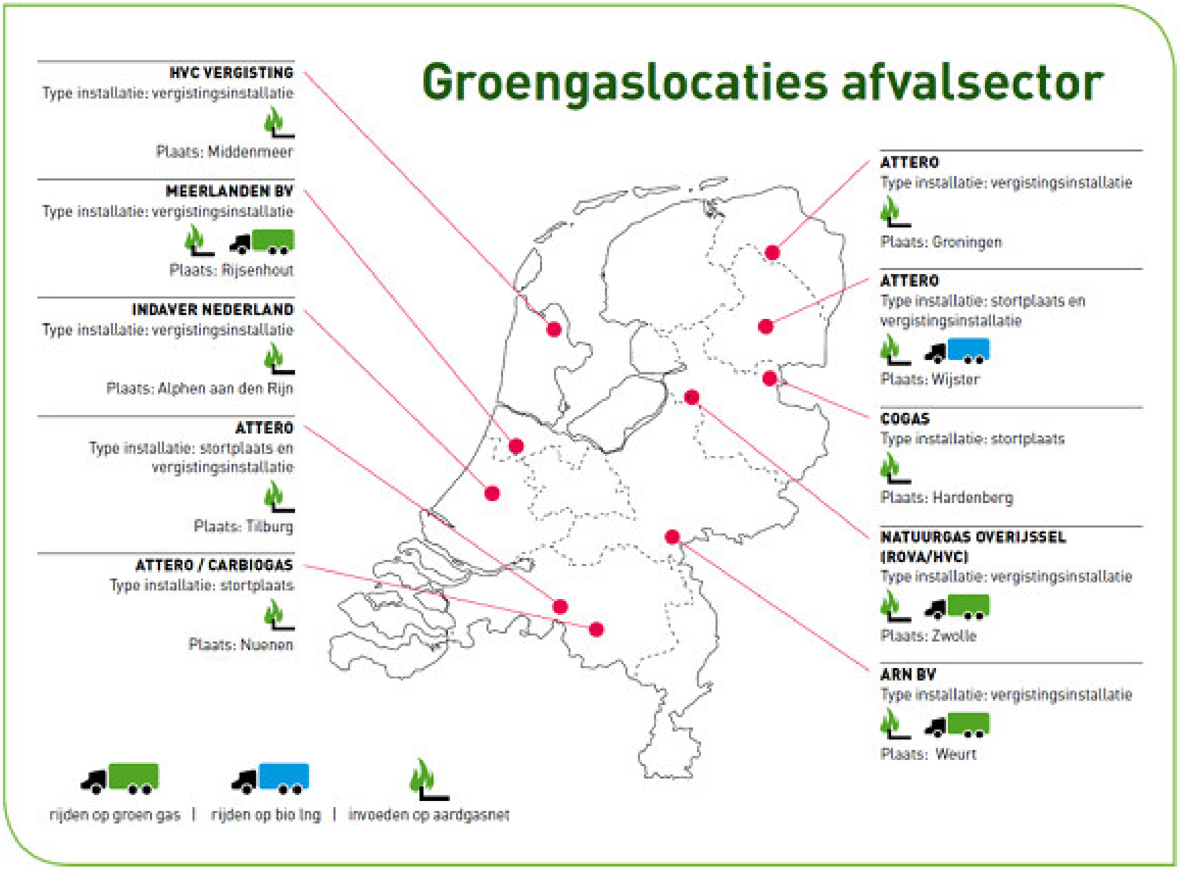

Fig. 6. Upgraded biogas production sites in the Netherlands

Finally, the gas quality requirement for biomethane allows a hydrogen content of 12% (Table VI), substantially higher than the specification for natural gas.

Methane number is important when the content of H_2 and/or C_3H_8 is relatively high (which causes low Methane number).

Table VI. Allowed composition of biomethane in Netherlands

Quality component	Conform advice Gastec	
	Limit	Unit
Fysical properties		
Calorific upper value	31,6 – 38,7	MJ/m$^{3}_{n}$
Wobbe-index	43,46-44,41	MJ/nm^{3}
Other properties		
Water dew point	–10(8 bar)	°C
Temperature (in te voeden gas)	0 – 20	°C
Sulfur (total)	45	mg/m$^{3}_{n}$
Inorganic bound sulfur (H_2S)	5	mg/m$^{3}_{n}$
Mercaptanes	10	mg/m$^{3}_{n}$
Odorant content (THT)	> 10, nom 18<40	mg/m$^{3}_{n}$
Ammoniac	3	mg/m$^{3}_{n}$
Organo chlorine compounds	50	mg/m$^{3}_{n}$
Organo fluorine compounds	25	mg/m$^{3}_{n}$
Hydrogen chloride (HCl)	1	Ppm
Hydrogen cyanide (HCN)	10	Ppm
Carbon monoxide (CO)	1	Mol%
Carbon dioxide in dry gas grids (CO_2)	6	Mol%
BTX (benzene, toluene, xylene)	500	Ppm
Aromatic hydrocarbons	1	Mol%
oxygen in dry gas grids	0,5 (3)	mol%
Hydrogen	12	vol%/ m$^{3}_{n}$
Methane number [1]	> 80	–
Dust	Technical free	–
Siloxanes	5	Ppm
Smellability (odorised biogas)	Sufficient	–

4.2. ITALY[9]

4.2.1. Italian grid

The NG grid in Italy is divided into 2 levels of distribution: a primary level that covers the national and regional distribution and a secondary level for the local distribution.

The primary transport distribution is a network operating at high pressure in large diameter pipes, which crosses the country from north to south and transports gas to the interconnection with the regional transport networks (at high and medium pressure).

The national and regional primary gas transport system is operated by 10 companies, including 7 operating exclusively on regional networks. Next picture shows Italian grid:

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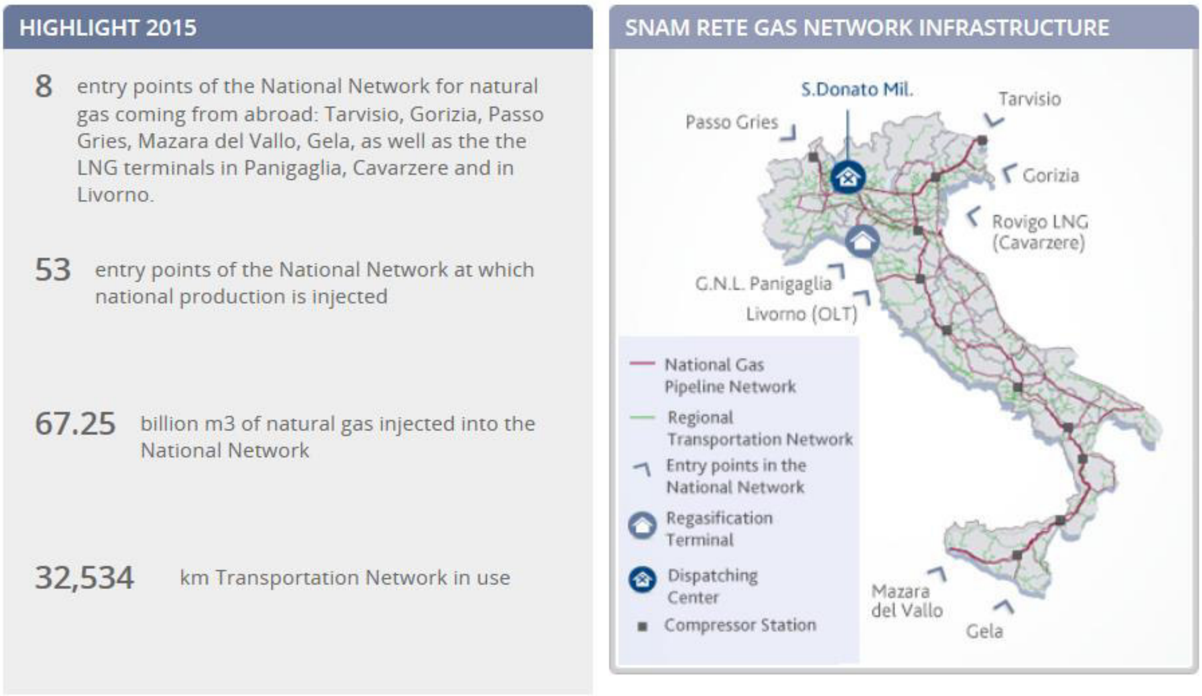
[9] Source: SAES



HIGHLIGHT 2015

8 entry points of the National Network for natural gas coming from abroad: Tarvisio, Gorizia, Passo Gries, Mazara del Vallo, Gela, as well as the the LNG terminals in Panigaglia, Cavarzere and in Livorno.

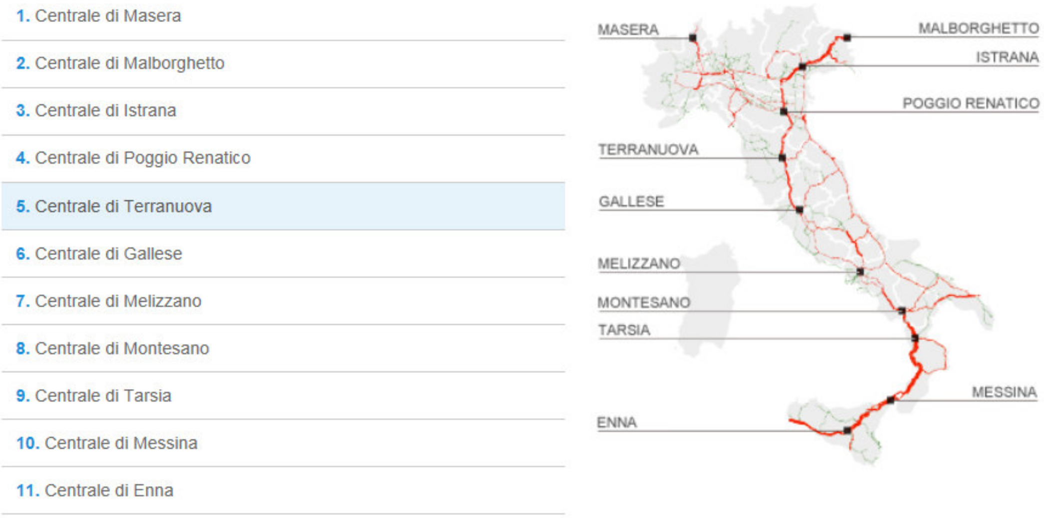
53 entry points of the National Network at which national production is injected

67.25 billion m3 of natural gas injected into the National Network

32,534 km Transportation Network in use

Fig. 7. SNAM Rete Gas Infrastructure

Snam Rete Gas[10], the company that managed the national and regional network, operates 11 **Compressor Stations**, located along the National Network, which increase gas pressure in the pipelines up to the level required to ensure flow continuity. Compression stations compress natural gas received from the Transportation Network to make it possible to inject it into the reservoirs.



1. Centrale di Masera
2. Centrale di Malborghetto
3. Centrale di Istrana
4. Centrale di Poggio Renatico
5. Centrale di Terranuova
6. Centrale di Gallese
7. Centrale di Melizzano
8. Centrale di Montesano
9. Centrale di Tarsia
10. Centrale di Messina
11. Centrale di Enna

Fig. 8. Reservoirs in Italian grid

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[10] Information collected from the SNAM web site

Once imported or re-gasified, gas is injected into the Transmission Network at the Entry Points in order to be transported to local distribution networks, to withdrawal points along the Regional Network, or to large final clients, either thermoelectric plants or industrial consumers.

The point of interconnection between the regional transport network, and the local distribution network (the secondary network, which measures a total of approximately 200,000 km) is the reduction and metering station (RE.MI. station) where the gas pressure is reduced, accounted and odorized.

Fire safety rules for accumulation and distribution of the use of natural gas with density not greater than 0.8 are approved in the decree DM24/11/84. Pipeline is classified according to the pressure:

a) Pipelines, 1° species: carried out to maximum pressure in the range 24-75 bar.

b) Pipelines, 2° Species: carried out to maximum pressure of over 12bar and lower than or equal to 24 bar.

c) Pipelines 3° species: carried out to maximum pressure of over 5 bar and less than or equal to 12 bar.

d) Pipelines 4° Species: carried out to maximum pressure of over 1.5 bar and lower than or equal to 5 bar.

e) Pipelines 5° Species: carried out to maximum pressure of over 0.5 bar and less than or equal to 1.5bar.

f) Pipelines 6° Species: pipelines for maximum operating pressure of more than 0.04bar and less than or equal to 0.5bar.

g) Pipelines 7° Species: carried out to maximum pressure lower or equal to 0.04bar.

The working pressure is dependent of the use of gas and its characteristics are defined in UNI regulations:

Table VII. Range of working pressures in Italy

UNI number	Inlet Pressure (bar)	Outlet Pressure (bar)	Type of use
10619	Up to 12	No limitation	Industrial or similar
10619	Up to 12	0.04 to 0.5	Medium Pressure Distribution,
10390	5 to 12	Up to 0.04	Low Pressure Distribution. domestic
8827	0.04 to 5	Up to 0.04	Low Pressure Distribution. domestic

The RE.MI (REgolazione e MIsura) cabin is a very important interface point between the national pipeline and the local distributor and the point where other gases are injected into grid.

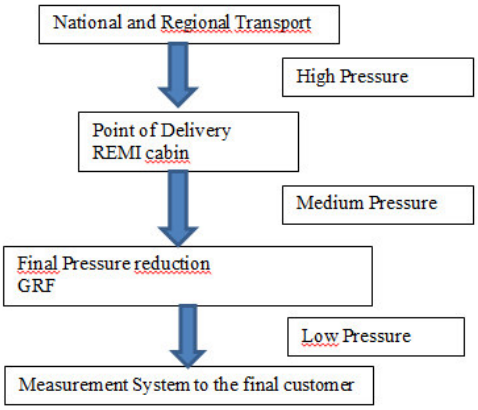

Fig. 9. Schematic Italian grid

4.2.2. Experimental conditions for Italian´s Grid

The chemical composition (%) of the natural gas in the Italian grid depends on the source as it can be seen in the table below:

Table VIII. Composition of the Italian natural gas

HC	National	Lybian	Russian	Dutch	Algerian
Methane	99.2	81.40	97.64	88.35	83.00
Ethane	0.40	9.40	0.99	4.30	7.50
Other Hydrocarbons	0.14	2.30	0.44	1.35	3.30
Carbon Dioxide	0.01	1.20	0.09	1.30	0.20
Nitrogen	0.25	0.50	0.84	4.20	6.00
Carbon Monoxide	-	0.20	-	-	-
Hydrogen	-	5.00	-	-	-

And the average physical parameters:

Table IX. Physical parameters of Italian natural gas

Parameter	Unit	National	Lybian	Russian	Dutch	Algerian
Higher Heating Value	Kcal/Sm^3	9043	9534	9121	9054	9580
Lower Heating Value	Kcal/Sm^3	8144	8609	8227	8169	8662
Absolute density	Kg/Sm^3	0.68	0.75	0.74	0.76	0.81
Relative density		0.55	0.61	0.60	0.62	0.66
Cp	Kcal/Kg°C	0.52	0.5	0.49	0.48	0.47
V flame propagation	cm/sec	33.47	45.36	32.58	32.02	32.08

4.2.3. Regulations for the injection of biomethane into the Natural Gas Grid

Italy is the third producer of biogas (after China and Germany) in the world, with more than 1500 installations at the end of 2015 producing more than 2 billion m^3 of biogas every year. However there are only 6 installations involved in the generation of biomethane, 5 of them just for demonstrative purpose. The interest for these types of installation is growing and there are 20 new installations in the authorization phase capable to deliver 250-1000 m^3/h each.

The conditions for the injection of Biomethane are regulated by UNI11537, April 2016 not yet released. After its final approval, the document will be reviewed by the CEN/TC 408 Project Committee – Natural Gas and biomethane for use in transport and biomethane for injection in the natural gas grid. The UNI document indicates the following chemical-physical characteristics:

Table X. Conditions for biomethane injection in Italy

Parameter	Symbol	Value	Units of measure
Higher Heating Value	HHV	≥ 34,95 ≤ 45,28	MJ/Sm^3
Wobbe index	WI	≥ 47,31 ≤ 52,33	MJ/Sm^3
Relative density	ρ	≥ 0,5548 ≤ 0,8	-
Dew point of water	≤ - 5°C at 7 000 kPa		
Dew point of hydrocarbons	≤ 0 ° C in rel. pressure range 100 kPa - 7000 kPa		
Oxygen content	O_2	≤ 0,6	%mol
Carbon dioxide content	CO_2	≤ 3	%mol

Parameter	Symbol	Value	Units of measure
Hydrogen sulfide content	H_2S	≤ 6,6	mg/Sm^3
Content of sulphur and mercaptans	-	≤ 15,5	mg/Sm^3
Total sulphur content		≤ 150	mg/Sm^3

Parameter	Symbol	Value	Unit of measure
Total Si content	Si	≤ 1	mg/Sm^3
Carbon monoxide content	CO	≤ 0,1	%mol
Ammonia content [a)]	NH_3	≤ 10	mg/Sm^3
Ammines content [b)]		≤ 10	mg/Sm^3
Hydrogen content	H_2	≤ 0,5	% Vol
Fluorine content [c)]	F	< 3	mg/Sm^3
Chlorine content [c)]	Cl	< 1	mg/Sm^3;
Compressor oil content [d)]			
Powders [d)]			

[a)] If it is demonstrated the absence of liquid water in the biomethane it may be omitted the measurement of ammonia <u>only for the injection into the distribution network</u>

[b)] If it is demonstrated the absence of liquid water in the biomethane it may be omitted the measurement of ammines <u>only for the injection into the distribution network</u>

[c)] The limit values for F and Cl will be expressed by CEN in a subsequent CEN / TR currently being studied. The values shown here are considered prudent at the present state of knowledge

[d)] Regarding the oil content from the compressor and powders, biomethane must be free of or does not exceed a minimum amount that render unacceptable biomethane for end users. This condition is fulfilled by the use of cartridge filters that retain 99% of the solid particles > 5 [μm] and 99% of liquid particles ≥ 10 [μm]. To maintain effective filtration capacity, equipment must be subject to periodical audits as prescribed in the UNI 10702 and UNI 9571-1 for applicable parts.

4.2.4. Injection of hydrogen into the Italian natural Gas Grid

Being H_2 a gas with chemical and physical properties well different from Natural Gas or Methane, its injection in the grid is rather critical. For the time being, in Italy, only a few preliminary theoretical studies have been carried out by Politecnico di Milano, Energy Department.

This group has simulated the propagation of 5% H_2 injection along the grid by changing the NG load. The impact of the main parameters is:

- **Pressure drop**: it is estimated that the impact of the presence of 5% H_2 in NG on the pressure drop is negligible.
- **Density**: on the contrary the variation of the density due to the presence of H_2 is significant and could have an impact on the management of the pipeline.
- **Gas Velocity**: the density reduction and the addition of H_2 cause a small increase of the velocity.
- The **Higher Heating Value** is affected by the presence of H_2, the higher the H_2 concentration the lower the HHV; the trend of the HHV versus time follows the H_2 injection.
- **Wobbe Index**: the impact of H_2 is rather complex because it determines two effects: first the increase of the compressibility factor and a decrease of the molecular weight of the mixture lead to a WI increase proportional to its square root; second the reduced HHV of the mixture generates a proportional reduction of the WI.

More detailed information is available in the paper `Dynamic modelling of natural gas quality within transport pipelines in presence of hydrogen injections´ prepared by Giulio Guandalini, Paolo Colbertaldo, Stefano Campanari; Applied Energy, March 2016.

The following figures show the impact of H_2 presence on the Higher Heating value and on the Wobbe Index, determined by Giulio Guandalini *et al.*: the higher is the H_2 concentration, the lower are both the Higher Heating Value and the Wobbe Index.

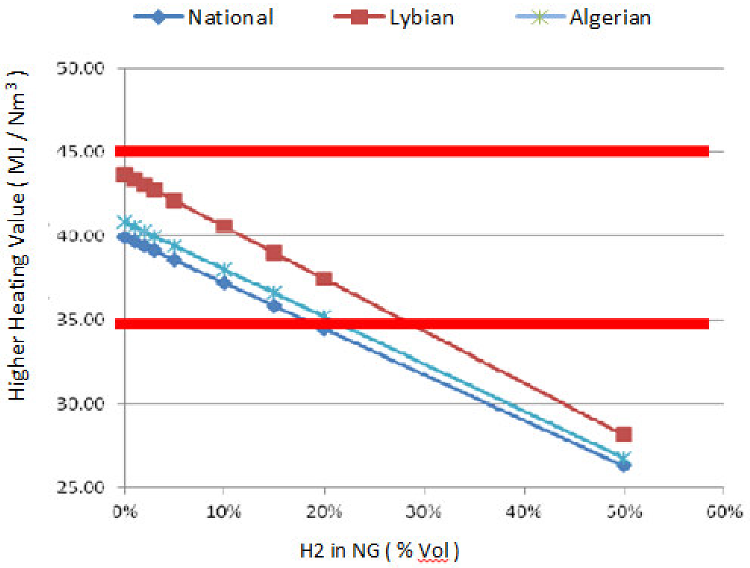

Fig. 10. HHV vs. H2 concentration in Natural gas (adapted from "Power-to-gas" – Guandalini Giulio)

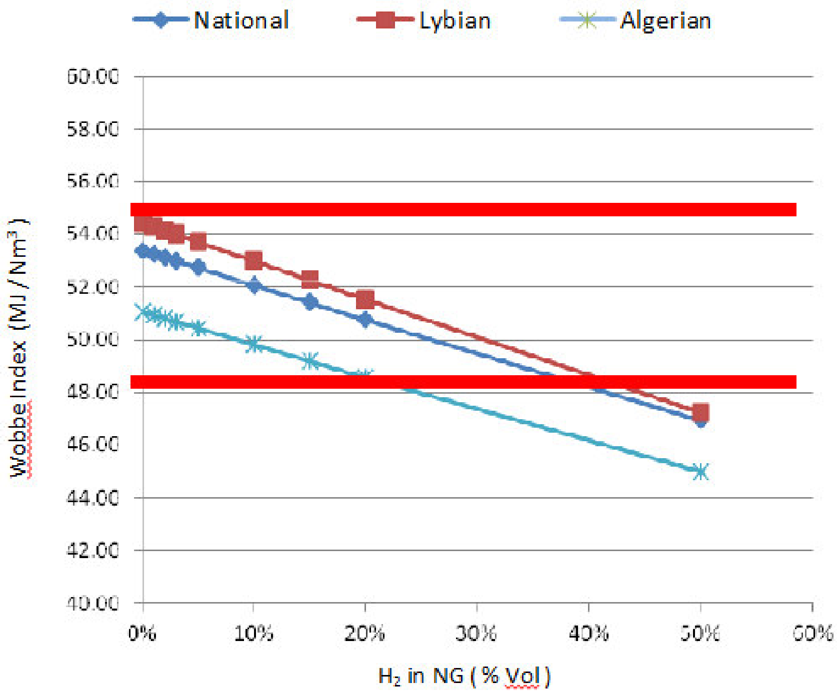

Fig. 11. Wobbe Index vs. H_2 concentration in Natural gas (adapted from "Power-to-gas" – Guandalini Giulio)

Considering only these physical parameters, for concentrations up to 20% H_2 in NG, both parameters remain within the acceptability threshold, although as it is explained above, other aspects limit the amount of Hydrogen injected.

4.3. SPAIN[11]

4.3.1. Spanish Grid

Natural gas supply

Spain is a net importer of natural gas. The natural gas is bought both liquid by ship, as liquefied natural gas (LNG), and gaseous (NG) by gas pipeline. Liquefaction and regasification plants change the gas state to enable its transportation.

Natural Gas comes from Europe or Maghreb:

- Four gas pipes to import natural gas from France, Portugal and Magreb.
- Six regasification plants: in Barcelona, Cartagena, Bilbao, Sagunto, Mugardos y Huelva.

Next picture shows the Spanish gas structure.

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[11] EDP own sources

Fig. 12. Natural Gas pipes and regasification plants in Spain

Specifically, during 2015 the natural gas came from:

Table XI. Origin of the Spanish natural gas

Source	2015 (GWh)
Algeria GN	175.344
Algeria GNL	43.401
Nigeria GNL	43.324
Qatar GNL	33.139
Peru GNL	10.794
T&T GNL	12.754
Norway GNL	7.984
National GN	776
Oman GNL	964

France	36.902
Total	365.382

Quality parameters of gas are mainly based on its higher heating value.

Table XII. Higher Heating Value of Spanish natural gas

	Spanish fields	France connection	Magreb gas pipe	Medgaz
Higher heating value (MJ/m^3 (n))	43.099-39.172	41.904	41.882	42.091
Higher heating value (kWh/m^3 (n))	11.972-10.881	11.640	11.634	11.692

Quality specifications are set in Spanish resolution of September the 22th of 2011[12]

Table XIII. Quality specifications of gas in Spain

Parameter	Minimum	Maximum	Units of measure
Higher Heating Value	10.26	13.26	kWh/m^3
Wobbe index	13.403	16.058	kWh/m^3
Relative density	0.555	0.700	m^3/m^3
Total sulphur content	--	50	mg/m^3
H_2S + COS as S	--	15	mg/m^3
RSH (as S)	--	17	mg/m^3
O_2	--	[0.01]	%mol
CO_2	--	2.5	%mol
Dew point of water	--	+2	ºC a 70 bar (a)
Dew point of hydrocarbons	-	+5	ºC a 1-70 bar (a)
Dust		Technically pure	--

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[12] *Resolución de 22 de septiembre de 2011, de la Dirección General de Política Energética y Minas, por la que se modifica el protocolo de detalle PD-01 «medición» de las normas de gestión técnica del sistema gasista.BOE-A-2011-15496*

Storage of natural gas

In Spain there are three underground storages of different capacity: Serrablo in Huesca and Gaviota in Vizcaya in the North of Spain and Yela in Guadalajara in the centre of Spain. Total storage capacity is reflected in next table:

Table XIV. Gas storage capacity in Spain

Parameter	Amount	Units of measure
Working Gas	2710	NMm^3
Cushion gas-removable	707	NMm^3
Cushion gas- no removable	2364	NMm^3
Total	**5781**	**NMm^3**
Maximum injection	18,3	NMm^3/d
Maximum Production	27,5	NMm^3/d

Transportation of natural gas

Transport of natural gas in Spain is a regulated activity which operates in two types of infrastructures:

- **Basic grid**: it is composed of regasification plants, primary transmission gas pipelines (working pressure > 60bar) and basic underground storage facilities. There are 18 compression stations along the grid to maintain the working pressure. This basic grid is formed by:
  - Backbone networks: they have interconnected gas pipelines needed to guarantee security of supply and gas system performance. It is managed by ENAGAS[13].
  - Networks of local influence: to help gas natural supply.
- **Secondary transmission grid**: made up gas pipelines working at 16-60bar. This grid is managed by private companies[14].

Gas compression stations

There are 19 compression stations to help the transportation of natural gas from the entry points to the end users. Its distribution is showed in next map:

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[13] Spanish main TSO and Technical Manager of gas system
[14] Such as EDP, GNF, Endesa, among others

Fig. 13. Compression stations in Spanish natural gas grid

Distribution of natural gas

The distribution grid carries the natural gas to the end user. Pipelines have a lower diameter and pressure than those of the transportation grid. Depending on the customer, the natural gas is served at a certain pressure. This pressure is adapted in the ERMS (RMS in English- Regulation and Measurement Stations) which are located in the interconnection points between transport and distribution grids.

There are three pressure ranges (in bar):

- High pressure (APA): $4<P\leq 16$
- Medium pressure:
  - MPB: $0,4<P \leq 4$
  - MPA: $0.05<P\leq 0,4$
- Low pressure: $P<0.05$ (domestic users)

The HYGRID prototype will be designed for maximum operation of 10 bar, thus it could be tested in either the medium pressure range grids or some of the high pressure range grids.

Materials employed

Pipelines of transport grid (P>16 bar) are made of steel. In Spain there are about 13.500 km of steel pipelines with a diameter from 2" up to 38" and higher.

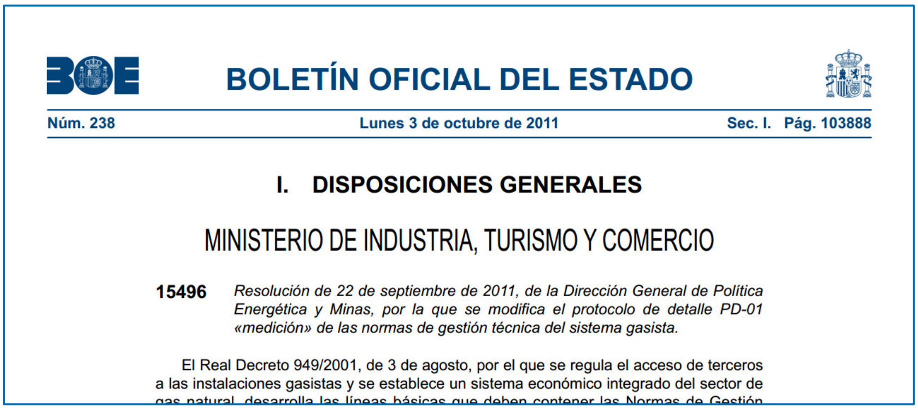
Pipelines of distribution grid are made of different materials depending on the working pressure:

- 4 < P ≤ 16 bar: mainly steel pipelines but also of PE100.
- 0.4<P≤ 4 bar: a 94% of polymeric pipes (PE80 and PE100) followed by steel pipes almost a 6%. There are negligible amounts of Cu or ductile cast.
- 0.05<P≤ 0,04 bar: mainly polymeric pipes (PE80 and PE100) and negligible amounts of ductile cast and steel.
- P≤ 0.05 bar: a 83% of polymeric pipes (PE80 and PE100), followed by a 16% of ductile cast and negligible amounts of steel and fibre cement.

4.3.2. Regulations for the injection of biomethane into the natural gas grid

Two national laws regulate the injection of other gases to the natural gas grid:

Resolution of September the 22 of 2011: where measurement, quality and odorization regulations are set for unconventional gases.



BOLETÍN OFICIAL DEL ESTADO

Núm. 238 Lunes 3 de octubre de 2011 Sec. I. Pág. 103888

I. DISPOSICIONES GENERALES

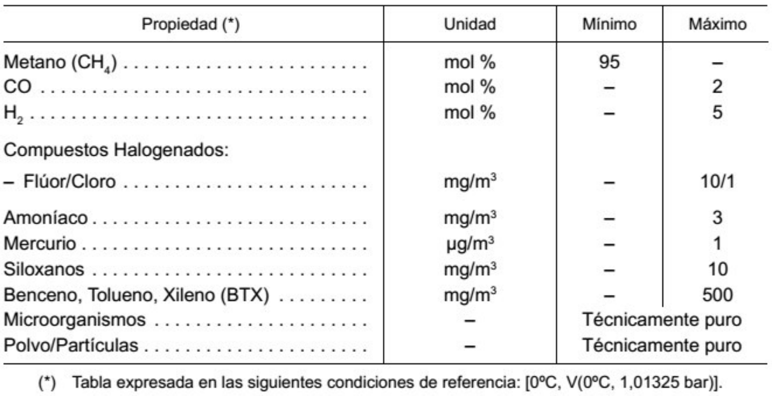
MINISTERIO DE INDUSTRIA, TURISMO Y COMERCIO

15496 *Resolución de 22 de septiembre de 2011, de la Dirección General de Política Energética y Minas, por la que se modifica el protocolo de detalle PD-01 «medición» de las normas de gestión técnica del sistema gasista.*

El Real Decreto 949/2001, de 3 de agosto, por el que se regula el acceso de terceros a las instalaciones gasistas y se establece un sistema económico integrado del sector de

Fig. 14. First page of mentioned resolution

Resolution of December the 21 of 2012: where composition of unconventional gases is set in order to inject them in gas grid. Specifications are showed in the table below. The first column contains gases, the second one the units employed, the third is the minimum concentration permissible and the last one the maximum. Microorganisms and dust are not allowed at all. In case of biomethane, a 0.3% of O_2 when $[CO_2] < 2$ mol% and water dew point ≤ -8ºC.



Propiedad (*)	Unidad	Mínimo	Máximo
Metano (CH_4)	mol %	95	–
CO	mol %	–	2
H_2	mol %	–	5
Compuestos Halogenados:			
– Flúor/Cloro	mg/m³	–	10/1
Amoníaco	mg/m³	–	3
Mercurio	µg/m³	–	1
Siloxanos	mg/m³	–	10
Benceno, Tolueno, Xileno (BTX)	mg/m³	–	500
Microorganismos	–	Técnicamente puro	
Polvo/Partículas	–	Técnicamente puro	

(*) Tabla expresada en las siguientes condiciones de referencia: [0ºC, V(0ºC, 1,01325 bar)].

Fig. 15. Allowed composition for injecting unconventional gases in Spanish grid

4.3.3. Injection of hydrogen into the Spanish natural gas grid

The European Committee for Standardization (CEN) has promoted an European Standard (EN 16726:2015) concerning the specification of gas quality of gases of group H to enhance the free flow of gas within the internal EU market.

This specification is being transposed to Spanish regulation through an UNE regulation developed by AENOR (the national association for normalization and certification). The document is under revision and has been coded as UNE-EN-16726.

In both documents, the injection of hydrogen into the natural gas grid is permitted and they explain calculations to obtain methane number of gaseous fuels for engines when hydrogen is added.

Hydrogen-Admissible Concentrations in natural gas system

In this standard the possibility of injecting hydrogen into the natural gas grid is indicated as follows:

There are proposals to inject hydrogen (H_2) 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 the GERG study “Admissible Hydrogen Concentrations in Natural Gas Systems” (see Bibliography) 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 (GERG is the European Gas Research Group, Brussels):

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 dihydrogen sulphide; the consumption of hydrogen, and the plugging of reservoir rock. A limit value for the maximum acceptable hydrogen concentration in natural gas cannot be defined at the moment. (hydrogen-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 hydrogen fraction in natural gas of 1 vol% or even lower. 5 vol % 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, a case by case analysis is recommended.

These conclusions are the same as those set in this deliverable.

4.4. EUROPEAN GAS GRID[15]

The European gas network has been established gradually during the last 70 years.

Generally, the European gas infrastructure is quite young and replacement is only considered a major issue in a few Member States. Initially, the European gas system was developed around national gas fields in Southern France, Northern Italy, Germany and Romania.

The gas infrastructure map has been divided into 4 regions: i) The Northern Region, ii) The South Western Region, iii) The South-Eastern Region, and a sub-region iv) Baltic integration region. The criteria for those regions are primarily the origin of the main source and secondary source of gas, geographical distances to new sources and pooling of gas storage.

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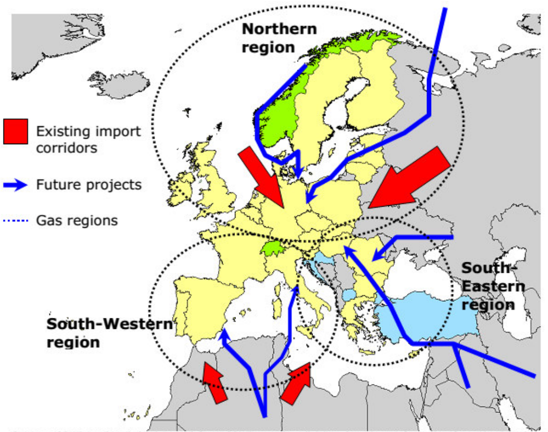
[15] EDP own sources



Source: COWI produced, background from COWI mapping division, based on information from the Petroleum Economist, (2008 edition).

Fig. 16. Existing main import corridors and future strengthening projects

Table XV. Description of gas regions. (Underlined: Bridging countries are in more than one region)

Northern	South-Eastern	South-Western	Baltic
Netherlands Belgium Ireland UK Germany Denmark Sweden Luxembourg Finland Poland Lithuania Latvia Estonia Czech Rep. France (Norway)	Austria Bulgaria Czech Rep., Greece Hungary Italy Romania Slovakia Slovenia Germany Cyprus (Turkey) (Croatia)	Spain Portugal France, Italy (Switzerland)	Finland Estonia Latvia Lithuania Poland

Gas transmission by pipeline is the transportation of gas over large distances and under high pressure. The pressure is typical over 80 bars and the pipeline diameter above ø500 mm. The flow is established by a number of compressor stations along the pipeline, and measurement and regulation stations are used to regulate and measure actual flow and gas conditions. Underground storage is gas stored under high pressure in caves, underground formations, depleted fields, etc. Each Member State has a distinct control and supervision system for handling daily operations of the gas transmission system.

The European gas grid is shown in the next picture. The internal transmission grid is especially dense in areas with many import points. Because of the cost of transportation, the gas is normally consumed as close as possible to the source. Therefore only few pipelines internally are dedicated to transmission over large distances. Underground gas storage facilities are used to balance demand and supply. Especially Germany, Italy and Austria have high storage capacity.

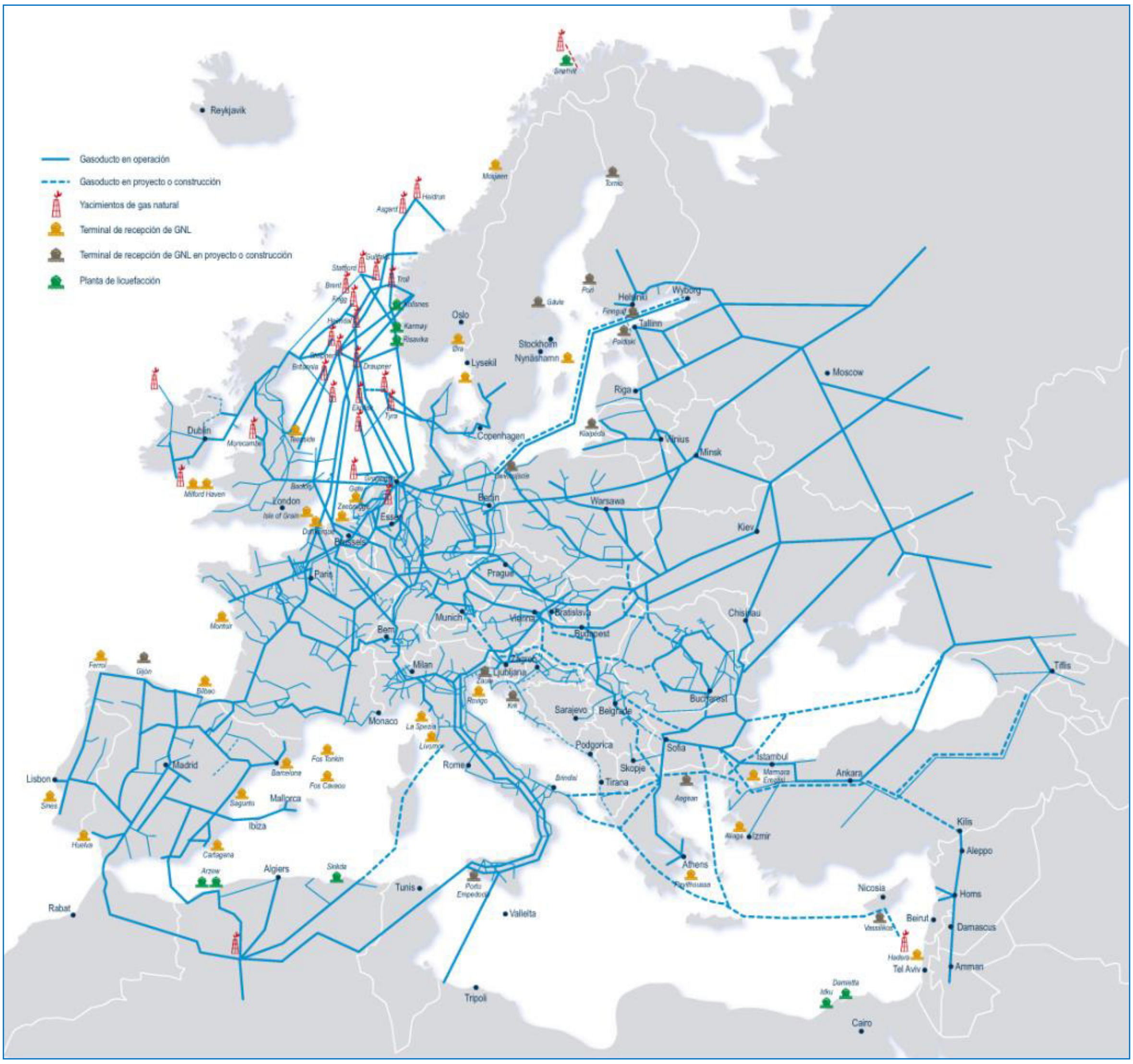


Fig. 17. European Gas Grid

4.4.1. European regulations to inject hydrogen in gas grid

As it was explained above, there is an European standard to harmonize gas quality in the European grid to allow free distribution of gas among the UE members. In this rule, hydrogen injection in gas grid is considered (the text is reproduced in section 4.3.3. Injection of hydrogen into the Spanish natural gas grid). This shows the significance that hydrogen will have in a near future and the importance of developing the appropriate technology to inject and extract hydrogen from gas grids.

5. CURRENT TECHNOLOGIES FOR SEPARATION OF HYDROGEN. STATE-OF-THE-ART

5.1. PSA

Currently, Pressure Swing Adsorption (PSA) is the mature technology used in refineries to produce high purity hydrogen. Hydrogen hardly adsorbs on usual adsorbent materials allowing removal of most contaminants. The sorbent materials used in PSA are carefully chosen to adsorb non-hydrogen compounds at elevated pressure (typically 10–30 bar). Multiple materials and layers of packing are typically used, which are tailored to the specific gas composition entering the bed. In this way, hydrogen is delivered at high pressure and the non-hydrogen materials are released at low pressure. PSA works efficiently for streams with high hydrogen concentrations. For example downstream a steam reformer where hydrogen concentration could be as high as 75%, a PSA would need pressurizing 1.3 volumes of gas per volume of hydrogen produced. On the other hand, if the hydrogen in the NG grid is maximum 10%, using a PSA would require pressurizing 10 volumes of gas per volume of H_2 produced and to a high pressure ratio, which would be very inefficient. For example in order to extract hydrogen from a NG distribution line at 4 bar, compressing to a pressure ratio suitable for PSA of about 8.8 would consume 20 kWh/kgH2 by the compressor alone (without even considering BOP). If the compression is not done upstream of the PSA, then the off-gas needs to be pressurized for re-injection into the NG grid which is an equally bad situation..

One important factor to take into account is the level of impurities as they define the size of the bed. PSA packing layers have two general operating regimes. The upstream portion of the bed is typically saturated with gas during operation and does the bulk of the extraction. The downstream portion is the fine polishing section and reduces the concentration of impurities that break through with hydrogen. Thus, the size of the PSA is strongly impacted by the concentration of non-hydrogen species entering the bed.

As lower concentrations of hydrogen are considered, the concentration of non-hydrogen gas species increases. This means that it would be necessary to compress larger quantities of gas to recover smaller quantities of hydrogen. To increase the hydrogen purity it could be necessary a second-stage PSA or other purification process such as membrane purification.

Hydrogen separation can also be done by means of cryogenic separation. Although liquefying hydrogen through cryogenic processes removes all impurities present in hydrogen (to almost undetectable levels), the energy needed to cool hydrogen down to -253 °C is about 30% of the stored energy. In addition, there is always a boil-off of hydrogen in the tank. The following table summarizes the advantages and disadvantages of the different hydrogen separation methods available.

5.2. MEMBRANES

Membrane technology is another industry-practiced technology for hydrogen extraction and purification. Membrane technologies work very efficiently with relatively high hydrogen concentrations. The purity of product gas can be high at very low fractional recovery but monotonically decreases as recovery increases, as the relative slower co-permeation of impurities proceeds to a greater degree. Most applications using membrane technology industrially recover the bulk hydrogen at 95-99% purity.

Several membranes have been developed for the purification of hydrogen. In all cases the hydrogen permeates through the membranes much more readily than (most) other compounds; sometimes hydrogen permeates even exclusively (i.e. in Pd-membranes). To support an appreciable flux, a differential partial pressure of hydrogen would be necessary.

The actual mechanism for the separation of hydrogen and contaminants may be based on either solution diffusion, molecular sieving and/or surface diffusion, depending on the actual type of membrane.

For all membrane processes, to support an appreciable flux a partial pressure difference must exist, hence the crude hydrogen has to be compressed. Like in PSA processes, the attainable yield and purity of the product of hydrogen are strongly dependent of the pressure; in practice relatively high pressures are often applied (>10bar). This is an economic optimization, since a higher pressure results in higher fluxes and hence a smaller required membrane surface area, but this is offset by the higher compression costs.

Low temperature membranes

Polymeric membranes are applied on an industrial scale for recovery of hydrogen from purge streams, recycle streams etc. In these processes, hydrogen selective membranes are used, most often applied in the form of hollow-fibre modules. It concerns dense membranes made of polymeric materials. Several suppliers exist, each with their own membranes (not exhaustive):

- Air Products (Prism process)
- Air Liquide (Medal process)
- UOP (Polysep process)

In the next Figure a schematic representation of a hollow fibre membrane for hydrogen purification, as applied in Air Liquid's Medal process, is showed.

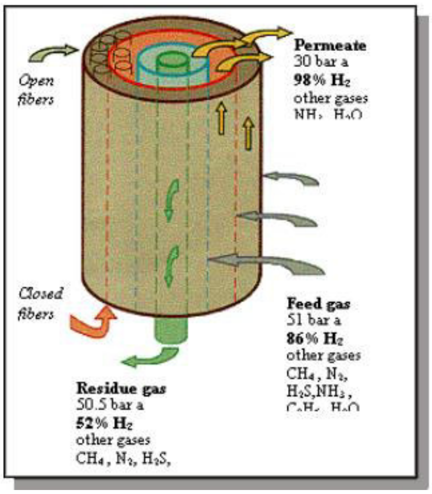


Fig. 18. Schematic representation of a hollow fibre membrane for hydrogen purification.

In a hollow fibre module, the pressurized feed gas enters the hollow fibre bundle from the tube side; compounds like nitrogen, methane and argon stay mostly on the pressurized shell side, whereas most of the hydrogen is collected at a lower pressure on the inner tube side.

Permeation occurs by a solution-diffusion mechanism caused by the (partial) pressure difference between shell and inner tube sides. The separation is based on different permeation rates through the membrane. In the next figure the relative permeation rates of different gases compared to hydrogen through low temperature polymeric membranes are presented. In this way, a “fast” gas like hydrogen is separated from “slow” gases such as carbon monoxide, methane or other hydrocarbons.

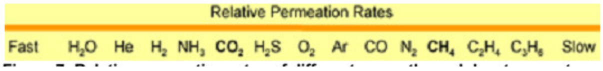


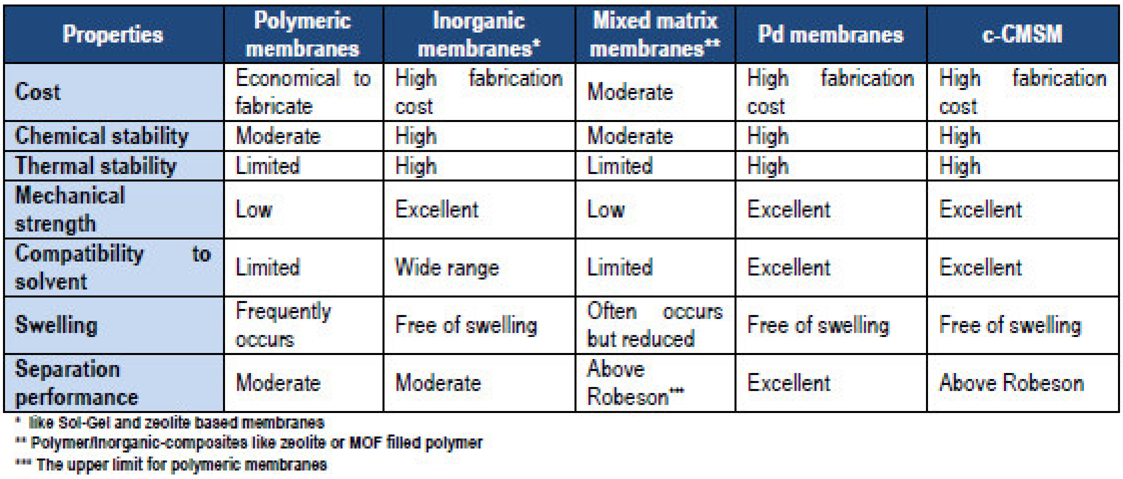
Fig. 19: Relative permeation rates of different gases through low temperature polymeric membranes.

From previous Figure it can be concluded that hydrogen (H_2) can be selectively separated from methane (CH_4), since hydrogen permeates a lot faster than methane.

One troublesome characteristic of polymeric membranes is that highly selective membranes tend to have poor permeability, while highly permeable membranes have low selectivity. The selectivity and permeability of membranes are visualized using a Robeson plot in which the best polymeric membranes form an “upper bound”. To surpass that bond, polymers which contain pores with molecular sieving properties (PIM) and mixed matrix membranes in which polymeric membranes are modified adding inorganic nanoparticles, metal-organic frameworks (MOF) are being developed. TECNALIA is participating in the M4CO2 project (being in charge of hollow fiber spinning) where MMMs are being developed showing good separation performances for pre-combustion (H2/CO2 separation). However, the maturity level, cost and availability of the materials used and performance of the membranes will hamper their application in low H2 blends into the natural gas grids and at the scales required.

On the other hand, among the best inorganic membranes, silica membranes show low H2 permeation and good selectivity. However, they are not long term stable and are very difficult to prepare without defects. Based on the data reported in Table X1 and results from recent projects, the best selection for the H2/NG separation are palladium based membranes or a combination of c-CMSM and palladium based membranes

Table XVI. Comparison of properties of various membrane materials



Properties	Polymeric membranes	Inorganic membranes*	Mixed matrix membranes**	Pd membranes	c-CMSM
Cost	Economical to fabricate	High fabrication cost	Moderate	High fabrication cost	High fabrication cost
Chemical stability	Moderate	High	Moderate	High	High
Thermal stability	Limited	High	Limited	High	High
Mechanical strength	Low	Excellent	Low	Excellent	Excellent
Compatibility to solvent	Limited	Wide range	Limited	Excellent	Excellent
Swelling	Frequently occurs	Free of swelling	Often occurs but reduced	Free of swelling	Free of swelling
Separation performance	Moderate	Moderate	Above Robeson***	Excellent	Above Robeson

* like Sol-Gel and zeolite based membranes
** Polymer/Inorganic-composites like zeolite or MOF filled polymer
*** The upper limit for polymeric membranes

Palladium membranes.

Palladium-based membranes have received a growing interest for the separation and purification of hydrogen from various resources. In addition, palladium membranes can be used as an integrated membrane reactor where the separation process is coupled with catalytic reactions. Palladium membranes have comparatively very high hydrogen flux and exclusive perm-selectivity for hydrogen due to the unique permeation mechanism. Since the permeation flux is inversely proportional to the membrane thickness, development of composite membranes with a thickness of less than 5 μm have been intensively studied in order to attain high hydrogen flux and to minimize the material cost[16].

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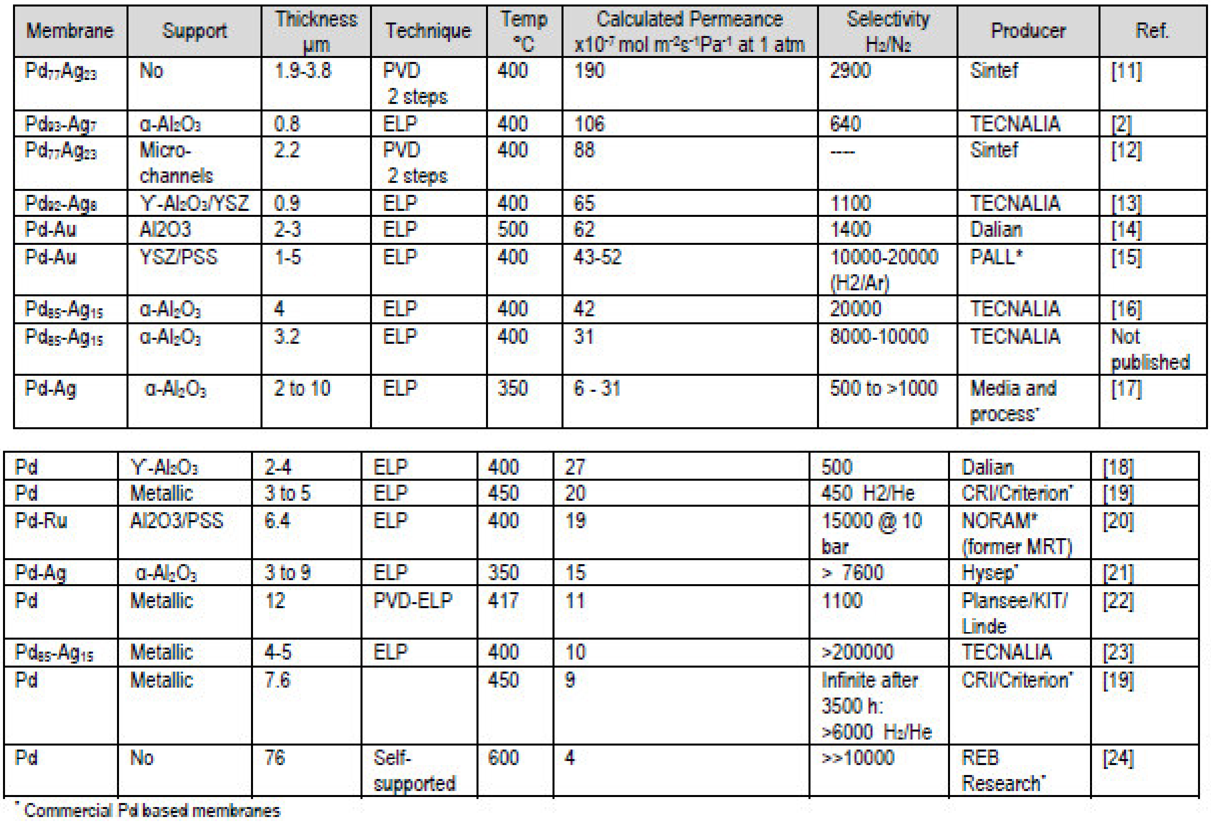
[16] L. Shi, A. Goldbach, H. Xu, High-flux H2 separation membranes from (Pd/Au)n nanolayers, Int. J. Hydrogen Energy. 36 (2011) 2281–2284. doi:10.1016/j.ijhydene.2010.11.056.
PALL, Hydrogen Reactor for Hydrogen Production, n.d. http://www.pall.com/pdfs/OEM-Media-Membranes-and-Materials/Hydrogen_Reactor_for_Hydrogen_Production.pdf.
E. Fernandez, A. Helmi, K. Coenen, J. Melendez, J.L. Viviente, D.A. Pacheco Tanaka, et al., Development of thin Pd–Ag supported membranes for fluidized bed membrane reactors including WGS related gases, Int. J. Hydrogen Energy. (2014) 1–14. doi:10.1016/j.ijhydene.2014.08.074.
Mediaandprocess.com, (n.d.). http://www.mediaandprocess.com/products/products02.html.
A. Goldbach, F. Bao, C. Qi, C. Bao, L. Zhao, C. Hao, et al., Evaluation of Pd composite membrane for pre-combustion CO2 capture, Int. J. Greenh. Gas Control. 33 (2015) 69–76. doi:10.1016/j.ijggc.2014.12.003.

Table XVII. Hydrogen permeation properties of commercial and the best th in Pd based membranes



Membrane	Support	Thickness µm	Technique	Temp °C	Calculated Permeance x10^{-7} mol m^{-2}s^{-1}Pa^{-1} at 1 atm	Selectivity H_2/N_2	Producer	Ref.
$Pd_{77}Ag_{23}$	No	1.9-3.8	PVD 2 steps	400	190	2900	Sintef	[11]
Pd_{93}-Ag_7	α-Al_2O_3	0.8	ELP	400	106	640	TECNALIA	[2]
$Pd_{77}Ag_{23}$	Micro-channels	2.2	PVD 2 steps	400	88	----	Sintef	[12]
Pd_{92}-Ag_8	Y-Al_2O_3/YSZ	0.9	ELP	400	65	1100	TECNALIA	[13]
Pd-Au	Al2O3	2-3	ELP	500	62	1400	Dalian	[14]
Pd-Au	YSZ/PSS	1-5	ELP	400	43-52	10000-20000 (H2/Ar)	PALL*	[15]
Pd_{85}-Ag_{15}	α-Al_2O_3	4	ELP	400	42	20000	TECNALIA	[16]
Pd_{85}-Ag_{15}	α-Al_2O_3	3.2	ELP	400	31	8000-10000	TECNALIA	Not published
Pd-Ag	α-Al_2O_3	2 to 10	ELP	350	6 - 31	500 to >1000	Media and process*	[17]
Pd	Y-Al_2O_3	2-4	ELP	400	27	500	Dalian	[18]
Pd	Metallic	3 to 5	ELP	450	20	450 H2/He	CRI/Criterion*	[19]
Pd-Ru	Al2O3/PSS	6.4	ELP	400	19	15000 @ 10 bar	NORAM* (former MRT)	[20]
Pd-Ag	α-Al_2O_3	3 to 9	ELP	350	15	> 7600	Hysep*	[21]
Pd	Metallic	12	PVD-ELP	417	11	1100	Plansee/KIT/Linde	[22]
Pd_{85}-Ag_{15}	Metallic	4-5	ELP	400	10	>200000	TECNALIA	[23]
Pd	Metallic	7.6		450	9	Infinite after 3500 h: >6000 H_2/He	CRI/Criterion*	[19]
Pd	No	76	Self-supported	600	4	>>10000	REB Research*	[24]

* Commercial Pd based membranes

Table XVIII lists commercial available membranes and the membranes with the highest H2 permeation available in the literature. The world record H2 permeation membrane is reported by SINTEF (a) with a self-supported (4 cm long) membrane prepared by Physical Vapor deposition (PVD) in two steps. Firstly, films are sputtered from a Pd/Ag23 wt% target onto polished silicon single crystal substrates, then the films are carefully lifted off the silicon substrate and mounted in a self-supported configuration[17]. As expected, since no support is used, the H2 permeation is extremely high, however, the technique requires very expensive equipment, the films are difficult to handle and building large modules without leaking is

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P. Veenstra, M. Iyer, A. Nijmeijer, F. Geuzebroek, R. Moene, J. Saukaitis, Integrated Approach to CO2 Capture: Fuel Gas Decarbonisation, Energy Procedia. 63 (2014) 2054–2059. doi:10.1016/j.egypro.2014.11.221.
A. Li, T. Boyd, A. Gulamhusein, A. Mahecha-Botero, Towards Industrial Applications: Membrane and Fluidized Bed Reactor, in: Work. Pd-Membrane Technol. Scale-Up, 2015.
HySep, (n.d.). http://www.hysep.com/fileadmin/hysep/user/documents/B-09-010_hysep_A4_wb.pdf.
B. Dittmar, A. Behrens, N. Schödel, M. Rüttinger, T. Franco, G. Straczewski, et al., Methane steam reforming operation and thermal stability of new porous metal supported tubular palladium composite membranes, Int. J. Hydrogen Energy. 38 (2013) 8759–8771. doi:10.1016/j.ijhydene.2013.05.030.
[23] D.A.P.T. E. Fernandez, J.A. Medrano, J. Melendez, M. Parco, J.L. Viviente, M. van Sint Annaland, F. Gallucci, Preparation and characterization of metallic supported thin Pd-Ag membranes for high temperature hydrogen separation., Chem. Eng. J. submitted (2015).

[17] T.A. Peters, M. Stange, R. Bredesen, On the high pressure performance of thin supported Pd-23%Ag membranes-Evidence of ultrahigh hydrogen flux after air treatment, J. Memb. Sci. 378 (2011) 28–34.
N. Vicinanza, I.-H. Svenum, L.N. Næss, T.A. Peters, R. Bredesen, A. Borg, et al., Thickness dependent effects of solubility and surface phenomena on the hydrogen transport properties of sputtered Pd77%Ag23% thin film membranes, J. Memb. Sci. 476 (2015) 602–608.

difficult. In addition, the unsupported membranes are not stable to high pressures (the membrane deforms and performance decreases with the time) and there is a gradient in grain size over the sputtered Pd-Ag film with a larger fraction of smaller grains and higher average density of grain boundaries as the thickness is reduced. These problems are solved by depositing directly ultra-thin Pd based membranes directly on a porous support with very low resistance to gas passage by ELP by TECNALIA[18].

Dilute hydrogen poses a significant challenge for membrane technology. For example, if 10% hydrogen is fed into a membrane separator, and 70% recovery is being considered, the outlet composition of the gas would be approximately 3%. This means that to support the flux of the outlet elements of the membrane, the pressure ratio would need to be at least 33:1. So, if ambient-pressure hydrogen is recovered, the pressure of the natural gas would need to be at least 33atm (500psia). This is, again, an idealized scenario, and a significantly higher ratio than 33:1 would be needed to provide a driving force. Membrane technology for transmission pipelines may, however, be a good technology fit. Such pipelines often operate at pressures of about 1,000 psig, which provides sufficient driving force for hydrogen extraction. In such systems, the bulk of the process gas retains its pressure, and only a small amount of re-pressurization would be required to compensate for any device pressure drop.

CMS – Carbon Molecular Sieve membranes

CMSM have been considered as the next generation of gas separation membrane technology to work between 100 and 250 °C were polymeric membranes are not stable and Pd membranes have low permeation and stability and higher cost. CMSM are produced by the carbonization of a polymeric precursor under an inert atmosphere or vacuum. CMSM have a unique microporous structure, which allows them to discriminate gas molecules by size and shape.

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[18] D.A.Pacheco.Tanaka. J. Melendez, E. Fernandez, A. Helmi, F. Gallucci, P.L. Arias, Preparation and characterization of ultra-thin (<1 micron) Pd-Ag membranes on porous alumina support (100 nm pore size), in: 12th Int. Conf. Catal. Membr. React., 2015. D.A. Pacheco Tanaka, J. Okazaki, M.A. Llosa Tanco, T.M. Suzuki, 5 - Fabrication of supported palladium alloy membranes using electroless plating techniques, in: A. Doukelis, K. Panopoulos, A. Koumanakos, E.B.T.-P.M.T. for H.P. Kakaras Carbon Capture and Other Applications (Eds.), Woodhead Publ. Ser. Energy, Woodhead Publishing, 2015: pp. 83–99.

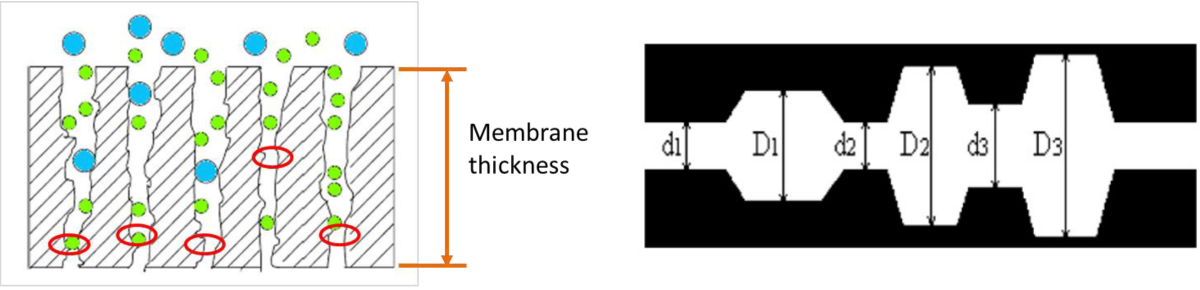

Fig. 20. Transport mechanism

CMS have a number of ultramicropores much higher than micropores, as it can be seen in next figure.

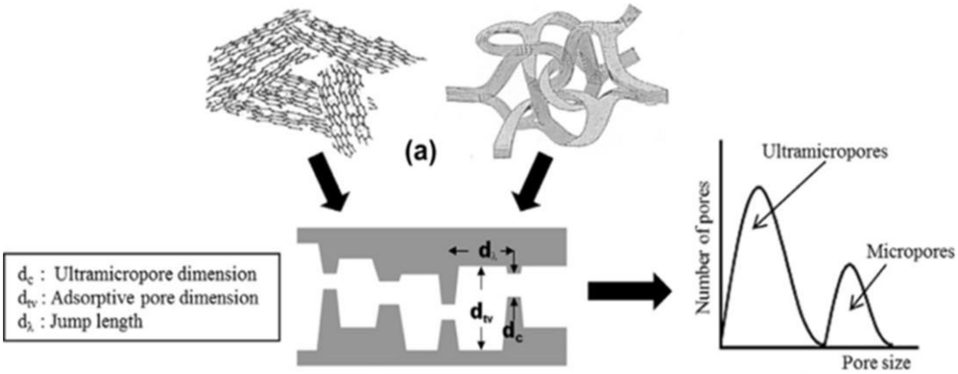

Fig. 21. Pores structure in CMS

The most common configuration of carbon membranes is tubular. Since permeation through membranes depends on the thickness and on the partial pressure difference, very-thin membranes (selective layer less than 5 µm) able to withstand high pressures are required. Very thin membranes are mechanically weak and are difficult to handle; therefore, supported membranes are preferred. Supported CMSM are prepared by carbonizing thin polymer precursor on a porous substrate.

Pacheco and M. Llosa reported for the first time the preparation of 5 cm long, 1 cm diameter supported defect free 3 µm thick composite alumina-CMSM from cheap polymer precursors.

The Robeson plot of the c-CMSM and Pd pore filled membranes is showed in Fig 28[19].the H_2/N_2 selectivity was 725 and the permeance to H2 was 145 x 10^{-9} $molm^{-2}$ s^{-1} Pa^{-1} at room temperature, values comparable with the best performing to Pd membranes at the same temperature. This c-CMS membrane can therefore be used instead of Pd for H2 separation processes involving hydrogen membranes at low temperature.

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[19] M.A. Llosa Tanco, D.A. Pacheco Tanaka, A. Mendes, Composite-alumina-carbon molecular sieve membranes prepared from novolac resin and boehmite. Part II: Effect of the carbonization temperature on the gas permeation properties, Int. J. Hydrogen Energy. 40 (2015) 3485–3496. doi:10.1016/j.ijhydene.2014.11.025

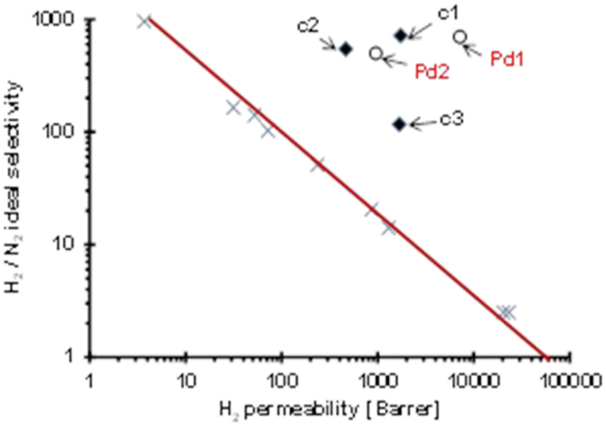


Fig. 22. Robeson plot of membranes developed in HyGrid Project

5.3. ELECTROCHEMICAL HYDROGEN SEPARATION (HYDROGEN PUMPING)

Electrochemical cells can selectively extract and compress hydrogen from gas mixtures. It is a more elaborate method for bulk hydrogen recovery. It operates on principles in common with fuel cell systems, using fuel cell stacks and passing the process gas across one side of the stack. By applying a current across the stack, hydrogen is atomically dissociated from the process gas and is re-associated into hydrogen on the product side. This process operates with very low differential pressure between the process gas and the product gas. Two technologies are used for electrochemical separation: one is based on Nafion and the other on PBI. Nafion is the more mature technology, but PBI is more desirable because the phosphoric acid conditions provide chemical resistance to sulphur contamination and its lower sensitivity to hydration, although water is needed.

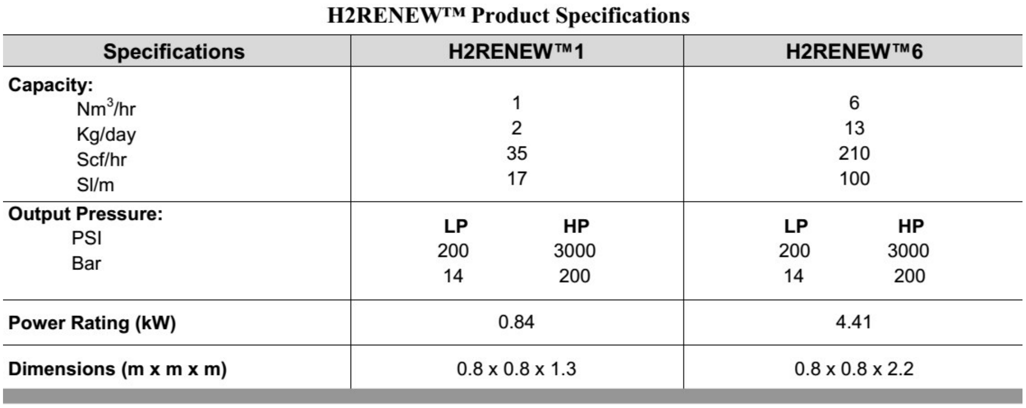
Electrochemical compression can be especially valuable at small scales where cost scaling factors for compressors become prohibitive. Unlike compressors, the scaling factor for electrochemical compression is much more linear with size. And because the membrane has few moving parts and avoids fuel cell degradation drivers (catalyst oxidation and contamination), maintenance costs would likely be low.

We have found specifications of a commercial Electrochemical Hydrogen Separation/Compresion (H2RENEW^{TM} Cell Stack) of the US Company Sustainable Innovations.

Fig. 23. Commercial Electrochemical Hydrogen Separation

Product specifications are showed in table below. Sustainable Innovations claims that purities as high as 99.999%, or greater, are attainable.

Table XVIII. H2RENEW^{TM} Product Specifications

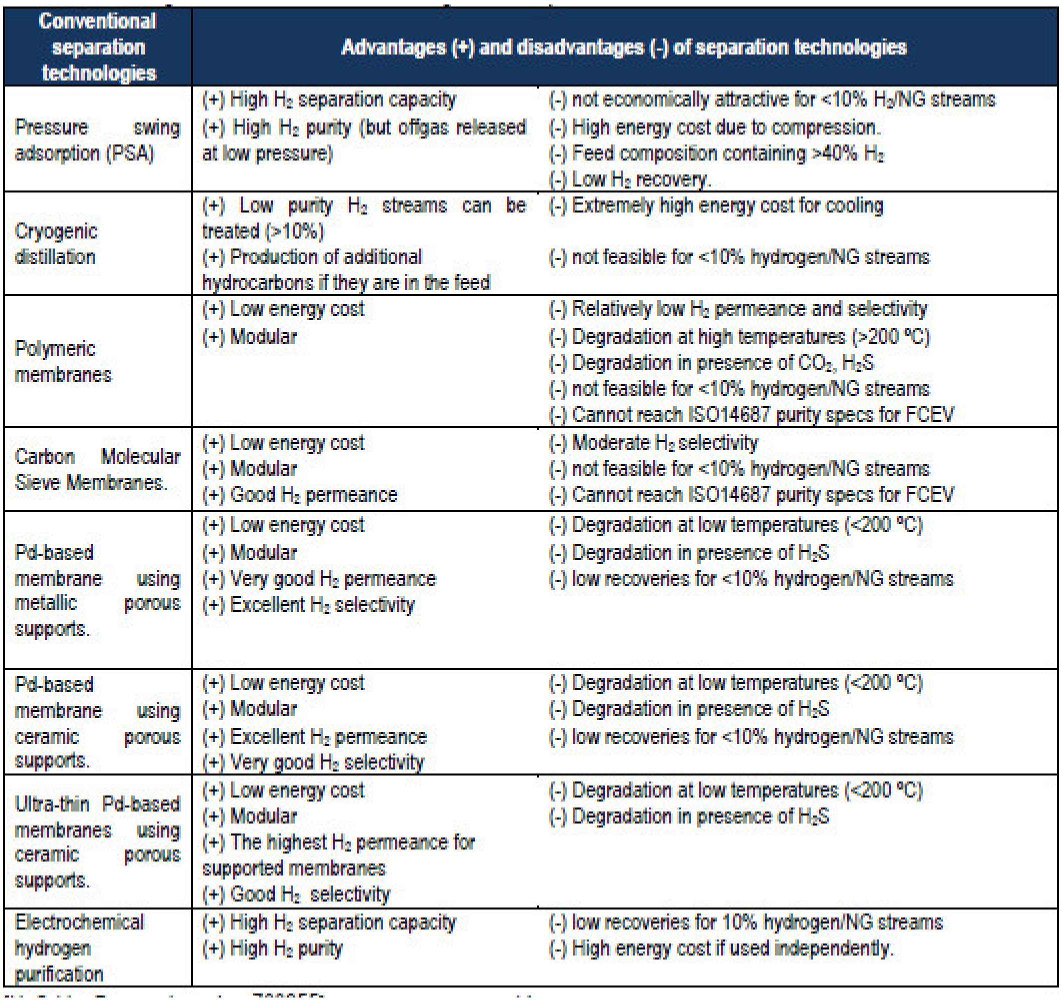


H2RENEW™ Product Specifications

Specifications	H2RENEW™1		H2RENEW™6	
Capacity:				
Nm^3/hr	1		6	
Kg/day	2		13	
Scf/hr	35		210	
Sl/m	17		100	
Output Pressure:	**LP**	**HP**	**LP**	**HP**
PSI	200	3000	200	3000
Bar	14	200	14	200
Power Rating (kW)	0.84		4.41	
Dimensions (m x m x m)	0.8 x 0.8 x 1.3		0.8 x 0.8 x 2.2	

The advantages and drawbacks of the technologies for H_2 separation are shown in Table XIX.

Table XIX: advantages and drawbacks of the technologies for H2 separation



Conventional separation technologies	Advantages (+) and disadvantages (-) of separation technologies	
Pressure swing adsorption (PSA)	(+) High H_2 separation capacity (+) High H_2 purity (but offgas released at low pressure)	(-) not economically attractive for <10% H_2/NG streams (-) High energy cost due to compression. (-) Feed composition containing >40% H_2 (-) Low H_2 recovery.
Cryogenic distillation	(+) Low purity H_2 streams can be treated (>10%) (+) Production of additional hydrocarbons if they are in the feed	(-) Extremely high energy cost for cooling (-) not feasible for <10% hydrogen/NG streams
Polymeric membranes	(+) Low energy cost (+) Modular	(-) Relatively low H_2 permeance and selectivity (-) Degradation at high temperatures (>200 °C) (-) Degradation in presence of CO_2, H_2S (-) not feasible for <10% hydrogen/NG streams (-) Cannot reach ISO14687 purity specs for FCEV
Carbon Molecular Sieve Membranes.	(+) Low energy cost (+) Modular (+) Good H_2 permeance	(-) Moderate H_2 selectivity (-) not feasible for <10% hydrogen/NG streams (-) Cannot reach ISO14687 purity specs for FCEV
Pd-based membrane using metallic porous supports.	(+) Low energy cost (+) Modular (+) Very good H_2 permeance (+) Excellent H_2 selectivity	(-) Degradation at low temperatures (<200 °C) (-) Degradation in presence of H_2S (-) low recoveries for <10% hydrogen/NG streams
Pd-based membrane using ceramic porous supports.	(+) Low energy cost (+) Modular (+) Excellent H_2 permeance (+) Very good H_2 selectivity	(-) Degradation at low temperatures (<200 °C) (-) Degradation in presence of H_2S (-) low recoveries for <10% hydrogen/NG streams
Ultra-thin Pd-based membranes using ceramic porous supports.	(+) Low energy cost (+) Modular (+) The highest H_2 permeance for supported membranes (+) Good H_2 selectivity	(-) Degradation at low temperatures (<200 °C) (-) Degradation in presence of H_2S
Electrochemical hydrogen purification	(+) High H_2 separation capacity (+) High H_2 purity	(-) low recoveries for 10% hydrogen/NG streams (-) High energy cost if used independently.

5.5. TSA – Drying Hydrogen

Depending on the application of the recovered hydrogen, water vapour has to be partly or virtually completely removed from the hydrogen product after the condenser. Drying is achieved by means of TSA (Thermal Swing Adsorption): this is an adsorption process in which the regeneration takes place by means of heating (compare to PSA, where regeneration is performed by decreasing the pressure).

TSA is applied for drying of air and other gases, and can be used for removal of other trace contaminants than water vapour as well. Adsorbents that can be used include silica gel, activated alumina and zeolites; the choice depends on the feed and product specifications. The regeneration temperature and adsorption heat are different for the varying adsorbents, hence the required heat input for regeneration differs as well.

Most often a TSA installation consists of two columns, of which one is in adsorption mode while the other one is being regenerated. This allows continuous operation. Heating for regeneration is usually performed by passing hot gas through the adsorber: this can be either a portion of the dry product gas or a portion of the wet feed gas. In the latter case the regeneration temperature has to be higher to compensate for the higher humidity of the gas. In HyGrid, no loss of hydrogen is accepted, hence the regeneration gas has to be recycled to the process after knocking out the desorbed water. This requires the inclusion of a recycle blower. Moreover, before feeding the regeneration gas back, water knock-out from the regeneration gas should be as complete as possible which may mean that a (small) chiller has to be included.

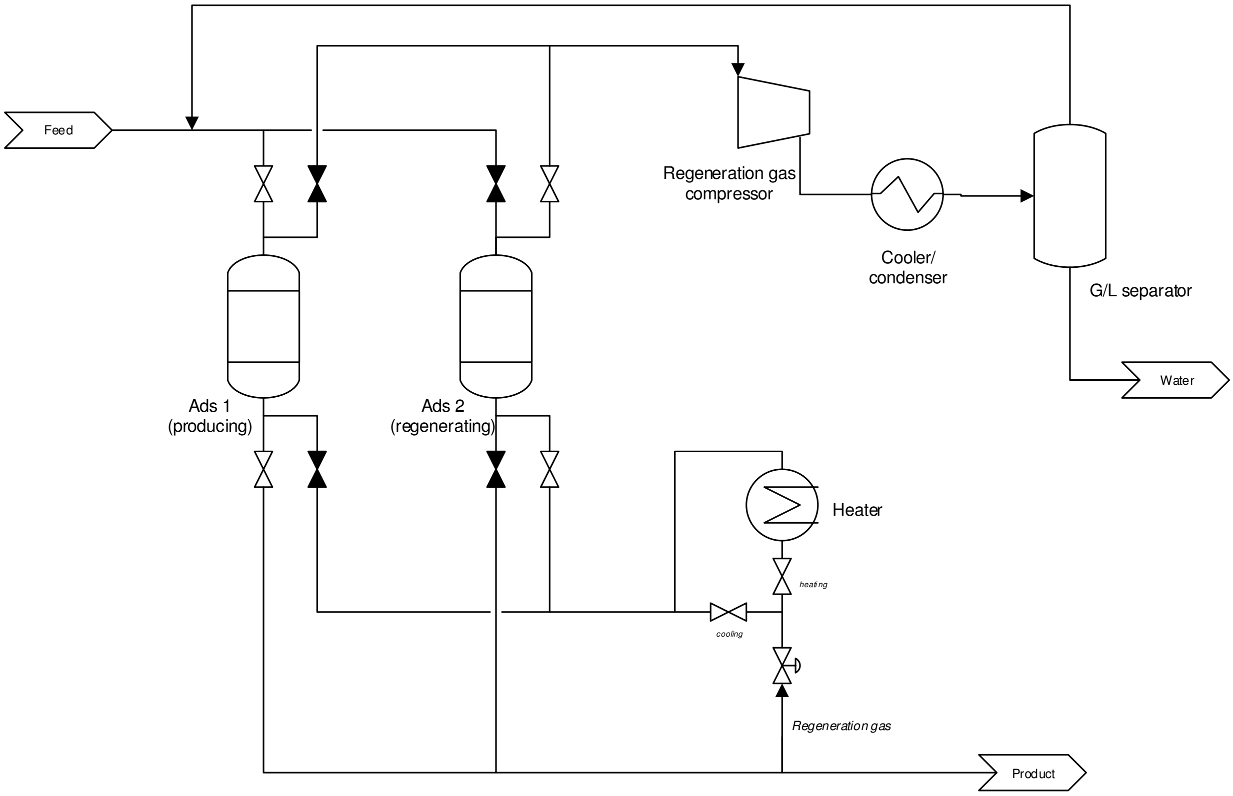


Fig. 24. Scheme of a TSA facility

Within HyGrid the feed stream to the TSA is water-saturated and is at low pressure, hence it contains a high humidity. For such conditions it is challenging to design a low-cost and energy efficient drying process. The release of adsorption heat limits the achievable product dew point, therefore the adsorbent should be carefully selected, keeping in mind the temperature dependency of the isotherms even during adsorption. The use of detailed models in the selection and design is mandatory. Possibly a chilling step prior to the TSA is necessary to reach a viable solution; the use of multiple sorbents might also be considered, although that will complicate the design and probably make it more expensive.

Heat integration may be applied to minimize the required heat input for regeneration.

6. HYDROGEN PRODUCT SPECIFICATION

The standard ISO 14687 rules the Hydrogen fuel specifications:

- Product specification ISO 14687:1999 - Part 1 All applications except proton exchange membrane (PEM) fuel cell for road vehicles.
- Product specification ISO 14687-2:2012 - Part 2: Proton exchange membrane (PEM) fuel cell applications for road vehicles.
- Product specification ISO/FDIS 14687-3:2013 - Part 3: Proton exchange membrane (PEM) fuel cell applications for stationary appliances.

Hydrogen fuel shall be classified according to different types and grade designations in accordance with its appliances (see Table XX).

Table XX. Hydrogen classification and applications

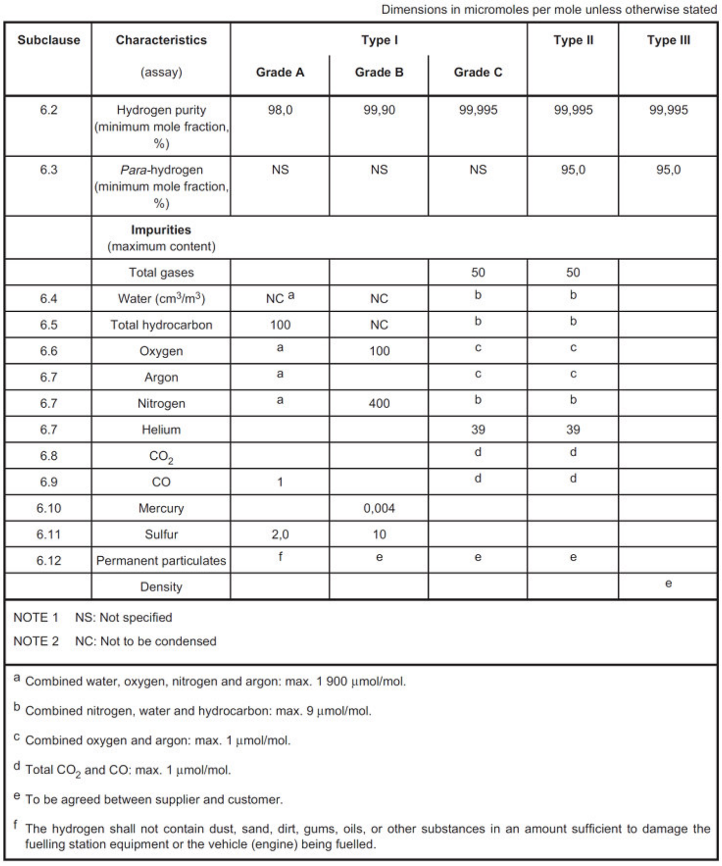
Type	State	Grade	Application
I	Gaseous	A	internal combustion engines/fuel cells for transportation; residential/commercial appliances
		B	industrial fuel, for use e.g. in power generation or as a heat energy source
		C	aircraft and space-vehicle ground support systems
		D	gaseous hydrogen fuel for PEM fuel cell road vehicle systems
		E	gaseous hydrogen fuel for PEM fuel cell stationary appliance systems
II	Liquid	C	aircraft and space-vehicle on-board propulsion and electrical energy requirements; land vehicles
		D	liquid hydrogen fuel for PEM fuel cell road vehicle systems
III	Slush	--	aircraft and space-vehicle on-board propulsion.

Type I, grade A, B, C, Type II, grade C and Type III, (applicable for all applications except PEM fuel cells), are defined in ISO 14687-1 (see Table XXI).

Type I, grade D and Type II, grade D, which are applicable for PEM fuel cells for road vehicles are defined in ISO 14687-2 (see Table XXII).

Type I, grade E, which are applicable for PEM fuel cells cell applications for stationary appliances are addressed in ISO 14687-3 (see Table XXIII).

Table XXI. Directory of limiting characteristics defined in ISO 14687



Dimensions in micromoles per mole unless otherwise stated

Subclause	Characteristics (assay)	Type I Grade A	Type I Grade B	Type I Grade C	Type II	Type III
6.2	Hydrogen purity (minimum mole fraction, %)	98,0	99,90	99,995	99,995	99,995
6.3	*Para*-hydrogen (minimum mole fraction, %)	NS	NS	NS	95,0	95,0
	Impurities (maximum content)					
	Total gases			50	50	
6.4	Water (cm³/m³)	NC [a]	NC	[b]	[b]	
6.5	Total hydrocarbon	100	NC	[b]	[b]	
6.6	Oxygen	[a]	100	[c]	[c]	
6.7	Argon	[a]		[c]	[c]	
6.7	Nitrogen	[a]	400	[b]	[b]	
6.7	Helium			39	39	
6.8	CO_2			[d]	[d]	
6.9	CO	1		[d]	[d]	
6.10	Mercury		0,004			
6.11	Sulfur	2,0	10			
6.12	Permanent particulates	[f]	[e]	[e]	[e]	
	Density					[e]

NOTE 1 NS: Not specified

NOTE 2 NC: Not to be condensed

[a] Combined water, oxygen, nitrogen and argon: max. 1 900 µmol/mol.

[b] Combined nitrogen, water and hydrocarbon: max. 9 µmol/mol.

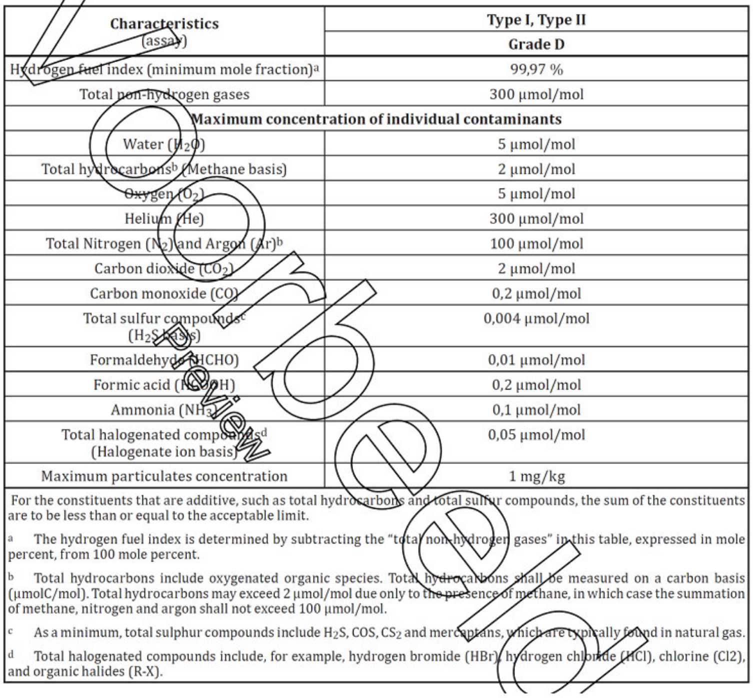
[c] Combined oxygen and argon: max. 1 µmol/mol.

[d] Total CO_2 and CO: max. 1 µmol/mol.

[e] To be agreed between supplier and customer.

[f] The hydrogen shall not contain dust, sand, dirt, gums, oils, or other substances in an amount sufficient to damage the fuelling station equipment or the vehicle (engine) being fuelled.

Table XXII. Directory of limiting characteristics defined by ISO 14687-2



Characteristics (assay)	Type I, Type II Grade D
Hydrogen fuel index (minimum mole fraction)[a]	99,97 %
Total non-hydrogen gases	300 µmol/mol
Maximum concentration of individual contaminants	
Water (H_2O)	5 µmol/mol
Total hydrocarbons[b] (Methane basis)	2 µmol/mol
Oxygen (O_2)	5 µmol/mol
Helium (He)	300 µmol/mol
Total Nitrogen (N_2) and Argon (Ar)[b]	100 µmol/mol
Carbon dioxide (CO_2)	2 µmol/mol
Carbon monoxide (CO)	0,2 µmol/mol
Total sulfur compounds[c] (H_2S basis)	0,004 µmol/mol
Formaldehyde (HCHO)	0,01 µmol/mol
Formic acid (HCOOH)	0,2 µmol/mol
Ammonia (NH_3)	0,1 µmol/mol
Total halogenated compounds[d] (Halogenate ion basis)	0,05 µmol/mol
Maximum particulates concentration	1 mg/kg

For the constituents that are additive, such as total hydrocarbons and total sulfur compounds, the sum of the constituents are to be less than or equal to the acceptable limit.

[a] The hydrogen fuel index is determined by subtracting the "total non-hydrogen gases" in this table, expressed in mole percent, from 100 mole percent.

[b] Total hydrocarbons include oxygenated organic species. Total hydrocarbons shall be measured on a carbon basis (µmolC/mol). Total hydrocarbons may exceed 2 µmol/mol due only to the presence of methane, in which case the summation of methane, nitrogen and argon shall not exceed 100 µmol/mol.

[c] As a minimum, total sulphur compounds include H_2S, COS, CS_2 and mercaptans, which are typically found in natural gas.

[d] Total halogenated compounds include, for example, hydrogen bromide (HBr), hydrogen chloride (HCl), chlorine (Cl2), and organic halides (R-X).

Table XXIII. Directory of limiting characteristics defined in 14687-3

Characteristics[a] (assay)	Type I, grade E		
	Category 1	Category 2	Category 3
Hydrogen fuel index (minimum mole fraction)	50 %	50 %	99,9 %
Total non-hydrogen gases (maximum mole fraction)	50 %	50 %	0,1 %
Water (H_2O)[b]	Non-condensing at all ambient conditions	Non-condensing at all ambient conditions	Non-condensing at all ambient conditions
Maximum concentration of individual contaminants			
Total hydrocarbons (C_1 basis)[c]	10 µmol/mol	2 µmol/mol	2 µmol/mol
Oxygen (O_2)	200 µmol/mol	200 µmol/mol	50 µmol/mol
Nitrogen (N_2), Argon (Ar), Helium (He) (mole fraction)	50 %	50 %	0,1 %
Carbon dioxide (CO_2)	Included in total non-hydrogen gases	Included in total non-hydrogen gases	2 µmol/mol
Carbon monoxide (CO)	10 µmol/mol	10 µmol/mol	0,2 µmol/mol
Total sulfur compounds[d]	0,004 µmol/mol	0,004 µmol/mol	0,004 µmol/mol
Formaldehyde (HCHO)	3,0 µmol/mol	0,01 µmol/mol	0,01 µmol/mol
Formic acid (HCOOH)	10 µmol/mol	0,2 µmol/mol	0,2 µmol/mol
Ammonia (NH_3)	0,1 µmol/mol	0,1 µmol/mol	0,1 µmol/mol
Total halogenated compounds[e]	0,05 µmol/mol	0,05 µmol/mol	0,05 µmol/mol
Maximum particulates concentration	1 mg/kg	1 mg/kg	1 mg/kg
Maximum particle diameter	75 µm	75 µm	75 µm

NOTE For the constituents that are additive (i.e. total hydrocarbons, total sulfur compounds and total halogenated compounds), the sum of the constituents shall be less than or equal to the specifications in the table. It is therefore important that the analytical method used measures the *total* concentration of these families of compounds, and not the concentration of single compounds within these families, which are subsequently summed to give a total amount of fraction. The latter approach risks a false negative being reported. For more details, see Clause 7.

[a] Maximum concentration of impurities against the total gas content shall be determined on a dry-basis.

[b] Each site shall be evaluated to determine the appropriate maximum water content based on the lowest expected ambient temperature and the highest expected storage pressure.

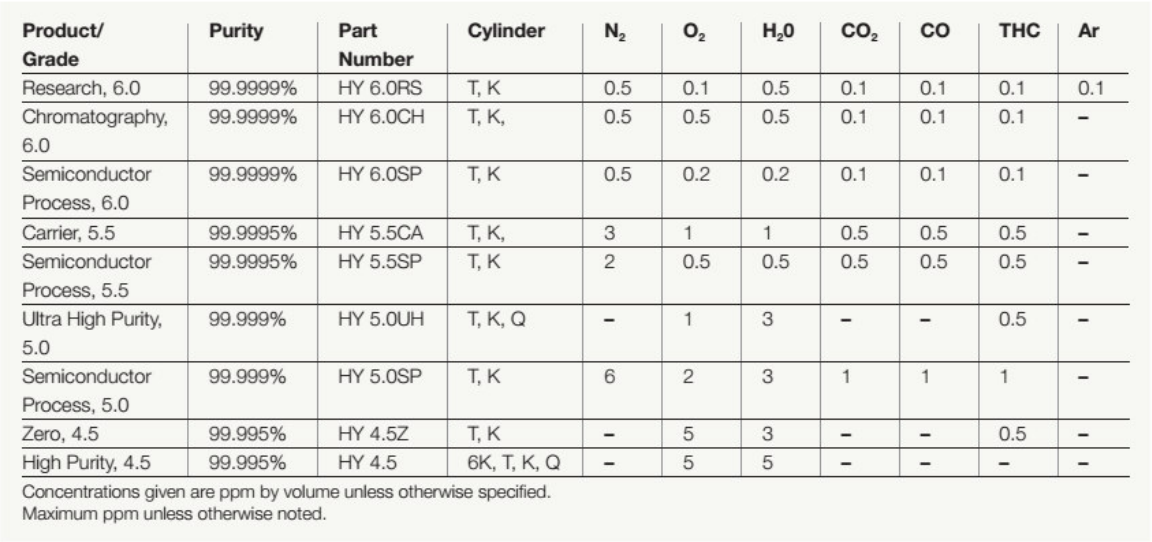
[c] Total hydrocarbons are measured on a carbon basis (µmolC/mol). The specification for total hydrocarbons includes oxygenated hydrocarbons. The measured amount fractions of all oxygenated hydrocarbons shall therefore contribute to the measured amount fraction of total hydrocarbons. Specifications for some individual oxygenated hydrocarbons (e.g. formaldehyde and formic acid) are also given in the table. These, however, also contribute to the measured amount fraction of total hydrocarbons. These species have been assigned their own specifications based on their potential to impair the performance of PEM fuel cells. Total hydrocarbons may exceed the limit due only to the presence of methane, in which case the methane shall not exceed 5 % for Category 1, 1 % for Category 2 or 100 µmol/mol of hydrogen fuel for Category 3.

d As a minimum, total sulfur compounds include H_2S, COS, CS_2 and mercaptans, which are typically found in natural gas.

e Includes, for example, hydrogen bromide (HBr), hydrogen chloride (HCl), chlorine (Cl_2), and organic halides (R-X).

Specifications for hydrogen bottled are stricter, reaching close 100% of hydrogen[20].

Table XXIV. Specifications for bottled hydrogen



Product/ Grade	Purity	Part Number	Cylinder	N_2	O_2	H_20	CO_2	CO	THC	Ar
Research, 6.0	99.9999%	HY 6.0RS	T, K	0.5	0.1	0.5	0.1	0.1	0.1	0.1
Chromatography, 6.0	99.9999%	HY 6.0CH	T, K,	0.5	0.5	0.5	0.1	0.1	0.1	–
Semiconductor Process, 6.0	99.9999%	HY 6.0SP	T, K	0.5	0.2	0.2	0.1	0.1	0.1	–
Carrier, 5.5	99.9995%	HY 5.5CA	T, K,	3	1	1	0.5	0.5	0.5	–
Semiconductor Process, 5.5	99.9995%	HY 5.5SP	T, K	2	0.5	0.5	0.5	0.5	0.5	–
Ultra High Purity, 5.0	99.999%	HY 5.0UH	T, K, Q	–	1	3	–	–	0.5	–
Semiconductor Process, 5.0	99.999%	HY 5.0SP	T, K	6	2	3	1	1	1	–
Zero, 4.5	99.995%	HY 4.5Z	T, K	–	5	3	–	–	0.5	–
High Purity, 4.5	99.995%	HY 4.5	6K, T, K, Q	–	5	5	–	–	–	–

Concentrations given are ppm by volume unless otherwise specified.
Maximum ppm unless otherwise noted.

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[20] http://www.praxair.com/gases/buy-compressed-hydrogen-gas-or-liquid-hydrogen

7. HYGRID TECHNOLOGY

HyGrid aims at developing an advanced high performance, cost effective separation technology for direct separation of hydrogen from natural gas networks.

The key objective of the HyGrid project is the design, scale-up and demonstration at industrially relevant conditions a novel membrane based hybrid technology for the direct separation of hydrogen from natural gas grids. The focus of the project will be on the hydrogen separation through a combination of membranes, electrochemical separation and temperature swing adsorption to be able to decrease the total cost of hydrogen recovery. The project targets a pure hydrogen separation system with power and cost of < 5 kWh/kgH_2 and < 1.5 €/kgH_2. A pilot designed for 25 kg/day of hydrogen will be built and tested.

To achieve this, HyGrid aims at developing novel hybrid system integrating three technologies for hydrogen purification integrated in a way that enhances the strengths of each of them: **Membrane separation technology is employed for removing H_2 from the "low H2 content" (e.g. 2-10 %)** followed by **electrochemical hydrogen separation (EHP) optimal for the "very low H_2 content" (e.g. <2 %)** and finally temperature swing adsorption (**TSA) technology to purify from humidity produced in both systems upstream**. The objective is to give a robust proof of concept and validation of the new technology (TRL 5) by designing, building, operating and validating a prototype system tested at industrial relevant conditions for a continuous and transient loads

The system will describe and evaluate the system performance for the different **pressure ranges within 0.03 to 80 bar (distribution to transmission)** and test the concept at **pilot scale in the 6-10 bar range**.

HyGrid will evaluate hydrogen quality production according to ISO 14687 in line not only with fuel cell vehicles (Type I Grade D) but also stationary applications (Type I grade A) and hydrogen fuelled ICE (Type I grade E category 3).

A complete energy and cost analysis will be carried out in detail.

Schematically, the HYGRID process is represented in Fig. 25.

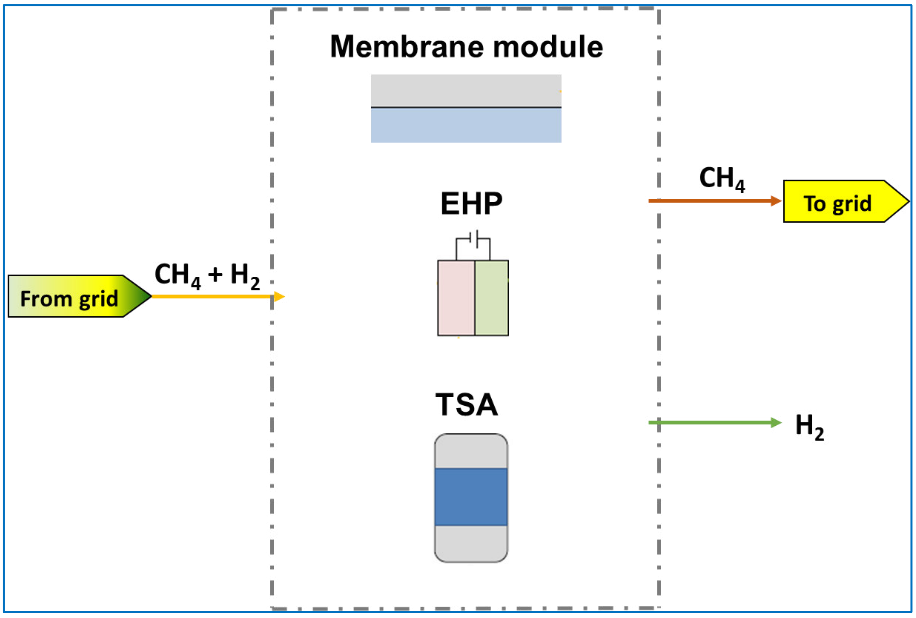

Fig. 25. HyGrid Process scheme

7.1. ELECTROCHEMICAL CELLS

Within project HyGrid electrochemical hydrogen extraction from a 2% H_2 in natural gas mixture is targeted. This functionality is part of a larger, hybrid membrane based hydrogen extraction system, capable of extracting hydrogen from its mixture with natural gas. The HyGrid system will become useful when natural gas grid infrastructures are used for hydrogen distribution, in addition to trucked hydrogen distribution and on-site production of hydrogen.

The electrochemical hydrogen purifier (EHP) is part of the HyGrid system, capable of recovering the majority of the remaining hydrogen from the retentate of the Pd-based membrane separator. In WP7 HYET will adapt its high hydrogen concentration electrochemical compressor technology for low concentration extraction application. WP4 (Electrochemical hydrogen separation development) will address the following objectives:

- Assimilation of the process/performance model of EHP as constructed in WP7 for electrochemical cell design.
- Theoretical modeling assisted optimum design of stack and gas distribution plate geometry for low concentration electrochemical hydrogen extraction (<3%).
- Optimum configuration of membrane-electrode-assembly for low concentration hydrogen extraction.
- Construction and testing of sub- and full size electrochemical compressor stacks for model validation and prototype preparation (in part also in WP6)

In order to limit the number of balance-of-plant components and to make the electrochemical hydrogen extraction cell more tolerant towards catalyst contaminants, the use of high temperature (T>120 ºC) proton exchange membranes is required. Liquid acid based membranes like the typical PBI/H_3PO_4 systems are not suitable because of acid leach out problems.

Purification and compression require membranes with:

- High mechanical integrity under high stress conditions.
- Low/zero humidity proton conduction.
- Low (hydrogen) gas permeability.

Within project HyGrid multiple membrane systems will be considered using the following approaches:

- PBI/H_3PO_4 systems modified with additives to limit H_3PO_4 leach out.
- Polymer/solid acid composites.
- Bonded acid polymer membranes for T>120 ºC operation.

7.2. TSA

The TSA unit in HyGrid is designed, constructed and tested in WP 5. The transient operation of the TSA is intrinsic to its operating mechanism. The behavior of the materials, and their response to the specific conditions required in HyGrid need to be better understood.

WP5 will tackle the technological needs for HyGrid with regards to the TSA purification step:

- Better comprehension of the behaviour and performance of the adsorption materials used in TSA.
- Understanding of the response of adsorbents to the dynamic temperature control.
- Implementation of the know-how gained through lab tests onto the up-scaled design.
- Design of prototype TSA unit for integration in pilot scale HyGrid system.
- Testing of pilot scale TSA unit.

7.3 MEMBRANES

The main objective of this WP is the development of cost effective tubular supported membranes for the recovery of hydrogen from low concentration streams (2% -10%) up to

99.97%, 99.9% and 98.0% H_2 purity for ISO14687 grade D, E category 3 and A respectively in the whole range of pressures of the Natural Gas Network. In order to achieve this, two different types of membranes will be developed up to TRL5:

- **Pd-based membranes** for the medium to the lowest Natural Gas Grid pressures (i.e. 30 mbar - 16 bar). TECNALIA will use the procedures developed in previous research activities (i.e. DEMCAMER, ReforCELL, FERRET, FluidCELL) for developing metallic and/or ceramic supported Pd-based thin and ultra-thin film membranes with ad-hoc properties. The target for the base case where distribution networks of Natural Gas (8-10bar) is the following:
  - ultra-thin Pd based membranes with selectivity (H_2/CH_4) ≥ 10.000 and
  - H_2 Permeance ≥ 10 x10-7 mol m^{-2} s^{-1} Pa^{-1} @ calculated at ΔP_{H2} 0.8 atm.
- **Carbon Molecular Sieve (CMS) membranes** for the high pressure range (i.e. 40-80 bar). TECNALIA will use procedures developed in previous research activities (TRL 3) for developing CMS membranes. The CMSM will be developed considering the case of transport Networks where pressure can reach up to 80 bars allowing for membranes less selective and/or permeable but with lower costs.

The membranes will be first characterised in this WP and later on in a small lab-scale setup of the prototype in WP6 and then, selected membranes (~40-45 cm long) will be manufactured, integrated in a separation module and, afterwards, the module integrated in the pilot prototype in WP7.

8. HYGRID OBJECTIVES

HyGrid will address not only fuel cell vehicles (type I grade D) but also stationary applications (type I grade A) and hydrogen fuelled ICE (type I grade E category 3).

The following requirements are relevant with respect to the HyGrid project:

- The required hydrogen content varies from 98% (grade A) to over 99.9% (grades D and E).
- The humidity demands vary widely, i.e. from very dry (5 ppmv, grade D) to noncondensing (which may come down to more than 1% v/v of H2O, grades A and E).
- The demands for hydrocarbon content are moderately to very strict: from 100 ppmv for grade A to 10 and 2 ppmv for grades D and E respectively.

Specifications of ISO 14687 will be taken into account to design the prototype.

The general flowsheet of a full-scale HyGrid system foresees that the natural gas is taken from the grid, compressed to overcome the system pressure drop (this concerns only a small compression ratio) and then heated to be fed into the membrane unit and subsequently the EHP unit to extract the hydrogen, before re-injection into the grid.

The composition and conditions of the intake natural gas (including potential hydrogen addition) depend on the geographic location and the place in the grid, and have been extensively reviewed in Chapter 4. Consequently, the pressure at which a full scale HyGrid unit could work may be in a low (0.03-1 bar), medium (1-10 bar) or high (10-80 bar) pressure range. Based on the current specifications for the hydrogen content of natural gas (which is often very low for high-pressure transportation grids) it may be argued that the most realistic case is application on a distribution grid at intermediate pressure. The prototype will be designed for a medium pressure range, i.e. the pressure will be limited to a maximum of 10 bar(a).

The hydrogen will be delivered at a low pressure, typically < 1 bar(g). Targeted operational costs of the system are < 1.5 €/kg H_2 (see DoW), with an electric energy consumption < 5 kWh/kg H_2.

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10. ANNEXES

- SAES Report
- HYGEAR Reports

HYGRID

FLEXIBLE HYBRID SEPARATION SYSTEM FOR H2 RECOVERY FROM NG GRIDS

FCH-2 GRANT AGREEMENT NUMBER: 700355

Start date of project: 01/05/2016 **Duration: 3 years**

WP2 – Industrial Specifications Definition

D2.1

Industrial specifications for a system to recover hydrogen from NG grids

Topic:	Development of technology to separate hydrogen from low-concentration hydrogen streams
Funding scheme:	Research and Innovation Action
Call identifier:	H2020-JTI-FCH-2015-1

Due date of deliverable: **31-07-2016**	**Actual submission date:**	**Reference period:**
Document classification code (*): **HYGRID-WP2-D2.1-DLR-SAES-12072016-version1.docx**		**Prepared by (**):** **SAES**

Version	DATE	Changes	CHECKED	APPROVED
v0.1	**12-07-2016**	**First Release**	**SAES**	**MSucci**

Project funded by the FCH-2 JU within the H2020 Programme (2014-2020)		
Dissemination Level		
PU	Public	
PP	Restricted to other programme participants (including the Commission Services)	
RE	Restricted to a group specified by the consortium (including the Commission Services)	
CO	Confidential, only for members of the consortium (including the Commission Services)	X
CON	Confidential, only for members of the Consortium	

(*) for generating such code please refer to the Quality Management Plan, also to be included in the header of the following pages

(**) indicate the acronym of the partner that prepared the document

Content

1. INTRODUCTION

This note briefly describes how the Natural Gas (NG) grid in Italy is set up. The conditions, currently under discussion and not yet approved, to inject biomethane into the grid are also indicated followed by some considerations regarding the injection of H2 into the grid.

2. THE NATURAL GAS GRID IN ITALY

The NG grid in Italy is divided into 2 levels of distribution: a primary level that covers the national and regional distribution and a secondary level for the local distribution.

The primary transport distribution is a network operating at high pressure in large diameter pipes, which crosses the country from north to south and transports gas to the interconnection with the regional transport networks (at high and medium pressure).
The national and regional primary gas transport system is operated by 10 companies, including 7 operating exclusively on regional networks; the main operator is Snam Rete Gas[1], which owns approximately 96% of the national transport network and regional, accounting for nearly 33,000 kilometers.

Natural gas imported into Italy is entered into the national grid through eigth entry points, at the interconnections with the 5 import pipelines:

- the Tag, at Tarvisio from Austria
- at Gorizia,
- the Transitgas at Gries Pass from the North of Europe
- the Transmed at Mazara del Vallo from Algeria passing through Tunisia
- the Greenstream at Gela from Lybia
- 3 entry points of LNG regasification terminals in Panigaglia (La Spezia), Rovigo (Cavarzere) and Livorno

Domestic production (the largest deposits are located in the Adriatic Sea, in Puglia, in Calabria and in the Po valley) is instead fed into the grid through the entry points from the production fields or their collection centers, as well as the storage of gas. There are 53 entry points of the National Network into which national production is injected[1].

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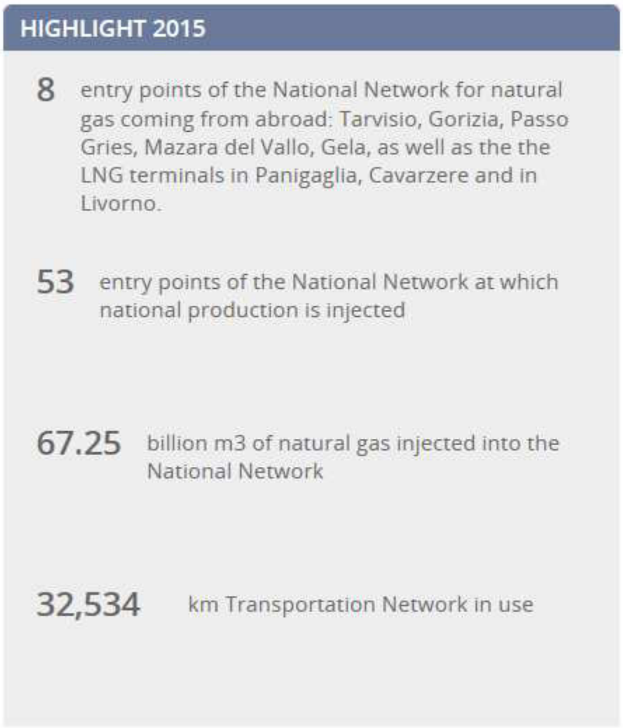
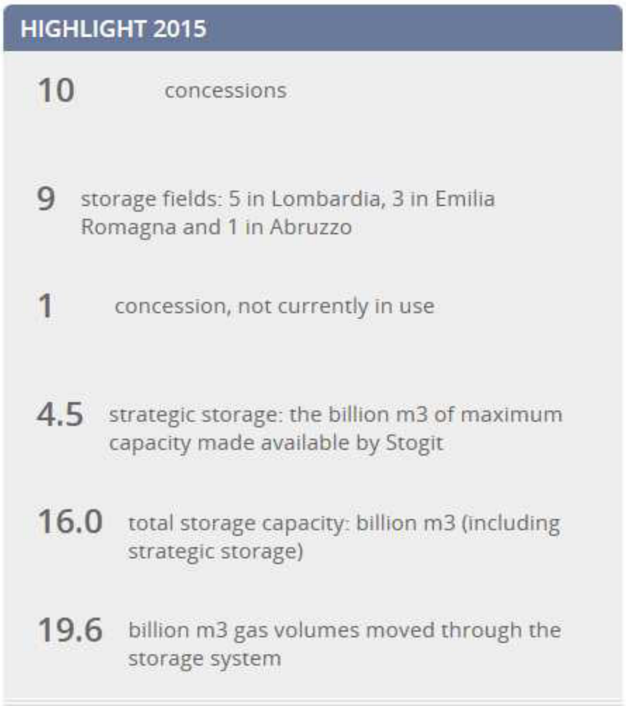
[1] Information collected from the SNAM web site



HIGHLIGHT 2015

8	entry points of the National Network for natural gas coming from abroad: Tarvisio, Gorizia, Passo Gries, Mazara del Vallo, Gela, as well as the the LNG terminals in Panigaglia, Cavarzere and in Livorno.
53	entry points of the National Network at which national production is injected
67.25	billion m3 of natural gas injected into the National Network
32,534	km Transportation Network in use

There are also 9 storage fields as shown below[2]:



HIGHLIGHT 2015

10	concessions
9	storage fields: 5 in Lombardia, 3 in Emilia Romagna and 1 in Abruzzo
1	concession, not currently in use
4.5	strategic storage: the billion m3 of maximum capacity made available by Stogit
16.0	total storage capacity: billion m3 (including strategic storage)
19.6	billion m3 gas volumes moved through the storage system

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[2] Information collected from the SNAM web site

The management of the gas storage system depends on the season: in the cold season natural gas is extracted from the fields while in the hot season, when the consumption is lower, it is injected in the fields.

Storage fields are depleted gas production reservoirs, located at average depths of between 1,000 and 1,500 meters below the surface.

Snam Rete Gas[3], the company that managed the national and regional network, operates 11 **Compressor Stations**, located along the National Network, which increase gas pressure in the pipelines up to the level required to ensure flow continuity. Compression stations compress natural gas received from the Transportation Network to make it possible to inject it into the reservoirs.

1. Centrale di Masera
2. Centrale di Malborghetto
3. Centrale di Istrana
4. Centrale di Poggio Renatico
5. Centrale di Terranuova
6. Centrale di Gallese
7. Centrale di Melizzano
8. Centrale di Montesano
9. Centrale di Tarsia
10. Centrale di Messina
11. Centrale di Enna

Once imported or regassified, gas is injected into the Transmission Network at the Entry Points in order to be transported to local distribution networks, to withdrawal points along the Regional Network, or to large final clients, either thermoelectric plants or industrial consumers.

The point of interconnection between the regional transport network, and the local distribution network (the secondary network, which measures a total of approximately 200,000 km) is the reduction and metering station (RE.MI. station) where the gas pressure is reduced, accounted and odorized.
After the REMI stations, the distribution network is at medium-pressure. Numerous final reduction stations are connected to decompress to a safe pressure for the domestic use. These cabins (called GRF, Gruppi di Riduzione Finale) then feed a low pressure distribution network to the individual meter of housing through the user connections.

In local distribution, there are 229 operators. Of these, the first 5 cover alone about 60% of the market.

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[3] Information collected from the SNAM web site

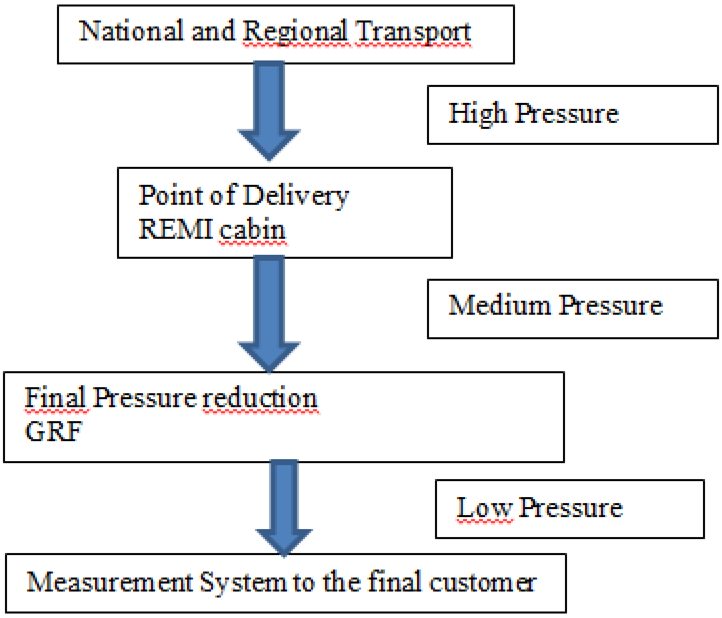
3. THE PRESSURE ALONG THE DISTRIBUTION NETWORK

The fire safety rules for accumulation and distribution of the use of natural gas with density not greater than 0.8 are approved in the decree DM24/11/84.
The following is the Classification of the pipeline according to the pressure:
a) Pipelines, 1° species: carried out to maximum pressure of more than 24 bar.
b) Pipelines, 2° Species: carried out to maximum pressure of over 12 bar and lower than or equal to 24 bar.
c) Pipelines 3° species: carried out to maximum pressure of over 5 bar and less than or equal to 12 bar.
d) Pipelines 4° Species: carried out to maximum pressure of over 1.5 bar and lower than or equal to 5 bar.
e) Pipelines 5° Species: carried out to maximum pressure of over 0.5 bars and less than or equal to 1.5 bar.
f) Pipelines 6° Species: pipelines for maximum operating pressure of more than 0.04 bars and less than or equal to 0.5 bar.
g) Pipelines 7° Species: carried out to maximum pressure lower or equal to 0.04 bar.

The Primary network, as described in the previous paragraph, is managed at High Pressure in the range **24-75 bar.**
The RE.MI (REgolazione e MIsura) cabin is a very important interface point between the national pipeline and the local distributor (which normally managed the REMI cabin).
In the REMI cabin the natural gas goes through the following steps:

- **Gas Filtration**: through a filtering system to ensure the interception of foreign bodies that could damage or cause malfunction of components and equipment installed downstream of the filter. The filter must be able to intercept particles larger than 5 microns (0.005 mm)
- **Preheating**: with the exception of the plants using pressures lower than 12 bar (1.2 MPa), the natural gas heating process is required and it is necessary to prevent excessive lowering of the product temperature from the reduction of pressure where the formation of ice could cause serious malfunction to the regulation apparatuses.
  In the reduction process, the gas loses about 0.7°C in temperature every bar of pressure.
- **Pressure regulation**: the part of the plant dedicated to the adjustment of the pressure is made up of all control and related accessories apparatuses. The regulations provide at least one emergency line able to guarantee the maximum flow rate.
- **Measure**: the fiscal measurement can be carried out in function of technical requirements both upstream and downstream of the adjustment groups.
- **Odorization**: in order to ensure the safe use of natural gas, the DM of 16 April 2008 according to the Law n. 1083 of December 6, 1971, requires the gas supply must be "odorized" to such an extent as to be perceived by human smell before reaching concentration levels which might result in dangerous conditions.
  The odorization process is regulated by different rules UNI 9463, 7132 and 7133 which provide guidance on the composition, properties, concentration, transport, use and storage.

For gases other than natural gas, the REMI station is the feed point into the distribution network.



After crossing the first reduction step (REMI), the natural gas has to undergo further pressure reductions, in order to ensure maximum safety during the transport to the end customer.
The plants that will ensure these further reductions are divided, as a function of the pressures upstream and downstream to the group, in three distinct types, for each of which the construction must be in compliance with the specific technical standards.

UNI number	Inlet Pressure (bar)	Outlet Pressure (bar)	Type of use
10619	Up to 12	No limitation	Industrial or similar
10619	Up to 12	Between 0.04 and 0.5	Medium Pressure Distribution,
10390	Between 5 and 12	Up to 0.04	Low Pressure Distribution. domestic
8827	Between 0.04 and 5	Up to 0.04	Low Pressure Distribution. domestic

Medium pressure (MP) is the pressure of natural gas, greater than 0.04 and less than or equal to 5 bar. Furthermore, according to the classification of the pipes as a function of operating pressure, there are specific standard "species": 4°, 5° and 6° species. The 6° species includes the values from 0.04 to 0.5 bar, the 5° from 0.5 to 1.5 bar, and the 4° from 1.5 to 5 bar. For security reasons and depending on the hydraulic conditions of the network, the distributor normally uses plants belonging to 5 ° or 6 ° species.

A further reduction of the pressure from Medium Pressure to Low Pressure BP (BP, Bassa Pressione), less than 40 mbar, typically 20 mbar, is necessary to ensure high safety levels.
The technical and safety requirements to be met are indicated by UNI:
◦UNI 8827 concerns the GRF control systems (Gruppi di Regolazione Finali) that feed the low pressure

pipelines up to the counter of the marketplace;
◦UNI 10619 provides guidelines for the construction of plants reduction that will feed directly from the network individually thermal power plants, industrial or artisanal users through GRM defined groups (Reduction and Measure Groups).

4. THE NATURAL GAS COMPOSITION

The chemical-physical characteristcs of the gas to be injected into the grid is regulated by the decree 19th February 2007 “Approval of the technical rule on physico-chemical characteristics and the presence of other components in the fuel gas to be conveyed”.
The following tables show the details of the composition and of the physical properties of natural gas:

Main Components

Component	Acceptable Limit	Unit of Measure
Methane	(*)	
Ethane	(*)	
Propane	(*)	
Iso-butane	(*)	
N-butane	(*)	
Iso-pentane	(*)	
N-pentane	(*)	
Esane and higher	(*)	
Nitrogen	(*)	
Oxygen	≤ 0.6	% mol
Carbon dioxide	≤ 3	% mol

(*) for these components the acceptable values are intrinsically limited by the acceptability range of the Wobbe Index

Trace Components

Component	Acceptable Limit	Unit of Measure
Hydrogen sulphide	≤ 6.6	mg/Sm^3
Mercaptans	≤ 15.5	mg/Sm^3
Total Sulphur	≤ 150	mg/Sm^3

Physical Properties

Property	Acceptable Limit	Unit of measure	Conditions
High Heating Value	34.95 – 45.28	MJ/Sm^3	
Wobbe index	47.31 – 52.33	MJ/Sm^3	
Relative density	0.5548 – 0.8		
Dew point of water	≤ -5	°C	At 7000K Pa
Dew point of hydrocarbons	≤ 0	°C	Between 100 – 7000 K Pa
Max. temperature	< 50	°C	
Min. temperature	> 3	°C	

Here below a table showing the average chemical composition (%) of the natural gas in the Italian grid depending on the source:

	National	Lybian	Russian	Dutch	Algerian
Methane	99.2	81.40	82.00	88.35	83.00
Ethane	0.40	9.40	3.20	4.30	7.50
Other Hydrocarbons	0.14	2.30	1.15	1.35	3.30
Carbon Dioxide	0.01	1.20	0.30	1.30	0.20
Nitrogen	0.25	0.50	3.30	4.20	6.00
Carbon Monoxide	-	0.20	-	-	-
Hydrogen	-	5.00	-	-	-

And the average physical parameters:

	unit	National	Lybian	Russian	Dutch	Algerian
Higher Heating Value	Kcal/Sm^3	9043	9534	9121	9054	9580
Lower Heating Value	Kcal/Sm^3	8144	8609	8227	8169	8662
Absolute density	Kg/Sm^3	0.68	0.75	0.74	0.76	0.81
Relative density		0.55	0.61	0.60	0.62	0.66
Cp	Kcal/Kg°C	0.52	0.5	0.49	0.48	0.47
V flame propagation	cm/sec	33.47	45.36	32.58	32.02	32.08

5. REGULATIONS FOR THE INJECTION OF BIOMETHANE INTO THE NATURAL GAS GRID

Italy is the third producer of biogas (after China and Germany) in the world with more than 1500 installations at the end of 2015 producing more than 2 billions m3 of biogas every year.
However there are only 6 installations involved in the generation of biomethane, 5 of them only for demonstrative purpose and not yet in operation that will handle flow rates in the range of 50-100 m3/h.
However the interest for these types of installation is growing and there are 20 new installations in the authorization phase capable to deliver 250-1000 m3/h each.
The conditions for the injection of Biomethane are regulated by UNI11537, April 2016 not yet released.
After its final approval, the document will be reviewed by the CEN/TC 408 Project Committee – Natural Gas and biomethane for use in transport and biomethane for injection in the natural gas grid.
The UNI document indicates the following chemical-physical characteristics:

Characteristic	Symbol	Value	Unit of measure
Higher Heating Value	HHV	$\geq 34,95 \leq 45,28$	MJ/Sm^3
Wobbe index	WI	$\geq 47,31 \leq 52,33$	MJ/Sm^3
Relative density	ρ	$\geq 0,5548 \leq 0,8$	-
Dew point of water $\leq$ - 5°C at 7 000 kPa			
Dew point of hydrocarbons $\leq$ 0 ° C in the pressure range from 100 kPa to 7000 kPa relative			
Oxygen content	O_2	$\leq 0,6$	%mol
Carbon dioxide content	CO_2	≤ 3	%mol
Hydrogen sulfide content	H_2S	$\leq 6,6$	mg/Sm^3
Content of sulphur and mercaptans	-	$\leq 15,5$	mg/Sm^3
Total sulphur content		≤ 150	mg/Sm^3

Characteristic	Symbol	Value	Unit of measure
Total Si content	Si	≤ 1	mg/Sm^3
Carbon monoxide content	CO	$\leq 0,1$	%mol
Ammonia content [a]	NH_3	≤ 10	mg/Sm^3
Ammines content [b]		≤ 10	mg/Sm^3
Hydrogen content	H_2	$\leq 0,5$	% Vol
Fluorine content [c]	F	< 3	mg/Sm^3
Chlorine content [c]	Cl	< 1	mg/Sm^3;
Compressor oil content [d]			
Powders [d]			

[a] If it is demonstrated the absence of liquid water in the biomethane it may be omitted the measurement of ammonia <u>only for the injection into the distribution network</u>

[b] If it is demonstrated the absence of liquid water in the biomethane it may be omitted the measurement of ammines <u>only for the injection into the distribution network</u>

[c] The limit values for F and Cl will be expressed by CEN in a subsequent CEN / TR currently being studied. The values shown here are considered prudent at the present state of knowledge

[d] Regarding the oil content from the compressor and powders, biomethane must be free of or does not exceed a minimum amount that render unacceptable biomethane for end users. This condition is fulfilled by the use of cartridge filters that retain 99% of the solid particles > 5 [µm] and 99% of liquid particles ≥ 10 [µm]. To maintain effective filtration capacity, equipment must be subject to periodical audits as prescribed in the UNI 10702 and UNI 9571-1 for applicable parts.

However the operating procedures to deliver biomethane into the Natural Gas grid have not been released yet.

6. INJECTION OF HYDROGEN INTO THE NATURAL GAS GRID

It is well known that renewable energy sources, solar and wind, could produce excess of energy. To avoid wasting the surplus of energy, there are studies to investigate the possibility to store the energy in batteries or to generate hydrogen by means of electrolyzers (Power to Gas, P2G).
Once hydrogen is generated it could be immediately used or stored; the biggest system to easily store hydrogen is the natural gas grid.
Studies on this matter have already been funded by the EU (for example the project NaturalHy) and are on going to understand the impact of the concentration of H2 into the natural gas grid. In fact there are applications where a high concentration of H2 can be an issue, for example:

- Methane used for cars; the metallic cylinders cannot accept H2 concentrations higher than 2%
- Domestic heaters could have problems to run with H2>2%

Being H2 a gas with chemical and physical properties well different from Natural Gas or Methane, its injection in the grid is rather critical.
For the time being, in Italy, only a few preliminary theoretical studies have been carried out by Politecnico di Milano, Energy Department.
This group has simulated the propagation of 5% H2 injection along the grid by changing the NG load. The impact of the main parameters is:

- Pressure drop: it is estimated that the impact of the presence of 5% H2 in NG on the pressure drop is negligible.
- Density: on the contrary the variation of the density due to the presence of H2 is significant and could have an impact on the management of the pipeline.
- Gas Velocity: the density reduction and the addition of H2 cause a small increase of the velocity
- the Higher Heating Value is affected by the presence of H2, the higher the H2 concentration the lower the HHV; the trend of the HHV versus time follows the H2 injection.
- Wobbe Index: the impact of H2 is rather complex because it determines two effects: first the increase of the compressibility factor and a decrease of the molecular weight of the mixture lead to a WI increase proportional to its square root; second the reduced HHV of the mixture generates a proportional reduction of the WI

More detailed information is available in the paper “Dynamic modeling of natural gas quality within transport pipelines in presence of hydrogen injections” prepared by Giulio Guandalini, Paolo Colbertaldo, Stefano Campanari; Applied Energy, March 2016.

The following figures show the impact of H2 presence on the Higher Heating value and on the Wobbe Index: the higher is the H2 concentration, the lower are both the Higher Heating Value and the Wobbe Index.

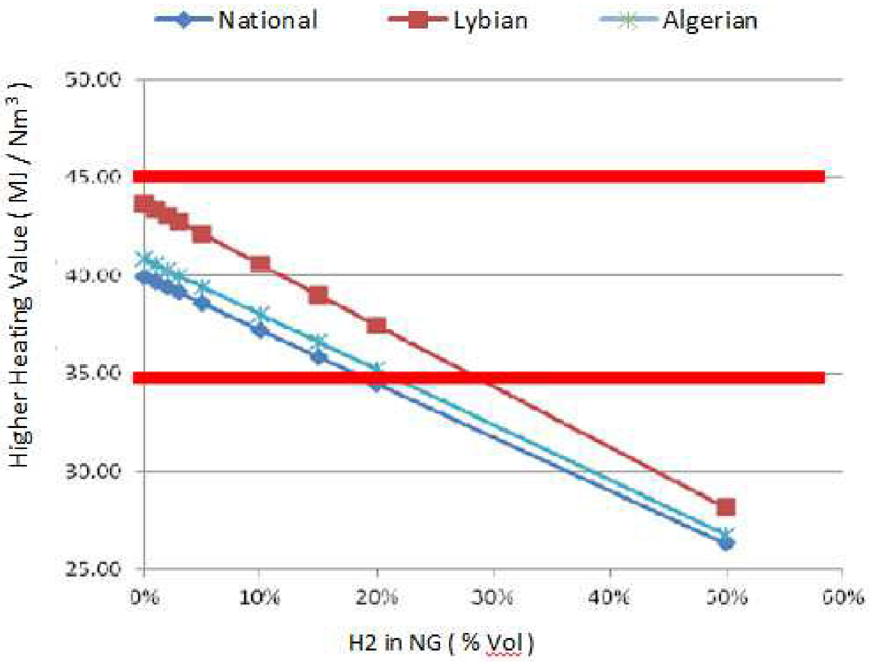


Figure 1. HHV vs. H2 concentration in Natural gas (adapted from “Power-to-gas” – Guandalini Giulio)

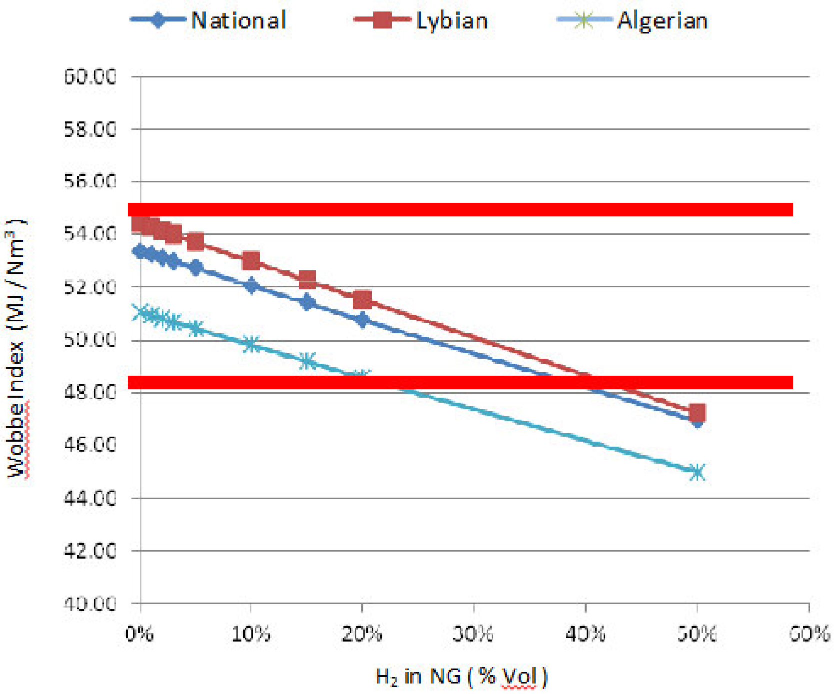


Figure 2. Wobbe Index vs. H2 concentration in Natural gas (adapted from “Power-to-gas” – Guandalini Giulio)

However, considering only these physical parameters, for concentrations up to 20% H2 in NG, both parameters remain within the acceptability threshold.

7. REFERENCES

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MEMO	
Company	EDP
For the attention of	Ángel María Gutiérrez Terrón
From	Marco Rep
Distribution	HyGrid Consortium
Date	23-6-2016
Document number	HYG-GRI-ME.001(2)
Subject	Hydrogen product specification
Pages	5

Dear Lucía,

Please find here the specs for hydrogen used in different applications (listed for fuel purposes, but not limited to fuel only):

Taken from:
Hydrogen fuel — Product specification ISO 14687:1999
Part 1: All applications except proton exchange membrane (PEM) fuel cell for road vehicles

Hydrogen fuel — Product specification ISO 14687-2:2012
Part 2: Proton exchange membrane (PEM) fuel cell applications for road vehicles

Hydrogen fuel — Product specification ISO/FDIS 14687-3:2013
Part 3: Proton exchange membrane (PEM) fuel cell applications for stationary appliances

Classification
Hydrogen fuel shall be classified according to the following types and grade designations:
a) Type I: Gaseous hydrogen
b) Type II: Liquid hydrogen
c) Type III: Slush hydrogen

Applications
Type I, grade A internal combustion engines/fuel cells for transportation; residential/commercial appliances;
Type I, grade B industrial fuel, for use e.g. in power generation or as a heat energy source;
Type I, grade C aircraft and space-vehicle ground support systems;
Type I, grade D gaseous hydrogen fuel for PEM fuel cell road vehicle systems;
Type I, grade E gaseous hydrogen fuel for PEM fuel cell stationary appliance systems.

Type II, grade C aircraft and space-vehicle on-board propulsion and electrical energy requirements; land vehicles;
Type II, grade D liquid hydrogen fuel for PEM fuel cell road vehicle systems.

Type III aircraft and space-vehicle on-board propulsion.

There is no equivalent grade A and B for Type II fuels.

As stated in the DoW, HyGrid will address not only fuel cell vehicles (type I grade D) but also stationary applications (type I grade A) and hydrogen fuelled ICE (type I grade E category 3). The following requirements are relevant with respect to the HyGrid project:

- The required hydrogen content varies from 98% (grade A) to over 99.9% (grades D and E).
- The humidity demands vary widely, i.e. from very dry (5 ppmv, grade D) to non-condensing (which may come down to more than 1% v/v of H_2O, grades A and E).
- The demands for hydrocarbon content are moderately to very strict: from 100 ppmv for grade A to 10 and 2 ppmv for grades D and E respectively.

Type I, grade A, B, C, Type II, grade C and Type III, which are applicable for all applications except PEM fuel cells applications, are defined in ISO 14687-1.

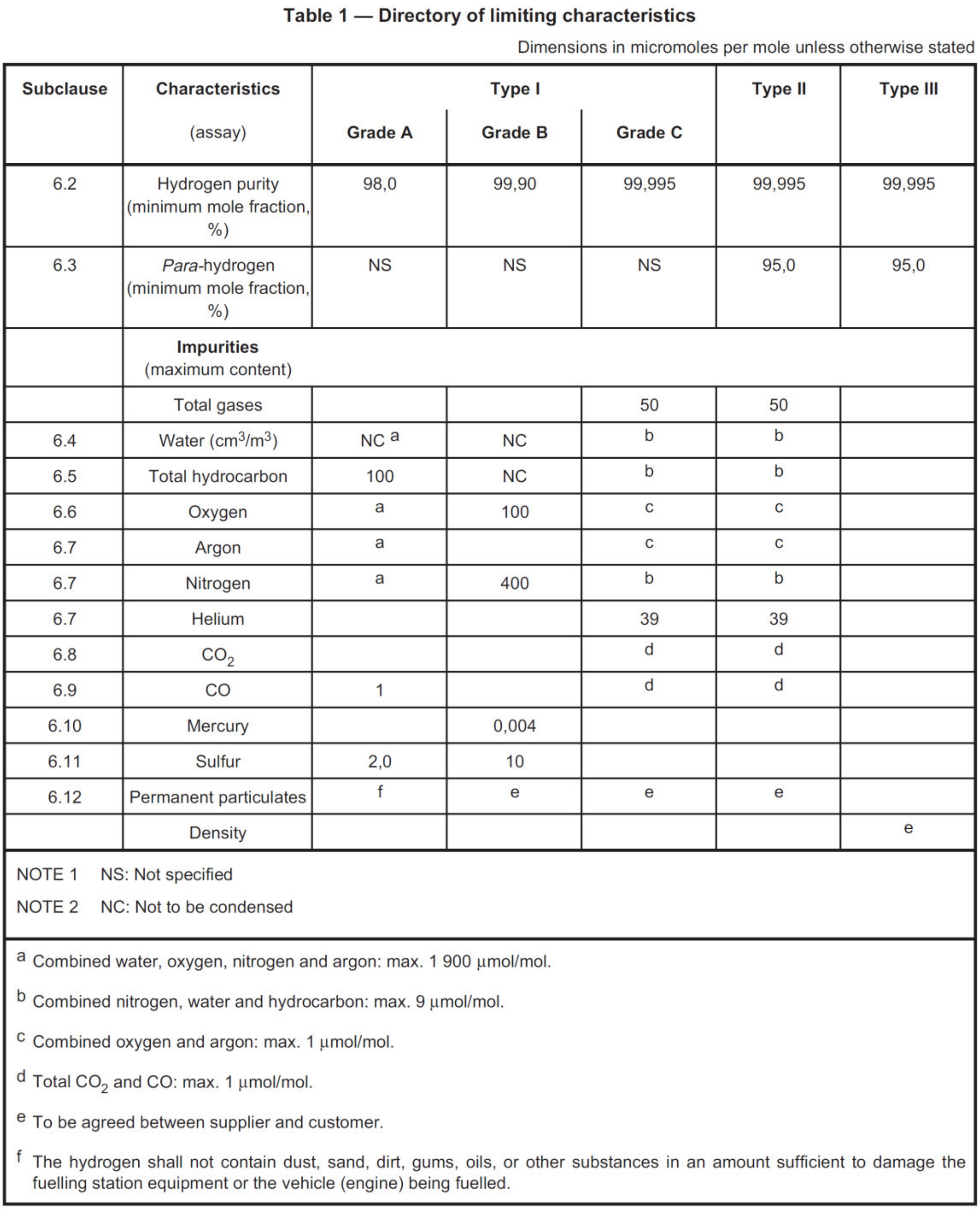

Table 1 — Directory of limiting characteristics

Dimensions in micromoles per mole unless otherwise stated

Subclause	Characteristics (assay)	Type I Grade A	 Grade B	 Grade C	Type II	Type III
6.2	Hydrogen purity (minimum mole fraction, %)	98,0	99,90	99,995	99,995	99,995
6.3	*Para*-hydrogen (minimum mole fraction, %)	NS	NS	NS	95,0	95,0
	Impurities (maximum content)					
	Total gases			50	50	
6.4	Water (cm^3/m^3)	NC [a]	NC	[b]	[b]	
6.5	Total hydrocarbon	100	NC	[b]	[b]	
6.6	Oxygen	[a]	100	[c]	[c]	
6.7	Argon	[a]		[c]	[c]	
6.7	Nitrogen	[a]	400	[b]	[b]	
6.7	Helium			39	39	
6.8	CO_2			[d]	[d]	
6.9	CO	1		[d]	[d]	
6.10	Mercury		0,004			
6.11	Sulfur	2,0	10			
6.12	Permanent particulates	[f]	[e]	[e]	[e]	
	Density					[e]

NOTE 1 NS: Not specified

NOTE 2 NC: Not to be condensed

[a] Combined water, oxygen, nitrogen and argon: max. 1 900 µmol/mol.

[b] Combined nitrogen, water and hydrocarbon: max. 9 µmol/mol.

[c] Combined oxygen and argon: max. 1 µmol/mol.

[d] Total CO_2 and CO: max. 1 µmol/mol.

[e] To be agreed between supplier and customer.

[f] The hydrogen shall not contain dust, sand, dirt, gums, oils, or other substances in an amount sufficient to damage the fuelling station equipment or the vehicle (engine) being fuelled.

Type I, grade D and Type II, grade D, which are applicable for PEM fuel cells for road vehicles are defined in ISO 14687-2.

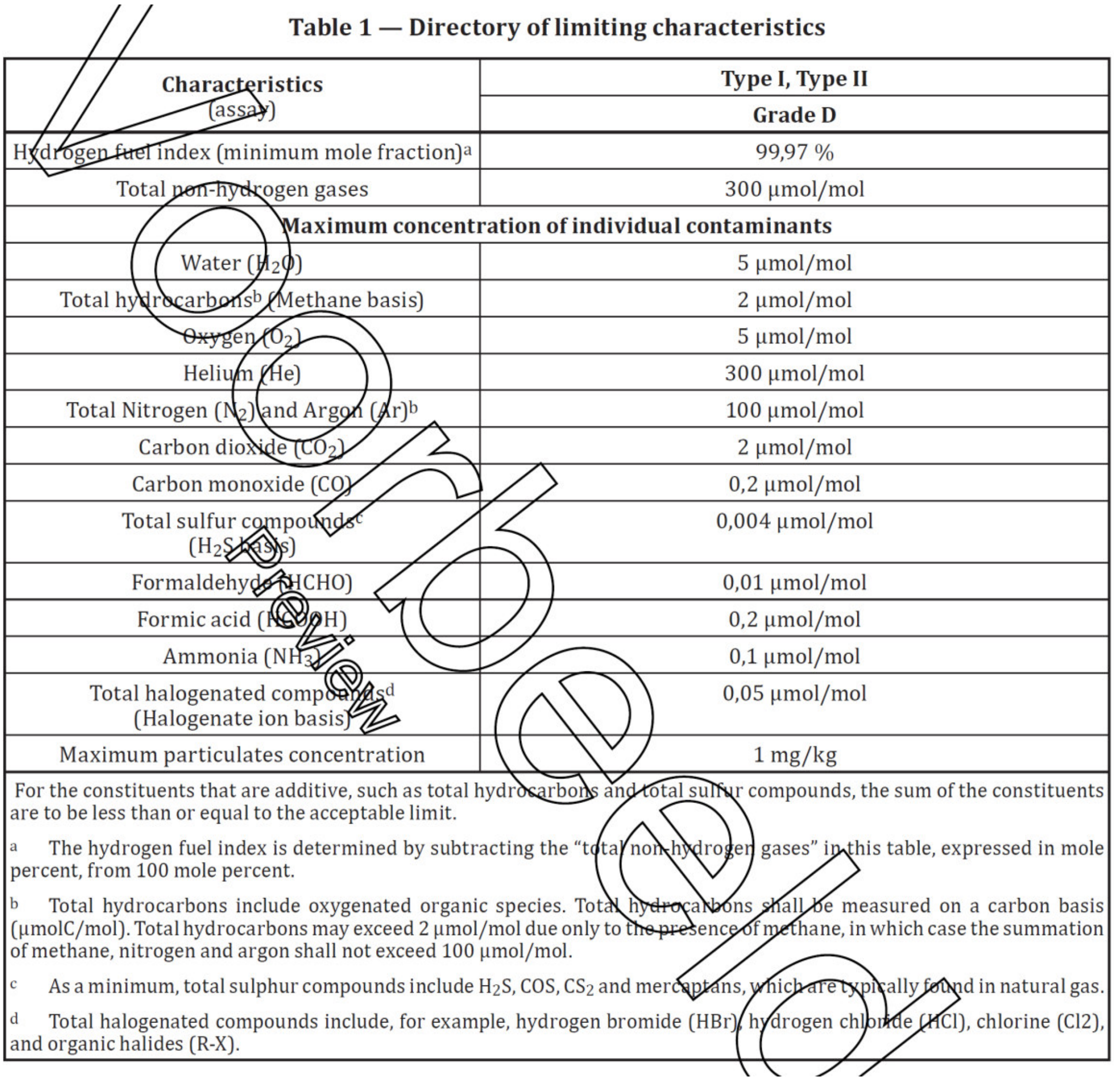

Table 1 — Directory of limiting characteristics

Characteristics (assay)	Type I, Type II
	Grade D
Hydrogen fuel index (minimum mole fraction)[a]	99,97 %
Total non-hydrogen gases	300 µmol/mol
Maximum concentration of individual contaminants	
Water (H_2O)	5 µmol/mol
Total hydrocarbons[b] (Methane basis)	2 µmol/mol
Oxygen (O_2)	5 µmol/mol
Helium (He)	300 µmol/mol
Total Nitrogen (N_2) and Argon (Ar)[b]	100 µmol/mol
Carbon dioxide (CO_2)	2 µmol/mol
Carbon monoxide (CO)	0,2 µmol/mol
Total sulfur compounds[c] (H_2S basis)	0,004 µmol/mol
Formaldehyde (HCHO)	0,01 µmol/mol
Formic acid (HCOOH)	0,2 µmol/mol
Ammonia (NH_3)	0,1 µmol/mol
Total halogenated compounds[d] (Halogenate ion basis)	0,05 µmol/mol
Maximum particulates concentration	1 mg/kg

For the constituents that are additive, such as total hydrocarbons and total sulfur compounds, the sum of the constituents are to be less than or equal to the acceptable limit.

[a] The hydrogen fuel index is determined by subtracting the "total non-hydrogen gases" in this table, expressed in mole percent, from 100 mole percent.

[b] Total hydrocarbons include oxygenated organic species. Total hydrocarbons shall be measured on a carbon basis (µmolC/mol). Total hydrocarbons may exceed 2 µmol/mol due only to the presence of methane, in which case the summation of methane, nitrogen and argon shall not exceed 100 µmol/mol.

[c] As a minimum, total sulphur compounds include H_2S, COS, CS_2 and mercaptans, which are typically found in natural gas.

[d] Total halogenated compounds include, for example, hydrogen bromide (HBr), hydrogen chloride (HCl), chlorine (Cl2), and organic halides (R-X).

Type I, grade E, which are applicable for PEM fuel cells cell applications for stationary appliances are addressed in ISO 14687-3.

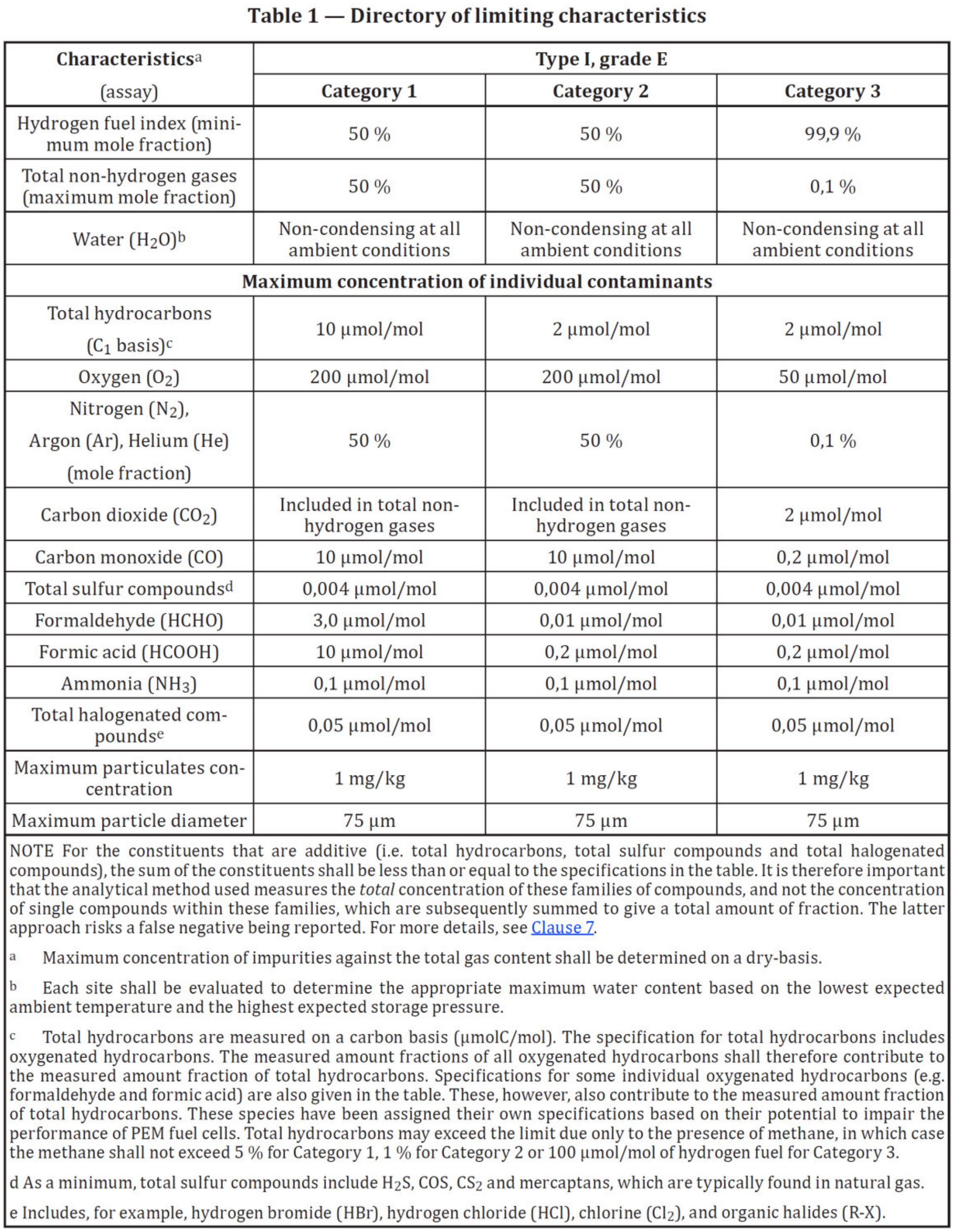

Table 1 — Directory of limiting characteristics

Characteristics[a] (assay)	Type I, grade E		
	Category 1	Category 2	Category 3
Hydrogen fuel index (minimum mole fraction)	50 %	50 %	99,9 %
Total non-hydrogen gases (maximum mole fraction)	50 %	50 %	0,1 %
Water (H_2O)[b]	Non-condensing at all ambient conditions	Non-condensing at all ambient conditions	Non-condensing at all ambient conditions
Maximum concentration of individual contaminants			
Total hydrocarbons (C_1 basis)[c]	10 µmol/mol	2 µmol/mol	2 µmol/mol
Oxygen (O_2)	200 µmol/mol	200 µmol/mol	50 µmol/mol
Nitrogen (N_2), Argon (Ar), Helium (He) (mole fraction)	50 %	50 %	0,1 %
Carbon dioxide (CO_2)	Included in total non-hydrogen gases	Included in total non-hydrogen gases	2 µmol/mol
Carbon monoxide (CO)	10 µmol/mol	10 µmol/mol	0,2 µmol/mol
Total sulfur compounds[d]	0,004 µmol/mol	0,004 µmol/mol	0,004 µmol/mol
Formaldehyde (HCHO)	3,0 µmol/mol	0,01 µmol/mol	0,01 µmol/mol
Formic acid (HCOOH)	10 µmol/mol	0,2 µmol/mol	0,2 µmol/mol
Ammonia (NH_3)	0,1 µmol/mol	0,1 µmol/mol	0,1 µmol/mol
Total halogenated compounds[e]	0,05 µmol/mol	0,05 µmol/mol	0,05 µmol/mol
Maximum particulates concentration	1 mg/kg	1 mg/kg	1 mg/kg
Maximum particle diameter	75 µm	75 µm	75 µm

NOTE For the constituents that are additive (i.e. total hydrocarbons, total sulfur compounds and total halogenated compounds), the sum of the constituents shall be less than or equal to the specifications in the table. It is therefore important that the analytical method used measures the *total* concentration of these families of compounds, and not the concentration of single compounds within these families, which are subsequently summed to give a total amount of fraction. The latter approach risks a false negative being reported. For more details, see Clause 7.

[a] Maximum concentration of impurities against the total gas content shall be determined on a dry-basis.

[b] Each site shall be evaluated to determine the appropriate maximum water content based on the lowest expected ambient temperature and the highest expected storage pressure.

[c] Total hydrocarbons are measured on a carbon basis (µmolC/mol). The specification for total hydrocarbons includes oxygenated hydrocarbons. The measured amount fractions of all oxygenated hydrocarbons shall therefore contribute to the measured amount fraction of total hydrocarbons. Specifications for some individual oxygenated hydrocarbons (e.g. formaldehyde and formic acid) are also given in the table. These, however, also contribute to the measured amount fraction of total hydrocarbons. These species have been assigned their own specifications based on their potential to impair the performance of PEM fuel cells. Total hydrocarbons may exceed the limit due only to the presence of methane, in which case the methane shall not exceed 5 % for Category 1, 1 % for Category 2 or 100 µmol/mol of hydrogen fuel for Category 3.

d As a minimum, total sulfur compounds include H_2S, COS, CS_2 and mercaptans, which are typically found in natural gas.

e Includes, for example, hydrogen bromide (HBr), hydrogen chloride (HCl), chlorine (Cl_2), and organic halides (R-X).

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MEMO	
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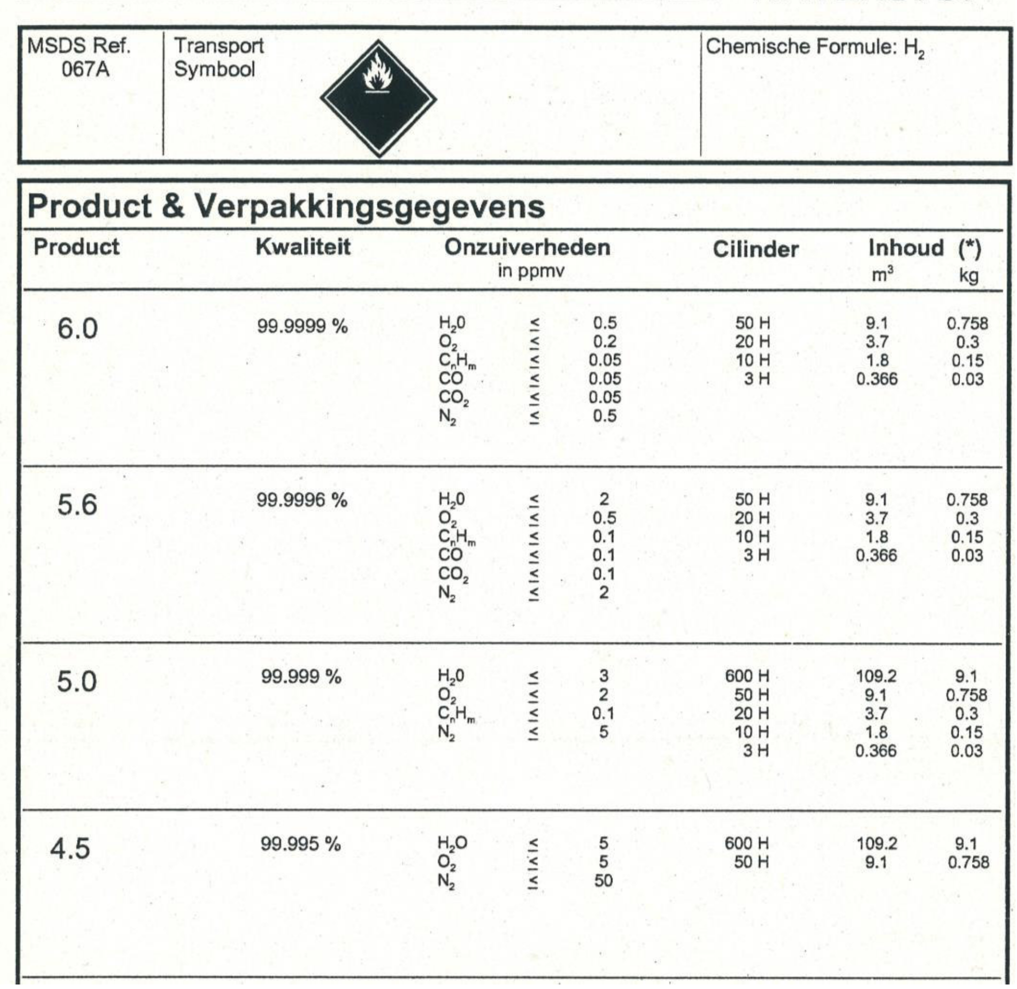
For the attention of	Ángel María Gutiérrez Terrón
From	Marco Rep
Distribution	HyGrid Consortium
Date	23-6-2016
Document number	HYG-GRI-ME.002(2)
Subject	Bottled hydrogen specification
Pages	2

Dear Lucia,

Please find here additional product qualities for bottled hydrogen (”waterstof” in Dutch) specifications (taken from Praxair).



WATERSTOF

MSDS Ref. 067A	Transport Symbool	Chemische Formule: H_2

Product & Verpakkingsgegevens

Product	Kwaliteit	Onzuiverheden in ppmv			Cilinder	Inhoud (*) m³	kg
6.0	99.9999 %	H_2O	≤	0.5	50 H	9.1	0.758
		O_2	≤	0.2	20 H	3.7	0.3
		C_nH_m	≤	0.05	10 H	1.8	0.15
		CO	≤	0.05	3 H	0.366	0.03
		CO_2	≤	0.05			
		N_2	≤	0.5			
5.6	99.9996 %	H_2O	≤	2	50 H	9.1	0.758
		O_2	≤	0.5	20 H	3.7	0.3
		C_nH_m	≤	0.1	10 H	1.8	0.15
		CO	≤	0.1	3 H	0.366	0.03
		CO_2	≤	0.1			
		N_2	≤	2			
5.0	99.999 %	H_2O	≤	3	600 H	109.2	9.1
		O_2	≤	2	50 H	9.1	0.758
		C_nH_m	≤	0.1	20 H	3.7	0.3
		N_2	≤	5	10 H	1.8	0.15
					3 H	0.366	0.03
4.5	99.995 %	H_2O	≤	5	600 H	109.2	9.1
		O_2	≤	5	50 H	9.1	0.758
		N_2	≤	50			

Column denotes:

- Kwaliteit = Quality
- Onzuiverheden = Impurities
- Cilinder = Cylinder
- Inhoud = Content

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MEMO	
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For the attention of	Ángel María Gutiérrez Terrón
From	Marco Rep
Distribution	HyGrid Consortium
Date	23-6-2016
Document number	HYG-GRI-ME.003(2)
Subject	Natural gas specifications The Netherlands
Pages	5

Dear Lucia,

In The Netherlands the gas network is divided in different operational pressures and owners;

HTL:
- Main transport line : high-pressure transmission lines
- Owner: Gasunie Transport Services (TSO)
- Operational pressure: $43 < p < 66$ bara (occasionally as high as 80 bar)
- H-gas or high calorific gas

RTL:
- Regional transmission lines
- Owner: Gasunie Transport Services (TSO)
- Operational pressure: $16 < p < 41$ bara
- G-gas or low calorific gas

RNB:
- Regional high pressure distribution grid
- Owner: Regional operator (DSO)
- Operational pressure: $1 < p < 4$ bara or $3 < p < 8$ bara
- G-gas or low calorific gas

RNB:
- Regional low pressure distribution grid
- Owner: Regional operator (DSO)
- Operational pressure: $40 < p < 100$ mbar
- G-gas or low calorific gas

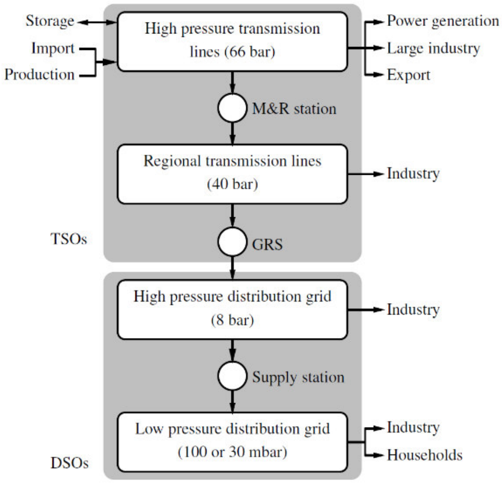

Fig. 1. Dutch gas grid supply chain

In The Netherlands approximately 80 large industrial consumers use H-gas or high calorific gas. All households and most businesses and buildings use G-gas [1] or low calorific gas.

The HTL grid that transports low-calorific gas delivers gas to the metering and regulating (M&R) stations, which reduce the gas pressure to approximately 40 bar and supply gas to several regional transmission lines (RTL) grids. The RTL grids transport the gas further into the country with a finer mesh of pipelines. The RTL grid delivers the gas to gas receiving stations (GRS), which reduce the gas pressure to 8 bar and supply gas to the high pressure distribution grids. The high pressure distribution grids transport the gas over longer distances and feed the gas

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[1] G-gas = Groningen gas

into the low pressure distribution grids via a supply station, which reduces the gas pressure to 100 mbar. The low pressure distribution grid supplies gas to households and smaller industry. At the entry points to homes the gas pressure is reduced to 30 mbar as most household appliances are designed to operate at approximately 30 mbar.

The map below shows the HTL transport lines, together with import and export connections.
Key:

- Transportation lines
    - yellow=H-gas, dark-grey=G-gas, light-grey=N2
- Import and export
    - Filled grey circles: feed points of gas into the grid
    - Circles with grey triangle: export station
    - Circles with letter L: storage of LNG
- Conversion
    - Half-filled grey circles: Underground storage
    - Circles with letter N: nitrogen injection stations (conversion of H to G gas)
    - Double circles: compressor stations
    - Bold grey circles: mixing stations
    - Control station (transfer to regional network; pressure reduction and odorisation)

From the website of Gasunie Transport Services a HR map can be downloaded showing both HTL and RTL gas grids and including locations of M&R stations, gas receiving stations etc.

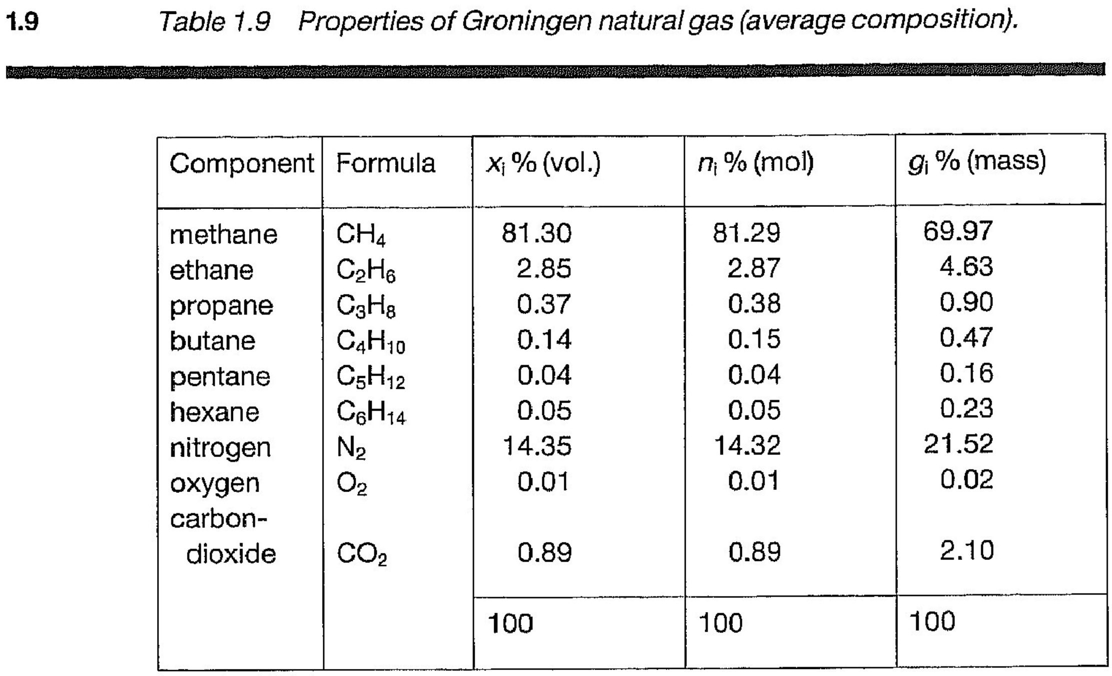
In below Table the gas quality requirement of G-gas is listed as fixed by the Dutch Government.

Gas quality		Value	Unit
Wobbe-index		43,46 – 44,41[1,2]	MJ/m^3(n)
Content higher hydrocarbons		≤ 5	mol% propane equivalent
Gas condensate		≤ 80	mg/m^3 (n) at −3 °C with every given pressure
Water dewpoint	in RTL and HTL	≤ −8	°C (at 70 bar(a))
	in RNB-net	≤ −10	°C (at 8 bar(a))
Temperature	in RTL and HTL	5 – 30	°C
	in RNB-net	5 – 20	°C
Oxygen content	in RTL and RNB-net	≤ 0,5	mol%
	in HTL	≤ 0,0005	mol%
Carbon dioxide content	in RTL and RNB-net	≤10,3	mol%
	in HTL	≤ 3	mol%
Hydrogen content	in RTL and HTL	≤ 0,02	mol%
	in RNB-net	≤ 0,5	mol%
Chlorine on basis of organo chlorine compounds		≤ 5	mg Cl/m^3(n)
Fluorine on basis of organo fluorine compounds		≤ 5	mg F /m^3(n)
Carbon monoxide (CO)		≤ 2.900	mg/m^3(n)
Pathogen microbes		≤ 500	aantal /m^3(n)
Dust particles with particle size > 5 µm		≤ 100	mg/m^3(n)
Sulfur content on basis of inorganic sulfur		≤ 5	mg S/m^3(n)
Sulfur content on basis of alkylthiols		≤ 6	mg S/m^3(n)
Total sulfur content	Before odorisation		
	Peak value	≤ 20	mg S/m^3(n)
	Year average	≤ 5,5	mg S/m^3(n)
	After odorisation		
	Peak value	≤ 31	mg S/m^3(n)
	Year average	≤ 16,5	mg S/m^3(n)
THT-content (odorant)	In HTL Flevoland, smellable gas	10 – 40	mg THT/m^3(n)
	in HTL: odorless gas	0	
	in RTL: smellable gas	10 – 40	mg THT/m^3(n)
	in RNB: smellable gas	10 – 40	mg THT/m^3(n)
Silicon content on basis of siliceous compounds		≤ 0,1	mg Si/m^3 (n)

The water dew point requirements correspond to about 44 ppmv H_2O for the RTL-HTL networks, and 325 ppmv H_2O for the RNB network.

It is allowed to feed in the RNB supply networks up to 0.5 mol% hydrogen gas to enable the addition of gas from sustainable sources. Both the HTL and RTL supply networks are not resistant towards higher concentrations hydrogen and thus the limit is set to 0.02 mol% hydrogen.

The general composition of G-gas is shown in next Table.



1.9 *Table 1.9 Properties of Groningen natural gas (average composition).*

Component	Formula	x_i % (vol.)	n_i % (mol)	g_i % (mass)
methane	CH_4	81.30	81.29	69.97
ethane	C_2H_6	2.85	2.87	4.63
propane	C_3H_8	0.37	0.38	0.90
butane	C_4H_{10}	0.14	0.15	0.47
pentane	C_5H_{12}	0.04	0.04	0.16
hexane	C_6H_{14}	0.05	0.05	0.23
nitrogen	N_2	14.35	14.32	21.52
oxygen	O_2	0.01	0.01	0.02
carbon-dioxide	CO_2	0.89	0.89	2.10
		100	100	100

Sources:
https://www.gasunietransportservices.nl/downloads-en-formulieren
http://wetten.overheid.nl/BWBR0035367/2016-04-01
http://www.rvo.nl/onderwerpen/duurzaam-ondernemen/energie-en-milieu-innovaties/projectbureau-nieuw-aardgas/
https://www.utwente.nl/ctw/opm/research/pm/research/publications/development_options_for_the_dutch_gas_distribution.pdf
http://eduweb.eeni.tbm.tudelft.nl/TB141E/?aardgas-transport
Physical Properties of Natural Gases, NV Nederlandse Gasunie, June 1988.

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MEMO	
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For the attention of	Ángel María Gutiérrez Terrón
From	Marco Rep
Distribution	HyGrid Consortium
Date	28-6-2016
Document number	HYG-GRI-ME.004(2)
Subject	Green gas specifications The Netherlands
Pages	3

Dear Lucia,

Upgrading crude biogas to natural gas quality guarantees the safety and integrity of the grid and end-users equipment. Green gas (renewable gas) is Bio-SNG, Biogas or Landfill gas which is upgraded to natural gas quality and must therefore meet the ‘Additional requirements for green gas injection into the regional gas grid,’ a set of requirements developed by the collective of Dutch grid operators together with biogas producers and is published in the Dutch official state papers [1]. These requirements are fixed to safeguard the interests of both producers and consumers of natural gas in The Netherlands.

Please find in below Table the gas quality requirement of green gas in The Netherlands. It may be noted that the allowed hydrogen content amounts to 12%, *i.e.*, substantially higher than the specification for natural gas.

In the Netherlands, producers of biogas have the option to upgrade biogas to green gas (with the quality equivalent to that of natural gas) and inject it either into the distribution grid at the maximum pressure of 8 bar, or into the transmission grid at the pressure of 40 to 80 bar. Most green gas producers choose to inject their gas into a distribution grid. This is due to

1) lower CAPEX costs:
    a. distribution grid located as close to the production facility as possible (to reduce the length of the pipeline connecting this facility to the distribution grid and hence the costs);
    b. different pipeline connection specifications (transmission grid operator’s requirements regarding the pipelines materials, diameter, length etc. which necessitate a larger investment in comparison to the requirements of the distribution grid operators),
    c. less stringent pressure demands on compressor.
2) lower OPEX costs:
    a. these are fully borne by the producer in the Netherlands (from 0 to max. 8 bar for the distribution grid are significantly lower in this case, compared to from 0 to 40 bar for the transmission grid).

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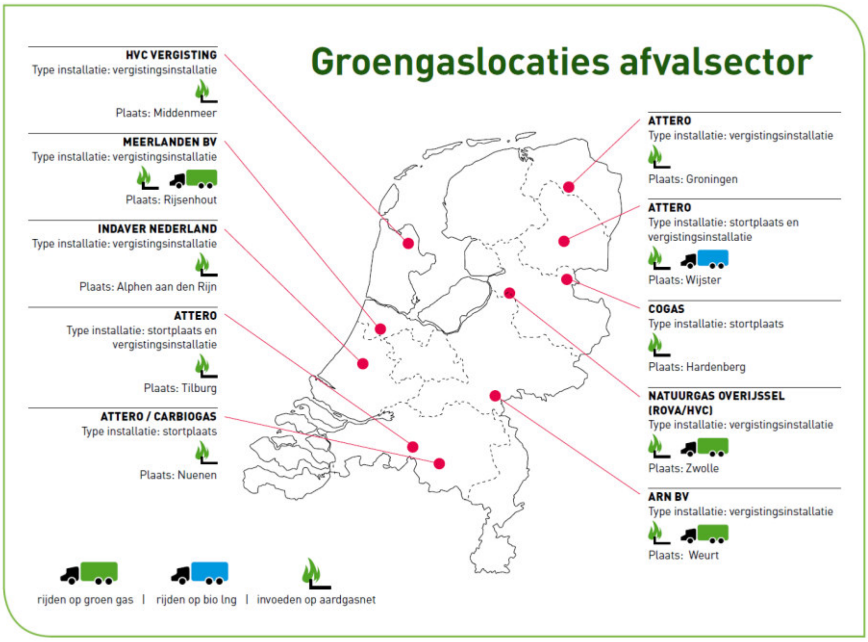
[1] *Staatscourant*, Nr. 21503 May 11, 2016, source: http://wetten.overheid.nl/BWBR0037926/2016-05-12

Quality component	Conform advice Gastec	
	Limit	Unit
Fysical properties		
Calorific upper value	31,6 – 38,7	MJ/m^3_n
Wobbe-index	43,46-44,41	MJ/nm^3
Other properties		
Water dew point	–10(8 bar)	°C
Temperature (in te voeden gas)	0 – 20	°C
Sulfur (total)	45	mg/m^3_n
Inorganic bound sulfur (H_2S)	5	mg/m^3_n
Mercaptanes	10	mg/m^3_n
Odorant content (THT)	> 10, nom 18<40	mg/m^3_n
Ammoniac	3	mg/m^3_n
Organo chlorine compounds	50	mg/m^3_n
Organo fluorine compounds	25	mg/m^3_n
Hydrogen chloride (HCl)	1	Ppm
Hydrogen cyanide (HCN)	10	Ppm
Carbon monoxide (CO)	1	Mol%
Carbon dioxide in dry gas grids (CO_2)	6	Mol%
BTX (benzene, toluene, xylene)	500	Ppm
Aromatic hydrocarbons	1	Mol%
oxygen in dry gas grids	0,5 (3)	mol%
Hydrogen	12	vol%/ m^3_n
Methane number [1]	> 80	–
Dust	Technical free	–
Siloxanes	5	Ppm
Smellability (odorised biogas)	Sufficient	–

[1] Important when relatively high content of H_2 and/or C_3H_8 (causes low Methane number)

In April 2013, 21 production locations for green gas were operating in the Netherlands, with an overall production capacity of 11900 Nm^3/hour; annual production approximately 90 million Nm^3/year [2]. The map below shows the main green gas production sites in the Netherlands [3].



Best regards,
Marco

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[2] Green-Gas-Grids: State of affairs on Biomethane in the Netherlands – National Roadmap, 2013, available at http://www.greengasgrids.eu/fileadmin/greengas/media/Markets/Roadmaps/D4.1_Roadmap_Netherlands_english.pdf

[3] Meer groen gas uit afval, Vereniging Afvalbedrijven, juni 2014, available at http://www.verenigingafvalbedrijven.nl/nieuws/nieuwsbericht/meer-groen-gas-uit-afval.html

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From	Marco Rep
Distribution	HyGrid Consortium
Date	8-7-2016
Document number	HYG-GRI-ME.005(2)
Subject	Upgrading technologies biogas
Pages	10

Dear Lucia,

Upgrading of biogas focusses on the removal of CO_2, in order to increase the caloric value of the gas. In addition, other components that are present in lower concentrations have to be removed, such as sulphur (in the form of H_2S), siloxanes, oxygen etc. The gas often also has to be dried. The following technologies for biogas to green gas are commonly applied:

- Pressure Swing Adsorption [1]
- Water scrubbing
- Organic physical scrubbing
- Amine scrubbing
- Membrane technology

Most of the mentioned technologies have to deal with methane losses through off-gases, which may pose a problem if the off-gas is to be vented to the atmosphere.

Next common technologies are applied to separate hydrogen from biogas:

- Pressure Swing Adsorption [1]
- Low temperature membrane separation
- High temperature membrane separation (under investigation)

Several more technologies are under investigation, however, their status is yet unclear.

Next pages show overview tables of technologies applied (and/or under investigation) for upgrading of biogas to green gas (Tables 1 and 2) or separation of hydrogen from biogas (Table 3 and Table 4). Table 4 is specifically addressed to membrane separation technology. Also comprehensive descriptions of technologies are presented in the next pages.

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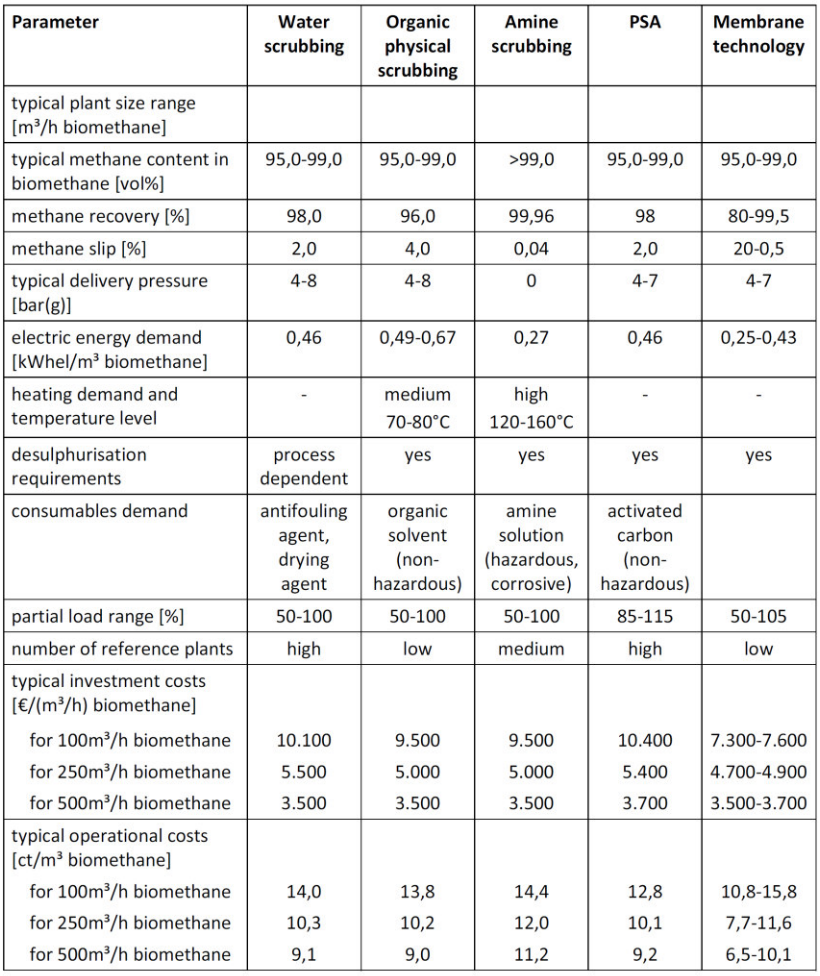
[1] Pressure Swing Asorption includes PSA, VSA and VPSA

In the next Table a comprehensive overview (and comparison) of the different upgrading technologies for biogas to green gas is presented [2].

Table 1: Comprehensive overview of the different upgrading technologies for biogas to green gas



Parameter	Water scrubbing	Organic physical scrubbing	Amine scrubbing	PSA	Membrane technology
typical plant size range [m³/h biomethane]					
typical methane content in biomethane [vol%]	95,0-99,0	95,0-99,0	>99,0	95,0-99,0	95,0-99,0
methane recovery [%]	98,0	96,0	99,96	98	80-99,5
methane slip [%]	2,0	4,0	0,04	2,0	20-0,5
typical delivery pressure [bar(g)]	4-8	4-8	0	4-7	4-7
electric energy demand [kWhel/m³ biomethane]	0,46	0,49-0,67	0,27	0,46	0,25-0,43
heating demand and temperature level	-	medium 70-80°C	high 120-160°C	-	-
desulphurisation requirements	process dependent	yes	yes	yes	yes
consumables demand	antifouling agent, drying agent	organic solvent (non-hazardous)	amine solution (hazardous, corrosive)	activated carbon (non-hazardous)	
partial load range [%]	50-100	50-100	50-100	85-115	50-105
number of reference plants	high	low	medium	high	low
typical investment costs [€/(m³/h) biomethane]					
for 100m³/h biomethane	10.100	9.500	9.500	10.400	7.300-7.600
for 250m³/h biomethane	5.500	5.000	5.000	5.400	4.700-4.900
for 500m³/h biomethane	3.500	3.500	3.500	3.700	3.500-3.700
typical operational costs [ct/m³ biomethane]					
for 100m³/h biomethane	14,0	13,8	14,4	12,8	10,8-15,8
for 250m³/h biomethane	10,3	10,2	12,0	10,1	7,7-11,6
for 500m³/h biomethane	9,1	9,0	11,2	9,2	6,5-10,1

The comprehensive descriptions of technologies are presented in the next pages [3,4,5].

Pressure swing adsorption

With this technique, carbon dioxide is separated from the biogas by adsorption, usually under elevated pressure. The adsorbing material, usually activated carbon or zeolites, is able to selectively retain some compounds of a mixture. In general carbon dioxide (CO_2) is adsorbed much more strongly than methane, enabling its removal from the biogas. The adsorbing material is regenerated by a sequential decrease in pressure before the column is reloaded again, hence the name of the technique. The efficiency of the process depends on temperature, pressure and the type of adsorbent,

An upgrading plant, using this technique, has four, six or nine vessels working in parallel, and each is equipped with a number of valves for the vessel interconnections, feed-, product- and off-gas lines. The pressure in the columns changes cyclically. One cycle usually has four basic steps: pressure build-up, adsorption, depressurization and regeneration. CO_2 from the raw biogas is captured in the adsorbent; when the adsorbing material in one vessel becomes

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[2] Biogas to Biomethane Technology Review, Contract Nr.: IEE/10/130, Del. Ref. Task 3.1.1, Vienna University of Technology, May 2012.

[3] Biogas upgrading, A. Petersson, A. Wellinger, Task 37, IEA BioEnergy, October 2009.

[4] Biogas Upgrading Technologies: State of Art Review in European Region, Jakub Niesner, David Jecha, Petr Stehl, *Chemical Engineering Transactions*, **Vol. 35**, 2013, 517-522 DOI:10.3303/CET1335086.

[5] Biogas and bio-syngas upgrading, Bailón Allegue, L. and Hinge, J., Danish Technological Institute, December 2012.

saturated the raw gas flow is switched to another vessel in which the adsorbing material has been regenerated. During regeneration the pressure is decreased in several steps. The gas that is desorbed during the first and possibly the second pressure drop may be sent to one of the other vessels, since it will contain some methane that was adsorbed together with CO_2. The gas desorbed in the following pressure reduction step, consisting largely of desorbed CO_2, is either led to the next column or if it is almost entirely methane free it is released to the atmosphere.
If hydrogen sulphide (H_2S)is present in the raw gas, it will be irreversibly adsorbed on the adsorbing material. In addition, water present in the raw gas can destroy the structure of the material. Therefore hydrogen sulphide and water needs to be removed before the PSA-column.
Maximum CH_4 yield is reportedly about 91 %, while a typical value of the CH_4 purity is 98 %.
Data gained from IEA indicate that PSA is used for wide range of biogas flow rate except high flow rates above 2,000 Nm^3/h.
PSA also enables to remove N_2 and O_2. Moreover PSA is also applied for cleaning and upgrading of hydrogen. Hydrogen hardly adsorbs on usual adsorbent materials allowing removal of most contaminants.

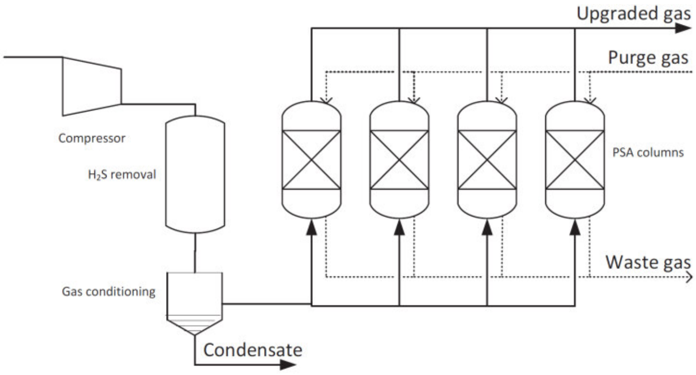


Figure 1: Process diagram for upgrading of biogas with PSA.

Water scrubbing

Water scrubbing represents a process based on physical absorption, employing water as a solvent for dissolving CO_2. Carbon dioxide has a higher solubility in water than methane, and will therefore be dissolved to a higher extent than methane, particularly at lower temperatures. In the scrubber column carbon dioxide is dissolved in the water, while the methane concentration in the gas phase increases. The gas leaving the scrubber has therefore an increased concentration of methane.
The water scrubbing process is usually carried out in a packed absorption column. Biogas is introduced at the bottom of the column and flows up. Water enters the column at the top and flows downward, so that mass transfer occurs in a counter-flow way. Purified biogas (biomethane) leaves the column at the top and water saturated with CO_2 is let out at the bottom. The scrubbed water stream is either regenerated in a desorption column and reused for absorption, or the water is used only for once in a single pass system. The system without recirculation can be suitable for plants with low cost water (e.g. waste water treatment facility). CO2 is released into atmosphere as an off-gas in case of water recirculation system or stays in the water in case of a single pass system.
In both cases, the water leaving the absorption column is transferred to a flash tank where the dissolved gas, which contains some methane but mainly CO_2, is released and transferred back to the raw gas inlet. If the water should be recycled it is transferred to a desorption column filled with plastic packing, where it meets a counter flow of air, into which carbon dioxide will be released. The water is cooled down to achieve the large difference in solubility between methane and carbon dioxide before it is recycled back to the absorption column.
Water scrubbing is the most common upgrading technique and plants are commercially available from several suppliers in a broad range of capacities. Data gained from IEA indicate that water scrubbing is used for a wide range of biogas flow rates, although the most preferred category belongs to higher flow rates of 500-2,000 Nm^3/h. The range of operating pressure is 6-12 bar. Maximum CH_4 yield is reportedly about 94 %. A typical value for the CH_4 purity is around 98%. Water scrubbing also enables to remove H_2S simultaneously, hence pretreatment for H_2S is not necessary. However, it is suitable to treat H_2S and also CO_2 after scrubbing.

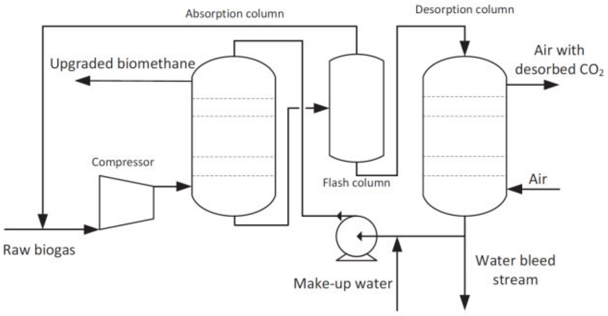


Figure 2: Schematic illustration of a water scrubber.

Organic physical scrubbing

Organic physical scrubbing is very similar to water scrubbing, with the important difference that the carbon dioxide is absorbed in an organic solvent such as polyethylene glycol. Carbon dioxide is more soluble in polyethylene glycol than in water and for the same upgrading capacity the flow of the liquid phase can be lower and so the plant can be smaller. The polyethylene glycol solution is regenerated by heating and/or depressurizing. Hydrogen sulphide, water, oxygen and nitrogen may be removed together with carbon dioxide. However, more often they are removed prior to upgrading. Selexol®, Rectosol® and Genosorb® are examples of trade names for liquids used in organic physical scrubbing.

The technological arrangement of organic physical scrubbing systems is similar to those for chemical scrubbing. The regeneration of the solvent is performed at higher temperature and energy demand than water scrubbing, but lower than chemical scrubbing. Pretreatment of H_2S is not required. Operating pressure is 7 - 8 bar. Maximum CH_4 yield is reportedly about 90 %. A typical value for the CH_4 purity is 93 - 98%. Data gained from IEA indicate that organic physical scrubbing is used primarily for higher flow rates (500-2,000 Nm^3/h).

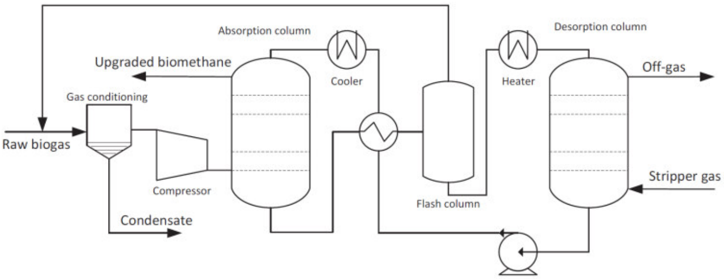


Figure 3: A simplified process flow diagram of a typical organic physical scrubbing process.

Chemical scrubbing

Chemical scrubbing, like water scrubbing, is based on dissolving CO_2 from biogas in a solvent, which in this case usually consists of an amine solution. However, the carbon dioxide is not only absorbed in the liquid, but also reacts chemically with the amine in the liquid. Consequently, the solvent can dissolve considerably much more CO_2 per unit volume in comparison to water. Since the chemical reaction is strongly selective, the methane loss might be as low as <0.1%. Part of the liquid is lost due to evaporation, and has to be replaced. The liquid in which carbon dioxide is chemically bound is regenerated by heating. The most employed solvents are monoethanolamine (MEA), diethanolamine (DEA) or diglycolamine (DGA). The technological arrangement of chemical scrubbers is similar to water scrubbers with regeneration. However, the regeneration of the solvent is performed at significantly higher temperature and energy demand.

If H_2S is present in the raw gas, it will be absorbed in the amine scrubber solution and higher temperatures will be needed for the regeneration. Therefore it is advisable to remove it before absorption in the amine scrubber.

Operating pressure is around 1 atm. Maximum CH_4 yield is reportedly about 90%. A typical value of the CH_4 purity is 99 %. Data gained from IEA indicate that chemical scrubbing is used for wide range of biogas flow rates, although the most preferred category belongs to medium flow rates of 500–1,000 Nm^3/h.

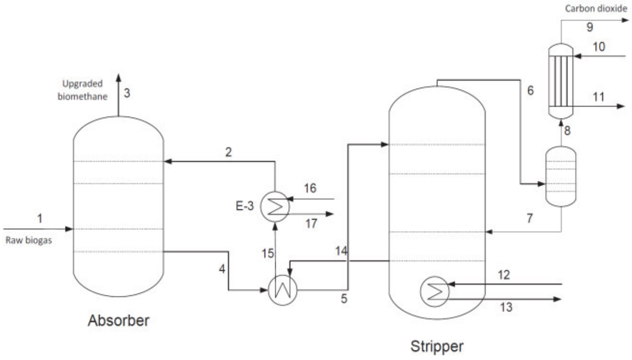


Figure 4: Simplified process flow diagram of an amine scrubber for biogas upgrading.

Membrane separation

Membrane separation is based on the selectivity of a membrane that allows different compounds to pass through at different rates. The mixture is split into two streams, the permeate fraction (compounds transferring through the membrane) and the retentate fraction (compounds passing by). In the case of biogas, the permeate consists mainly of CO_2 while the retentate consists mainly of CH_4.

Membranes can be made of polymers like silicone rubber or cellulose acetate. Another group of materials comprise polyimide or liquid membranes. Dry membranes for biogas upgrading are permeable to carbon dioxide, water and ammonia. Hydrogen sulphide, and oxygen permeate through the membrane to some extent while nitrogen and methane only pass to a very low extent. Usually membranes are in the form of hollow fibres bundled together. The process is often performed in two stages. Before the gas enters the hollow fibres it passes through a filter that retains water and oil droplets and aerosols, which would otherwise negatively affect the membrane performance. Additionally, hydrogen sulphide is usually removed by cleaning with activated carbon before the membrane.

There are two types of membrane systems: (1) high pressure, which employs gas flow both in permeate and retentate and (2) low pressure, which employs gas on the retentate side and liquid on the permeate side. Range of operating pressure is for high pressure systems 20-36 bar, for low pressure systems around 1 atm. Membrane separation is one of the classical methods for landfill gas upgrading. The first plants were built in the late 1970's in the US and later in the Netherlands. However, the early designs operating at elevated pressures (up to 30 bars) suffered from considerable methane losses (up to 25%). Newer designs operate around 8 bars with far lower methane losses.

Maximum CH_4 yield is reportedly about 78%. A typical value of the CH_4 purity is 90 - 97 %. This rather low performance of membrane separation (CH_4 purity and recovery) is obtained in single stage systems. But multistage systems can achieve better performance results (CH_4 purity 99 %, recovery 99.5 %) and therefore they are mandatory. Data gained from IEA indicate that membrane separation is used for low and medium flow rates, especially less than 300 Nm^3/h.

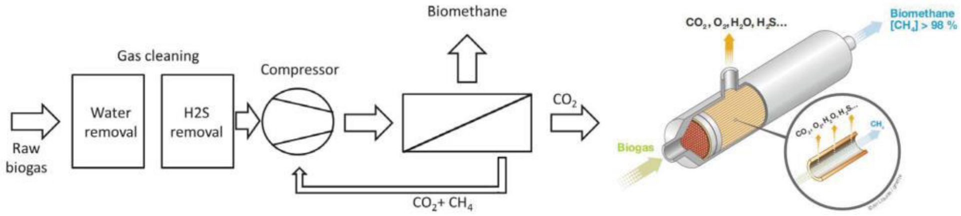
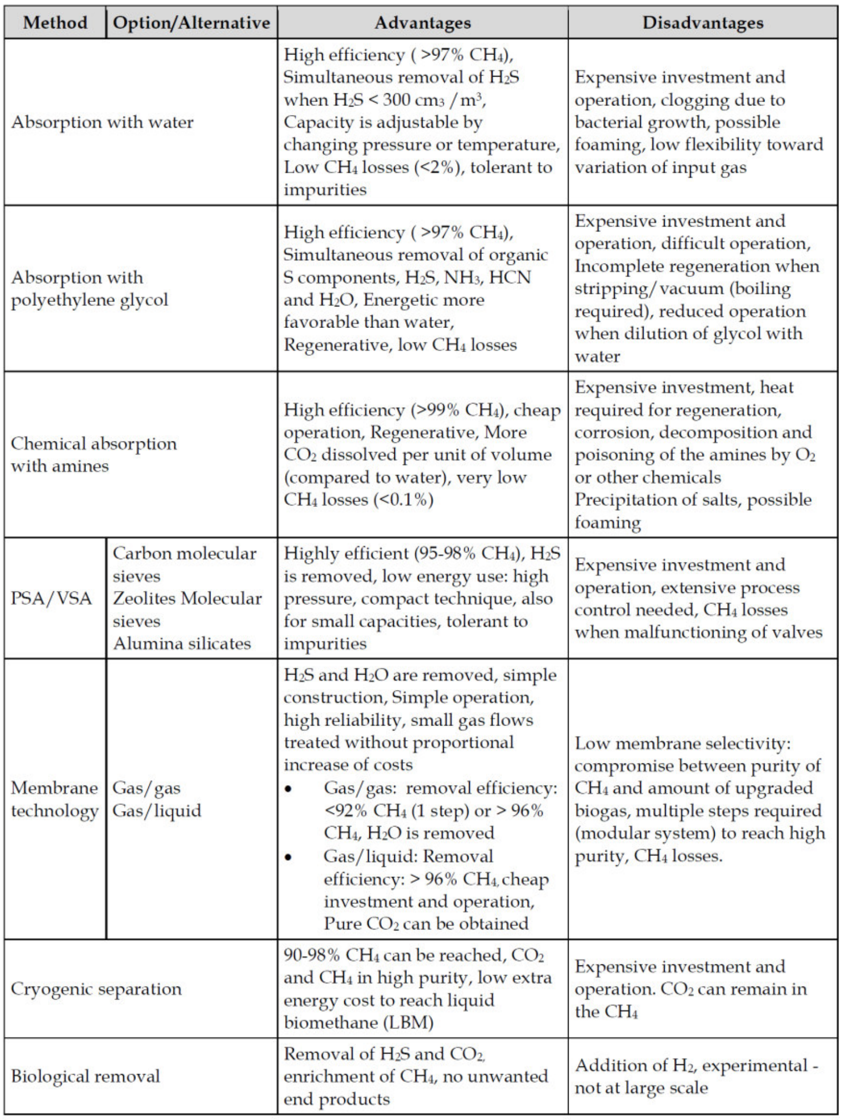


Figure 5: Typical design of a biogas upgrading unit with membranes.

In the next Table the advantages and disadvantages of the different upgrading technologies mentioned for biogas to green gas are listed [6].

Table 2: (Dis-)advantages of several upgrading technologies for biogas to green gas



Method	Option/Alternative	Advantages	Disadvantages
Absorption with water		High efficiency (>97% CH_4), Simultaneous removal of H_2S when H_2S < 300 cm_3 / m^3, Capacity is adjustable by changing pressure or temperature, Low CH_4 losses (<2%), tolerant to impurities	Expensive investment and operation, clogging due to bacterial growth, possible foaming, low flexibility toward variation of input gas
Absorption with polyethylene glycol		High efficiency (>97% CH_4), Simultaneous removal of organic S components, H_2S, NH_3, HCN and H_2O, Energetic more favorable than water, Regenerative, low CH_4 losses	Expensive investment and operation, difficult operation, Incomplete regeneration when stripping/vacuum (boiling required), reduced operation when dilution of glycol with water
Chemical absorption with amines		High efficiency (>99% CH_4), cheap operation, Regenerative, More CO_2 dissolved per unit of volume (compared to water), very low CH_4 losses (<0.1%)	Expensive investment, heat required for regeneration, corrosion, decomposition and poisoning of the amines by O_2 or other chemicals Precipitation of salts, possible foaming
PSA/VSA	Carbon molecular sieves Zeolites Molecular sieves Alumina silicates	Highly efficient (95-98% CH_4), H_2S is removed, low energy use: high pressure, compact technique, also for small capacities, tolerant to impurities	Expensive investment and operation, extensive process control needed, CH_4 losses when malfunctioning of valves
Membrane technology	Gas/gas Gas/liquid	H_2S and H_2O are removed, simple construction, Simple operation, high reliability, small gas flows treated without proportional increase of costs • Gas/gas: removal efficiency: <92% CH_4 (1 step) or > 96% CH_4, H_2O is removed • Gas/liquid: Removal efficiency: > 96% CH_4, cheap investment and operation, Pure CO_2 can be obtained	Low membrane selectivity: compromise between purity of CH_4 and amount of upgraded biogas, multiple steps required (modular system) to reach high purity, CH_4 losses.
Cryogenic separation		90-98% CH_4 can be reached, CO_2 and CH_4 in high purity, low extra energy cost to reach liquid biomethane (LBM)	Expensive investment and operation. CO_2 can remain in the CH_4
Biological removal		Removal of H_2S and CO_2, enrichment of CH_4, no unwanted end products	Addition of H_2, experimental - not at large scale

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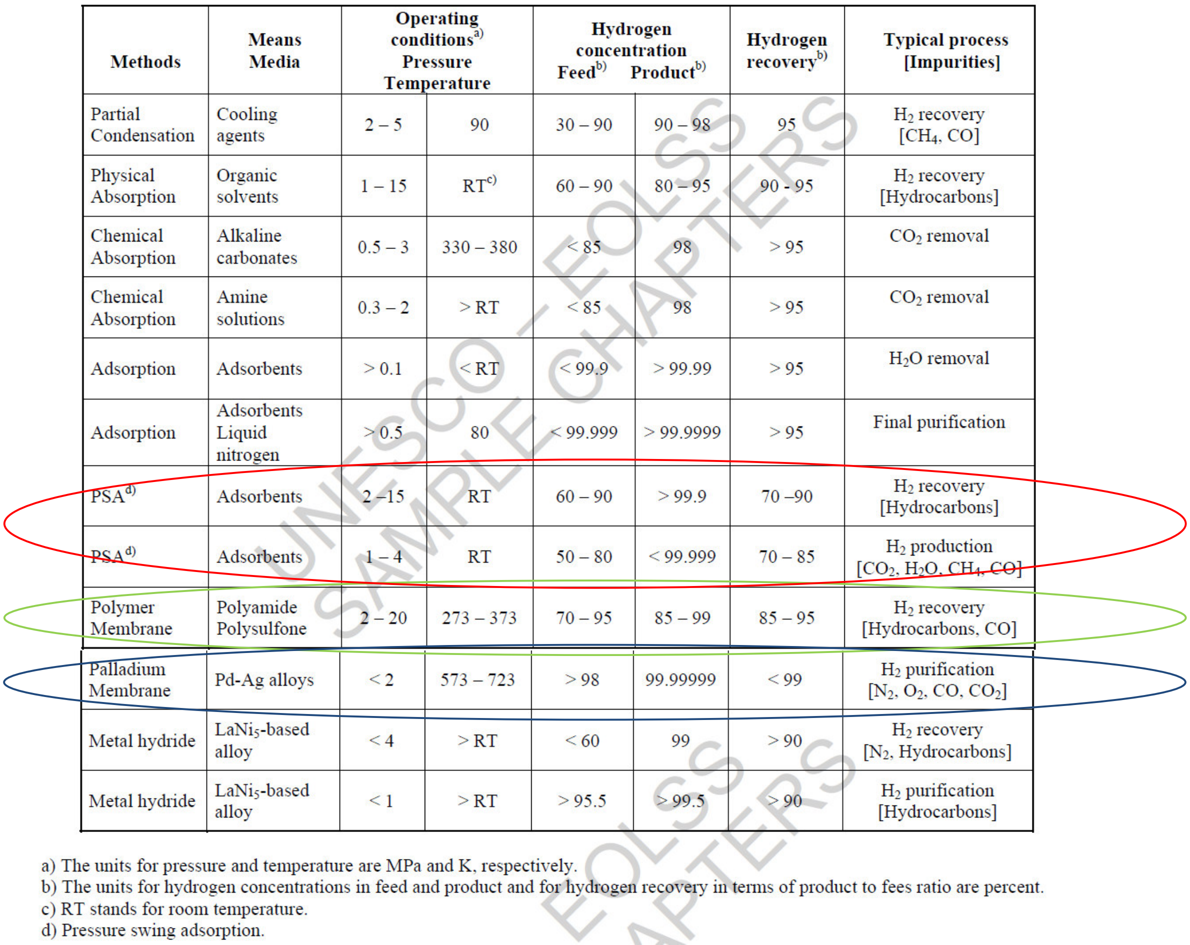
[6] Huertas, J.I. *et al.*, *Removal of H_2S and CO_2 from Biogas by Amine Absorption*, in Mass Transfer in Chemical Engineering Processes, Markoš, J. (*Eds.*), 2011, pp 133 - 150, ISBN: 978-953-307-619-5

In the next Table an overview (and comparison) of the different upgrading technologies for hydrogen from biogas gas is presented [7] showing, *a.o.*, operating conditions and typical hydrogen recovery. Highlighted in the red circle PSA upgrading, within the green circle the low temperature membrane separation (polymer membrane) and in the blue the high temperature membrane separation (palladium membrane).

Table 3: Overview of the different upgrading technologies hydrogen from biogas



Methods	Means Media	Operating conditions[a] Pressure	Temperature	Hydrogen concentration Feed[b]	Product[b]	Hydrogen recovery[b]	Typical process [Impurities]
Partial Condensation	Cooling agents	2 – 5	90	30 – 90	90 – 98	95	H_2 recovery [CH_4, CO]
Physical Absorption	Organic solvents	1 – 15	RT[c]	60 – 90	80 – 95	90 - 95	H_2 recovery [Hydrocarbons]
Chemical Absorption	Alkaline carbonates	0.5 – 3	330 – 380	< 85	98	> 95	CO_2 removal
Chemical Absorption	Amine solutions	0.3 – 2	> RT	< 85	98	> 95	CO_2 removal
Adsorption	Adsorbents	> 0.1	< RT	< 99.9	> 99.99	> 95	H_2O removal
Adsorption	Adsorbents Liquid nitrogen	> 0.5	80	< 99.999	> 99.9999	> 95	Final purification
PSA[d]	Adsorbents	2 – 15	RT	60 – 90	> 99.9	70 – 90	H_2 recovery [Hydrocarbons]
PSA[d]	Adsorbents	1 – 4	RT	50 – 80	< 99.999	70 – 85	H_2 production [CO_2, H_2O, CH_4, CO]
Polymer Membrane	Polyamide Polysulfone	2 – 20	273 – 373	70 – 95	85 – 99	85 – 95	H_2 recovery [Hydrocarbons, CO]
Palladium Membrane	Pd-Ag alloys	< 2	573 – 723	> 98	99.99999	< 99	H_2 purification [N_2, O_2, CO, CO_2]
Metal hydride	$LaNi_5$-based alloy	< 4	> RT	< 60	99	> 90	H_2 recovery [N_2, Hydrocarbons]
Metal hydride	$LaNi_5$-based alloy	< 1	> RT	> 95.5	> 99.5	> 90	H_2 purification [Hydrocarbons]

a) The units for pressure and temperature are MPa and K, respectively.
b) The units for hydrogen concentrations in feed and product and for hydrogen recovery in terms of product to fees ratio are percent.
c) RT stands for room temperature.
d) Pressure swing adsorption.

Clearly from previous Table it can be observed that the hydrogen concentrations in the feed are relatively high for both PSA (> 50% H_2) and membrane separation processes (> 70% H_2). H_2 recoveries increase from 70% (lowest end PSA) up to 98% (Pd-membrane).

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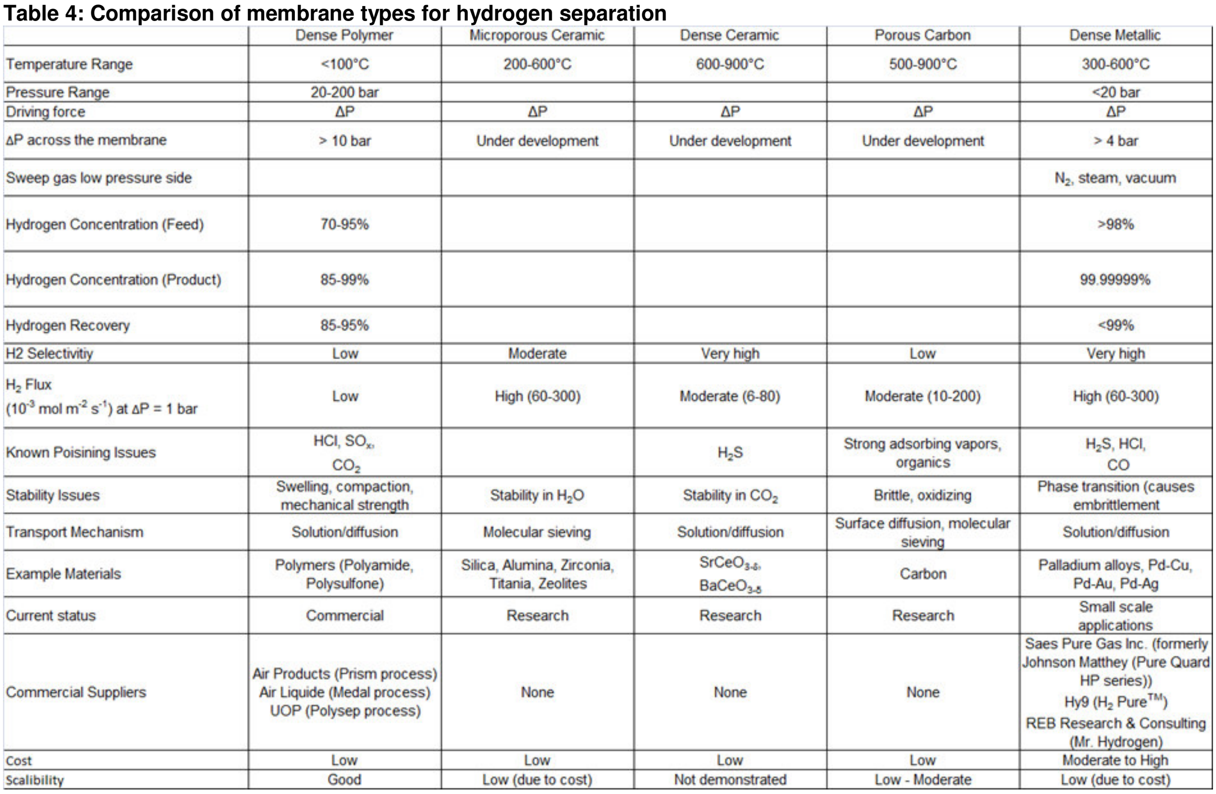
[7] Uehara, I., *Separation and Purification of Hydrogen*, in Energy Carriers and Conversion Systems with Emphasis on Hydrogen - Volume 1, Ohta, T. (*Eds.*), 2008, pp 268 - 282, ISBN: 978-1-905839-29-2 (eBook)

The next Table presents a comparison of different membrane types (membrane material, costs etc.) for hydrogen [8]. Of these, only the polymeric membranes have seen significant commercialization, although dense metal membranes (high temperature membrane) have been used for commercial applications in selected niche markets.

Table 4: Comparison of membrane types for hydrogen separation



	Dense Polymer	Microporous Ceramic	Dense Ceramic	Porous Carbon	Dense Metallic
Temperature Range	<100°C	200-600°C	600-900°C	500-900°C	300-600°C
Pressure Range	20-200 bar				<20 bar
Driving force	ΔP	ΔP	ΔP	ΔP	ΔP
ΔP across the membrane	> 10 bar	Under development	Under development	Under development	> 4 bar
Sweep gas low pressure side					N_2, steam, vacuum
Hydrogen Concentration (Feed)	70-95%				>98%
Hydrogen Concentration (Product)	85-99%				99.99999%
Hydrogen Recovery	85-95%				<99%
H2 Selectivitiy	Low	Moderate	Very high	Low	Very high
H_2 Flux (10^{-3} mol m^{-2} s^{-1}) at ΔP = 1 bar	Low	High (60-300)	Moderate (6-80)	Moderate (10-200)	High (60-300)
Known Poisining Issues	HCl, SO_x, CO_2		H_2S	Strong adsorbing vapors, organics	H_2S, HCl, CO
Stability Issues	Swelling, compaction, mechanical strength	Stability in H_2O	Stability in CO_2	Brittle, oxidizing	Phase transition (causes embrittlement
Transport Mechanism	Solution/diffusion	Molecular sieving	Solution/diffusion	Surface diffusion, molecular sieving	Solution/diffusion
Example Materials	Polymers (Polyamide, Polysulfone)	Silica, Alumina, Zirconia, Titania, Zeolites	$SrCeO_{3-\delta}$, $BaCeO_{3-\delta}$	Carbon	Palladium alloys, Pd-Cu, Pd-Au, Pd-Ag
Current status	Commercial	Research	Research	Research	Small scale applications
Commercial Suppliers	Air Products (Prism process) Air Liquide (Medal process) UOP (Polysep process)	None	None	None	Saes Pure Gas Inc. (formerly Johnson Matthey (Pure Quard HP series)) Hy9 (H_2 Pure^{TM}) REB Research & Consulting (Mr. Hydrogen)
Cost	Low	Low	Low	Low	Moderate to High
Scalibility	Good	Low (due to cost)	Not demonstrated	Low - Moderate	Low (due to cost)

The comprehensive descriptions of technologies are presented in the next pages.

Several membranes have been developed for the purification of hydrogen. In all cases the hydrogen permeates through the membranes much more readily than (most) other compounds; sometimes hydrogen permeates even exclusively (i.e. in Pd-membranes). The actual mechanism for the separation of hydrogen and contaminants may be based on either solution-diffusion, molecular sieving and/or surface diffusion, depending on the actual type of membrane. For all membrane processes, for permeation to occur a partial pressure difference must exist, hence the crude hydrogen has to be compressed. Like in PSA processes, the attainable yield and purity of the product of hydrogen are strongly dependent of the pressure; in practice relatively high pressures are often applied (>10 bara). This is an economic optimization, since a higher pressure results in higher fluxes and hence a smaller required membrane surface area, but this is offset by the higher compression costs.

Low temperature membranes

Low temperature membranes (polymeric membranes) are applied on an industrial scale for recovery of hydrogen from purge streams, recycle streams etc. In these processes, hydrogen-selective membranes are used, most often applied in the form of hollow-fibre modules. It concerns dense membranes made of polymeric materials. Several suppliers exist, each with their own membranes (not exhaustive):

- Air Products (Prism process)
- Air Liquide (Medal process)
- UOP (Polysep process)

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[8] Internal HyGear communication, 2013

In the next Figure a schematic representation of a hollow fibre membrane for hydrogen purification, as applied in Air Liquid‘s Medal process (http://www.medal.airliquide.com), is shown.

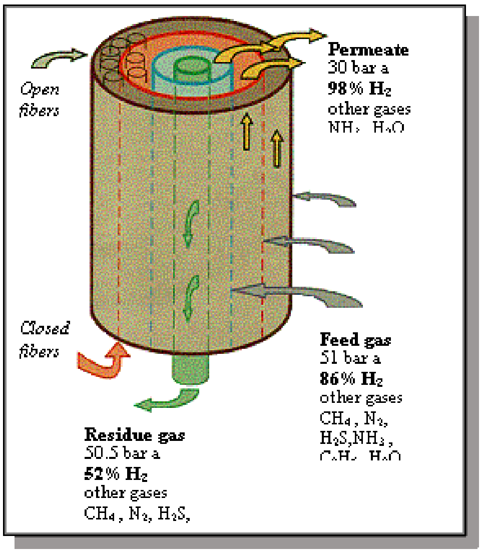

Figure 6: Schematic representation of a hollow fibre membrane for hydrogen purification.

In a hollow fibre module, the pressurized feed gas enters the hollow fibre bundle from the tube side; compounds like nitrogen, methane and argon stay mostly on the pressurized shell side, whereas most of the hydrogen is collected at a lower pressure on the inner tube side. Permeation occurs by a solution-diffusion mechanism caused by the (partial) pressure difference between shell and inner tube sides. The separation is based on different permeation rates through the membrane. In the next figure the relative permeation rates of different gases compared to hydrogen through low temperature polymeric membranes are presented (http://www.medal.airliquide.com). In this way, a “fast” gas like hydrogen is separated from “slow” gases such as carbon monoxide, methane or other hydrocarbons.

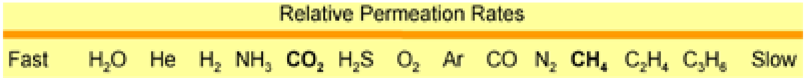

Figure 7: Relative permeation rates of different gases through low temperature polymeric membranes.

From previous Figure it can be concluded that hydrogen (H_2) can be selectively separated from methane (CH_4), since hydrogen permeates a lot faster than methane.

High-temperature membranes

High temperature membranes include dense metallic (Pd) and porous ceramic membranes (alumina, silica etc), as well as carbon molecular sieves (CMS). Typically, high-temperature membranes are highly selective for hydrogen, especially Pd-membranes. In combination with the reported stability issues and the state of development, the most suitable type would be a Pd-membrane. All high-temperature membranes require operating temperatures above 300°C. Moreover the use of sweep gas at the permeate (pure H_2) side is required. For the current application, the sweep gas would be steam as this can be separated from the hydrogen relatively easily (by cooling/condensing in the TSA). Most of the high temperature membranes are still under development and require high investment costs, but Pd-membranes are available for small scale applications (see Figure 8).

Figure 8: High-temperature Pd-based composite hydrogen separation membranes manufactured by CRI/criticatalyst.