Development of H_2 Safety Expert Groups and due diligence tools for public awareness and trust in hydrogen technologies and applications

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Authors:

Stefano Campanari (Politecnico di Milano)

Giulio Guandalini (Politecnico di Milano)

Gianluca Valenti (Politecnico di Milano)

Ennio Macchi (Politecnico di Milano)

Leonardo Rosés Grimaldi (Politecnico di Milano)

Gioele Di Marcoberardino (Politecnico di Milano)

Note: Author printed in bold is the contact person for this document.

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V1.0	2013-07-26	Initial draft - discriminating criteria - methodology and format definition	POLIMI	S. Campanari
V2.0	2013-08-29	Hydrogen production layouts	POLIMI	S. Campanari
V3.0	2013-09-28	Preliminary draft with all production cases	POLIMI	S. Campanari
V4.0	2013-10-10	Introduction to storage and transport	POLIMI	S. Campanari
V5.0	2013-10-31	Final draft	POLIMI	S. Campanari
V5.1	2013-10-31	Final document	POLIMI	S. Campanari

Contents

1 Executive Summary

Task 2.2 “Definition of a reference benchmark“ belongs to WP2 (Develop Analytical Framework). It has been developed a reference benchmark for the operating conditions of typical H_2 production, storage and distribution technologies.

The benchmark report is dedicated to industrialized and commercial technologies, or at least with an established early-market availability, having the most important impact on public awareness and trust in hydrogen technologies and applications, which is the target of H2TRUST. Due to that, it does not consider all possible unconventional or emerging technologies still featuring a low technology readiness level, although some of them are sometimes cited in the report.

The benchmark considers different cases for hydrogen production, classified according to the possible feedstock:

- natural gas and hydrocarbons (including LPG, ethanol, biogas), using reforming-based processes (either using steam reforming, autothermal reforming or through partial oxidation)
- solid or heavy fuels (including coal, biomass, refinery residues) through gasification / pyrolysis processes
- electricity through electrolysis

Moreover, the cases are divided according to the plant size and the required level of hydrogen purity, when these factors influence significantly the plant configuration with inclusion of new components which can be important by the point of view of safety.

In all cases the benchmark report defines a conceptual plant scheme, as well as the corresponding reference component operating conditions (e.g. streams pressure, temperature, chemical features in the most important points); moreover the report evidences in a qualitative way the relative size of the most important plant components.

Figure 1 shows a summary of the relevant plant configurations that are covered by the report.

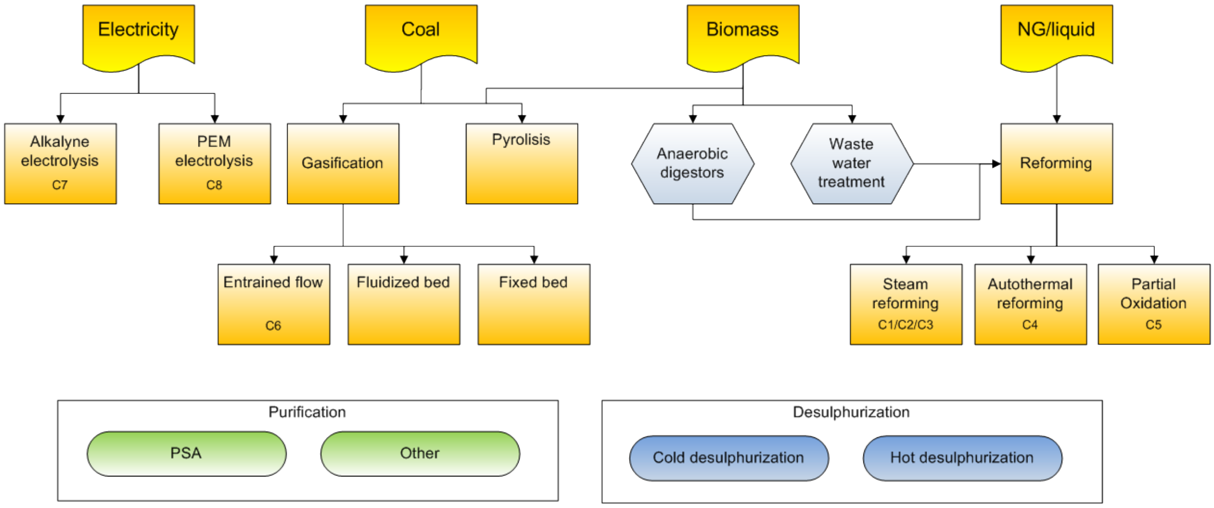

Figure 1. *Example of categories of plant configurations as considered in the benchmark report.*

Figure 2 gives an example of the first configuration (large scale hydrogen production through steam reforming from natural gas).

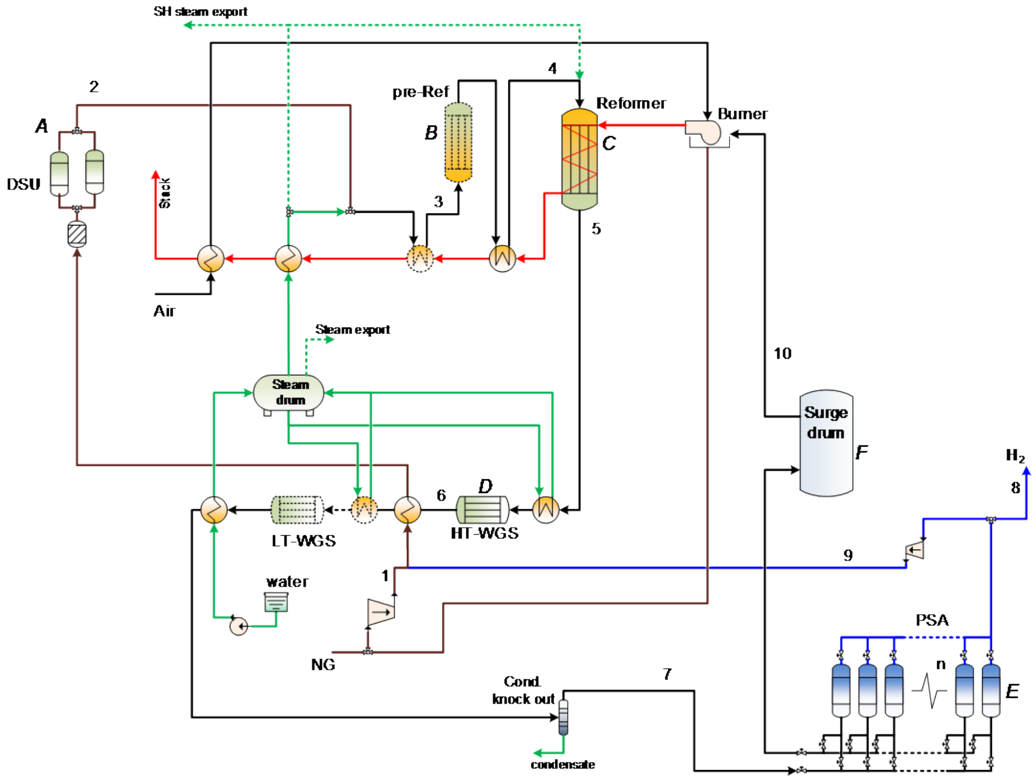

Figure 2. *Example of plant configuration as considered in the benchmark report (case C1 in Fig.1).*

For each type of plant, a corresponding table gives an example of the related stream operating conditions, and another table an example of component size evaluation. The relative size is evaluated only qualitatively as small (+), medium (++) or large (+++) aiming to evidence the presence of bulky equipment, especially when processing hazardous streams.

This approach can effectively support a subsequent safety evaluation, since an analysis of the recurrence of streams featuring high pressure / high temperature / high content of combustible, chemically reactive or toxic species, as well as the presence of large size reactors with hazardous contents, could address in evaluating how critical is a certain plant by the point of view of safety.

In the same way the benchmark report presents a definition of reference conditions for the compression / liquefaction / storage / transport / distribution phases, also here according to size and possible technologies. The corresponding overview of considered cases is shown in Figure 3.

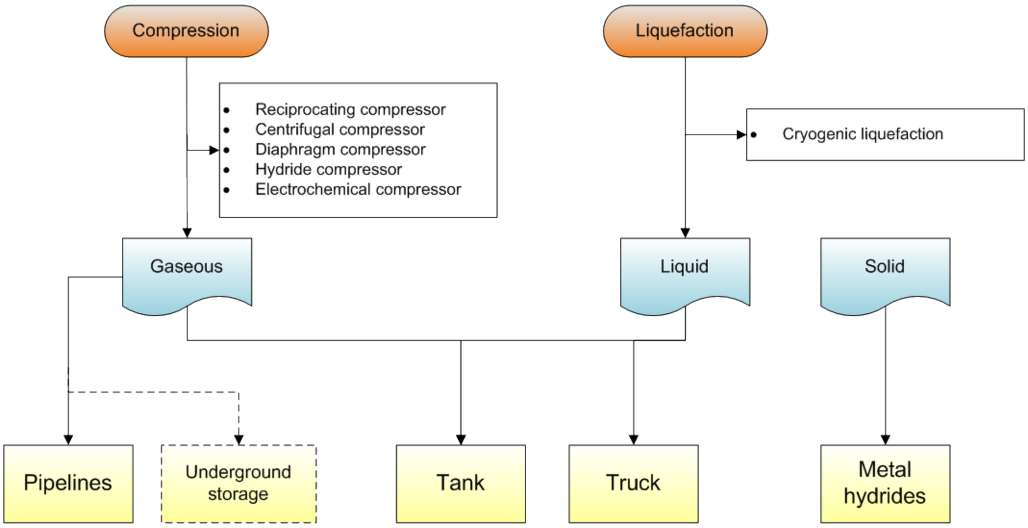

Figure 3. *Example of classification of storage / transport / distribution phases as considered in this benchmark report.*

A first draft of the benchmark report have been circulated to partners during M2 , evidencing a preliminary list of selected plant configurations with corresponding tables for typical stream operating conditions. A second version was circulated at M4. This is the final version (Deliverable D2.2) concluded at M5.

2 Introduction

This report from H2TRUST task 2.2 is a precursor to tasks 3.1 and 3.2 dedicated to data gathering about safety in the areas of production, storage and transportation. Within Task 2.2 POLIMI has set up and compiled an explicit reference benchmark report for typical production-storage-distribution technologies, which represents a key point for the subsequent safety analysis, focusing on their operating conditions and component features.

The benchmark report is dedicated to industrialized and commercial technologies, or at least with an established early-market availability, having the most important impact on public awareness and trust in hydrogen technologies and applications, which is the target of H2TRUST. Due to that, it does not consider all possible options for hydrogen production, distribution and storage and it excludes from a systematic analysis all options still featuring a low technology readiness level as well as unconventional or emerging technologies. Nevertheless, some of them are sometimes cited in the report for clarity of explanation and comparison, and a brief description addressing their operating principles is given in a dedicated chapter.

3 Methodology

The report is based on data collected from open literature on hydrogen production / distribution and storage, as well as from specific information provided by the partners. Where necessary, data are integrated with results of numerical simulations of specific plant configurations carried out using process simulation software (e.g. Aspen Plus®).

In the present report, firstly the conventional routes for hydrogen production are identified. A straightforward discrimination of the benchmark technologies used for hydrogen production considers the possible feedstock as hydrocarbons, solid fuels or electricity.

More precisely, the considered feedstocks for H2 production are the following:

- natural gas and hydrocarbons (including LPG, ethanol, biogas), using reforming-based processes (either using steam reforming, autothermal reforming or through partial oxidation)
- solid or heavy fuels (including coal, biomass, refinery residues) through gasification / pyrolysis processes
- electricity through electrolysis

The most common production routes are by far in the first and third category, namely natural gas steam reforming or electrolysis. Use of solid and heavy fuels specifically for hydrogen production is presently limited to rather few demonstration plants, whereas solid fuels and biomass are converted into syngas through gasification or pyrolysis and for the majority directly used without hydrogen purification or separation. The report will deal with the case of gasification of heavy residues, taken as a representative case, typically carried out in refineries where at least part of the syngas is purified to hydrogen for internal uses.

A further step into detailed discrimination of the technologies applied in hydrogen production takes into consideration other factors as production scale and grade of hydrogen purity required, when these factors influence significantly the plant configuration with inclusion of new components which can be important by the point of view of safety.

Figure 4 presents a schematic view of the different technologies applied to the conversion of raw material to hydrogen. This conceptual summary is taken as a starting point for the definition of plant designs addressed in this report.

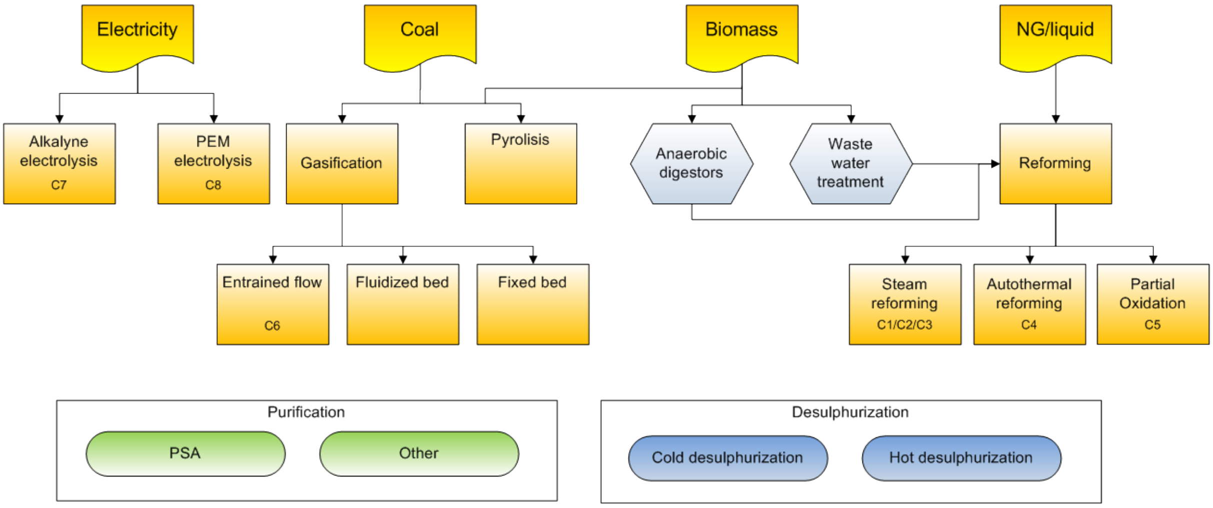

Figure 4. *Hydrogen production techniques considered in reference benchmark analysis, and related plant configurations (C1-C8).*

As anticipated in the introduction, this report analyses mature technologies used for production of hydrogen, focusing mostly on the processes which are most used as for today. Therefore the description in Figure 4 is not including technologies in early stage of development, R&D or niche applications, that are beyond the scope of this report. A comprehensive list could include other processing techniques, for instance solar driven thermochemical water splitting, adsorption enhanced reforming, microbial production, hydrocarbon decomposition, and so on. A brief description of these and other non-conventional technologies will be given in section 4.4.

Table 1 lists a summary of the relevant plant designs that are covered by this report.

In addition to the plant size, the table addresses a classification according to the following criteria:

- *Desulphurization*

  Desulphurization is applied to fuel and syngas feedstock ahead of catalytic reactors involved in the hydrogen production process. It can be divided in two categories, based on operating temperature. This implies a different arrangement in the plant configuration and different streams conditions.
- *Purity and purification*

  Usually highest purity is obtained by electrolysis plants or through PSA purification applied to syngas generated by SR plants. The size of the PSA section depends on the quantity of contaminants in the syngas (e.g. CO, CO2, N2) to be removed; ATR and POX plants using air as oxidant have a higher concentration of N2 and are generally not suitable for highest purity grades. Other purification routes include preferential oxidation, usually applied to smaller SR plants for CO removal, without influence on non-combustible contaminants. The grade of purity of the final product is defined with a standard decimal notation (e.g. High purity grade 4.0 for 99.99 % H2; Ultra High purity grade 5.5 for 99.9995 % H2 and so on).

Table 1: *List of hydrogen production plants discriminated by design criteria*

Feedstock	**Gas / liq. hydrocarbon fuel**					**Solid fuel**	**Electricity**	
Technology Criteria \ Plant	Steam reforming (large scale)	Steam reforming (small / medium scale)		Autothermal reforming	Partial oxidation	Gasification (Entrained flow)	Alkaline electrolysis	PEM electrolysis
NG/ liquid hydrocarbons	X	X	X	X	X			
Biogas		X	X					
Coal / heavy residues						X		
Electricity							X	X
Plant size (*)								
Small - medium		X	X				X	X
Large	X			X	X	X	X	
Desulfurization								
Hot	X			X		X	**n.a.**	
Cold		X	X					
Purity								
Grade 4.0-6.0	X		X			X	X	X
Grade 2.0 ÷ 4.0			X	X	X	X		
<99 %		X						
Purification								
PSA	X		X	X	X	X		
Other		X					X	X
Configuration	C1	C2	C3	C4	C5	C6	C7	C8

(*) small and medium size plants are intended here up to around 2000 Nm3/h

In all cases resulting from Figure 4 (labelled C1 to C8) it is defined a conceptual plant scheme, as well as the corresponding reference operating conditions (e.g. streams pressure, temperature, chemical features in the most important points).

Quantities are indicated with a range according to most common literature evidences. Mass flow rates are generally normalized towards a production of 1 Nm^3/h of hydrogen.

The stream specification may be completed with a note specifying the possible hazards (e.g. a fluid may be flammable, toxic, acid or caustic etc.).

Table 2: *Example of stream specifications*

Point	P	T	F	Composition (% molar)								Notes
	[bar$_a$]	[°C]	[*]	C_xH_y	H_2	CO	CO_2	H_2O	O_2	N_2	H_2S	
1	17 ÷ 37	120 ÷ 150	0.37 ÷ 0.41	94 ÷ 100	-	-	<2	-	<0.1	<5	<1	flammable
…	16 ÷ 36	600 ÷ 700	1.5 ÷ 2.1	16 ÷ 22	6 ÷ 11	<0.1	1 ÷ 3	68 ÷ 72	-	<1	<1 ppm	flammable
n	13 ÷ 33	800 ÷ 920	2.1 ÷ 2.8	0.4 ÷ 5	45 ÷ 48	7 ÷ 9	5 ÷ 7	35 ÷ 39	-	<1	<1 ppm	flammable / toxic

* All flows are in Nm^3/h relative to a production of 1 Nm^3/h of hydrogen.

Another key issue in a safety analysis is the physical quantity of hazardous substances which are present in a plant; as a first approximation, this quantity is proportional to the size of the plant equipment (e.g. reactors, vessels, storages). A quantitative definition of component size is not possible since it depends on a number of plant-specific features, ranging from the exact plant capacity to design specification of all its components. However, it is possible to give a qualitative indication of the presence of specially large pieces of equipment. Therefore another table (see the example of Table 3) evidences in a qualitative way the relative size of the most important plant components, classified as small (+), medium (++) or large (+++) aiming to evidence the presence of bulky equipment, especially when processing hazardous streams.

Table 3: *Example of component relative size*

Config. ref.	Description	Relative size
A	Desulfurization Unit	+
B	Pre-reformer	++
C	Reformer	++/+++
…	….	….
F	Surge drum	+++

In the same way the benchmark report presents a definition of reference conditions for the compression / liquefaction / storage / transport / distribution phases, also here according to size and possible technologies. The corresponding overview of considered cases is shown in Figure 5. Additional details about these technologies are given case by case in the corresponding sections.

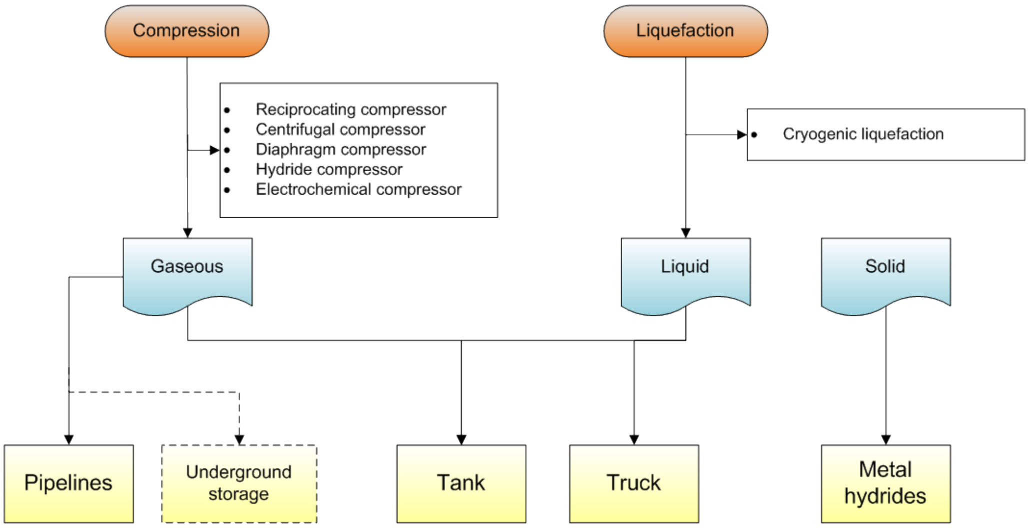

Figure 5. *Example of classification of storage / transport / distribution phases as considered in this benchmark report.*

4 Hydrogen production

This section describes the operating conditions of the hydrogen production technologies listed in Table 1. A first level of classification is based on the feedstock; therefore in section 4.1 production from natural gas, biogas and liquid fuels is analyzed. In section 4.2 production from solid feedstock is briefly addressed and in section 4.3 production from electricity is described. After a description of the available technologies and of their common characteristics, each section is divided in some paragraph related to the most relevant configurations. In section 4.4, other non-conventional technology are briefly described.

Main literature references for this section are ENI Encyclopaedia of Hydrocarbons [1], Hydrogen Fuel [2], Hydrogen Technology [3] and Gas purification [4]; other references are included in the text.

4.1 Production from natural gas, biogas and liquid fuels

Hydrogen production from gaseous and liquid fuels (natural gas, biogas, light hydrocarbons) is mainly based on two reactions. The first is steam reforming, namely (focusing on methane):

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \Delta\mathrm{H}^0_{298\ \mathrm{K}} = 206\ \mathrm{kJ/mol} \qquad (1)$$

that produces a mixture of carbon monoxide (*CO*) and hydrogen (*H_2*). To improve the conversion to hydrogen, usually a successive water gas shift reaction is included in the process:

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta\mathrm{H}^0_{298\ \mathrm{K}} = -41\ \mathrm{kJ/mol} \qquad (2)$$

Both reactions are carried out with proper catalysts to enhance the hydrogen production rate. Due to the strong endothermic nature of the steam reforming reaction, an external heat source is required; an alternative is the consumption of a fraction of the feeding in the reactor according to the exothermic combustion reaction:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad \Delta\mathrm{H}^0_{298\ \mathrm{K}} = -802\ \mathrm{kJ/mol} \qquad (3)$$

In some technologies, a partial oxidation of methane in oxygen or air sub-stoichiometric atmosphere is used to produce hydrogen and carbon monoxide:

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2 \qquad \Delta\mathrm{H}^0_{298\ \mathrm{K}} = -38\ \mathrm{kJ/mol} \qquad (4)$$

that also has to be promoted by a catalyst.

In case of presence of higher (C_{2+}) hydrocarbons, a preliminary step of *prereforming* is generally included, in order to crack longer hydrocarbon chains. The product stream is a syngas mixture of different species, whose composition strongly depends on the technology and the feeding; an hydrogen separation section, placed downstream the syngas production, is therefore mandatory.

The process of steam reforming for hydrogen production is used also with light hydrocarbons other than natural gas, such as naphtha, LPG, ethanol or diesel, though in much lesser cases. Such applications are mainly of specific interest with on-board reforming for mobile/portable applications. In general the reforming process of these hydrocarbons are quite similar to that of NG reforming; the main differences may fall on a more complex desulphurization system and the use of higher steam to carbon ratio to reduce coking.

Alternatively, a feasible way to reduce the impact of hydrogen production would be the use of biogas as feedstock. Typical technologies for biogas production can be anaerobic digesters of agricultural residues, landfill gas or waste water (sewage) treatment. This processes lead to a mixture of the same components of natural gas, but in a very different ratio, as exemplified in Table 4.

Table 4: *Comparison among different biogas and natural gas common compositions* [5]

Specie	Landfill biogas	Anaerobic digestor biogas	North Sea natural gas	Italian NG regulation limits	German NG regulation limits	Sweden NG regulation limits
CH_4 [$\%_{vol}$]	35÷65	53÷70	87	n.a.	n.a.	95÷99
H_2 [$\%_{vol}$]	0÷3	n.a.	n.a.	n.a.	< 5	n.a.
CO_2 [$\%_{vol}$]	15÷50	30÷47	1.2	< 3	< 6	sum up to 5 %
O_2 [$\%_{vol}$]	0÷5	0	0	< 0.6	< 3	
N_2 [$\%_{vol}$]	5÷40	0.2	0.3	n.a.	5÷40	
H_2S [ppm]	< 100	< 100	0	< 4.6	n.a.	n.a.
S [mg/Nm^3]	n.a.	n.a.	0	n.a.	< 30	< 23

The gas mixture could be then processed by a steam reforming plant. As evident, the methane content in biogas is much lower than in natural gas. Moreover, the higher sulphur content forces the implementation of larger purification systems, while the large amount of CO_2 has a negative influence on the WGS reaction. On the other hand, the dilution with an inert could be favourable by the point of view of safety.

However, hydrogen production from biogas is presently very poorly applied in real plants, since biogas is typically directly used as a fuel in power generation units located close to the biogas production facilities. Due to such limitation this option is not further addressed explicitly in this report.

As already mentioned, several other technologies could be chosen to produce hydrogen from gaseous or liquid hydrocarbons, based on different principles (e.g. steam-iron and chemical looping processes, plasma reforming, photoproduction, ...). Nevertheless, they are not used in commercial application and therefore just briefly described in this report (section 4.4).

4.1.1 Configuration 1 - Large scale steam reforming of natural gas

The first option addressed in this work is also the most widespread type of plant nowadays used for the production of large quantities of hydrogen. It is based on steam reforming of natural gas, typically carried out in fired tubular reforming (FTR) plants. This is the generally the most competitive technology for plant capacity up to approximately 250’000 Nm^3 of H_2 per hour.

A typical layout of a large scale steam reforming plant is shown in Figure 6, where main components and streams are evidenced.

Even if this kind of plant is essentially designed for H_2 production, it also usually shows a consistent export of superheated steam (typically used by adjacent industrial processes), produced by heat recovery from hot gas streams.

The main chemical reactor (C) is the *reformer,* which requires a heat source due to the strongly endothermic balance of reaction (1). In order to grant optimal mechanical and thermal resistance of the materials, the reaction takes place in catalyst filled vertical tubes that are externally irradiated by a flame. The catalyst is usually Ni-based in form of pellets or powders, which may have specific manipulation and handling hazards (e.g. toxicity); more active noble metals could be adopted as catalysts, but Ni is preferred due to its relatively lower cost.

A *pre-reforming* stage (B) can be introduced in case of presence of heavier hydrocarbons in the feeding stream (C_{2+} hydrocarbons, that can reach up to 10 % in common natural gas). The aim of this reactor is to decompose the larger hydrocarbon chains in CH_4, CO and H_2. This reactor is usually adiabatic and works at lower temperatures in order to reduce the risk and amount of solid carbon (coke) formation, which is easier from highly reactive heavy hydrocarbons molecules [6]. Also this reaction is generally enhanced by alumina-supported, Ni-based catalysts.

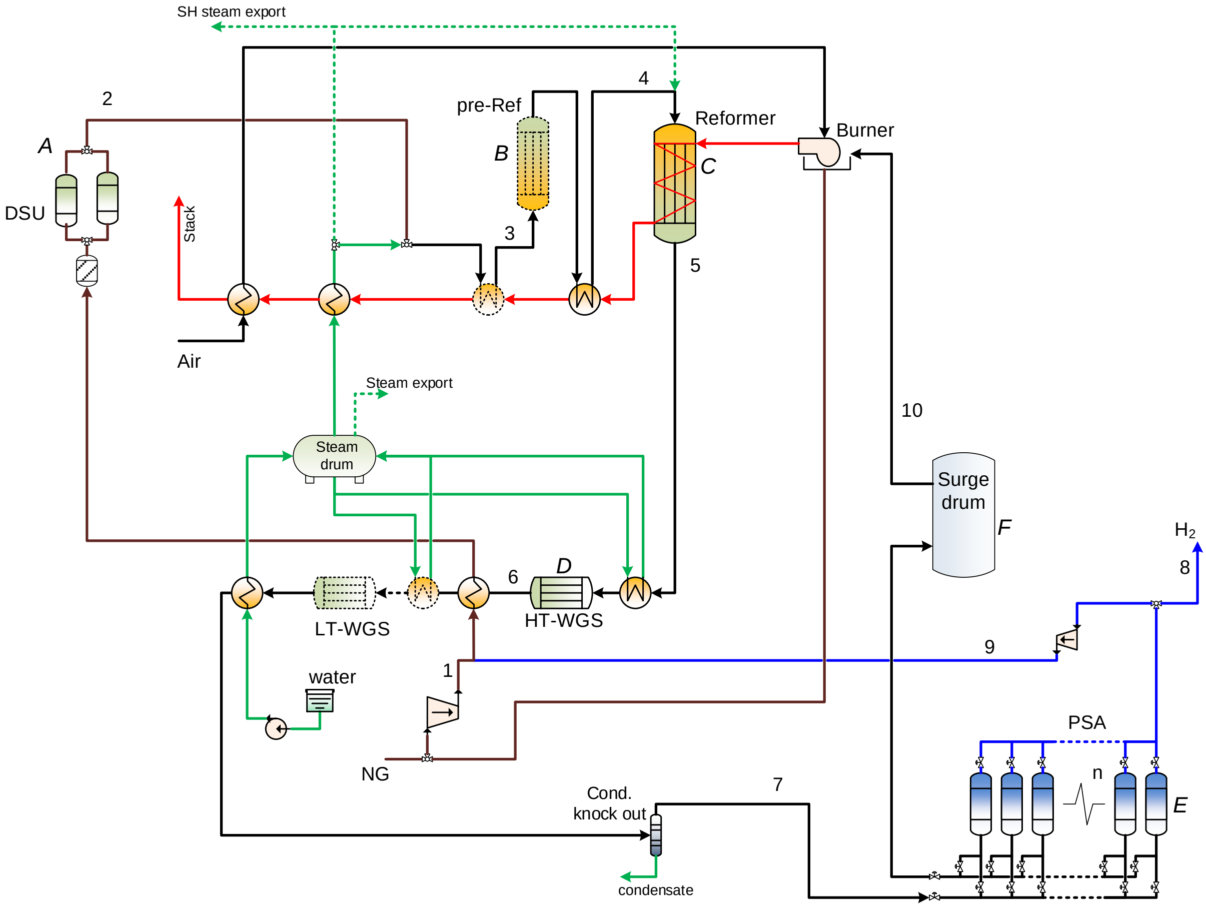

Figure 6: *Configuration 1 - Large scale steam reforming of natural gas*

The catalysts are very sensible to sulphur. Therefore the NG feedstock must be treated in a *desulfurization unit* (DSU), generally based on a two stage process starting with a catalytic hydrogenation of all the sulphur-organic compounds over a catalyst (typically Co-Mo at 290-370°C) to form H_2S. The second step is H_2S scrubbing by a ZnO bed (at about 340-390°C).

The reformer is usually operated at high temperatures (about 800-920 °C). Most industrial plants are operated at high pressures (up to 40 bar), despite the negative influence of the pressure on the reforming reaction equilibrium, in order to obtain pressurized H_2 and reduce the size of the reactor. Another relevant control parameter is the steam to carbon ratio (S/C), defined as the molar ratio H_2O/CH_4, which is usually maintained in the range 2.5÷3 in order to avoid carbon formation on the catalyst.

Downstream the reformer, a further section is dedicated to the *water gas shift* (WGS) reaction (2). To achieve higher CO conversion into hydrogen, two reactors with different catalysts are commonly used in series (D). The HT-WGS reactor usually relies on an ironchromium-based catalyst that works at about 400°C; on the other hand, the LT-WGS catalyst is generally Cu-Zn based and works at lower temperatures (200-300°C).

Finally, a purification process is used to remove the large amount of impurities (CO_2, CO, N_2) contained in the syngas. Large plants usually adopt a *pressure-swing adsorption* (PSA) system, based on a multiple adsorption bed system (molecular sieves of suitable pore size) where the adsorption and release of impurities is governed by periodical pressure changes (the so-called pressure swing) on the beds. The number of PSA vessels could be from 8 to 12. The large quantity of off-gas released by the beds during the release phase of impurities is stored in a *surge drum* (F) and used as secondary fuel for the reformer furnace. In some cases, the LT-WGS can be removed and a larger fraction of residual CO will be contained in the off-gas and finally burned in order to provide the reaction heat; nevertheless, in this case the PSA section has to be designed for higher off-gas flows.

A summary of common streams conditions is presented in Table 5.

Table 5: *Configuration 1 - Large scale SR - Operating conditions*

Point	**P**	**T**	**F**	**Composition (% molar)**								**Notes**
	[bar$_a$]	**[°C]**	**[*]**	**C_xH_y**	**H_2**	**CO**	**CO_2**	**H_2O**	**O_2**	**N_2**	**H_2S**	
1	17 ÷ 37	120 ÷ 150	0.37 ÷ 0.41	94 ÷ 100	-	-	<2	-	<0.1	<5	<1	flammable
2	16 ÷ 36	300 ÷ 400	0.37 ÷ 0.41	94 ÷ 100	<3	-	<2	-	<0.1	<5	<1 ppm	flammable
3	16 ÷ 36	400 ÷ 600	1.4 ÷ 2	20 ÷ 28	<1	-	<1	72 ÷ 80	-	<1	<1 ppm	flammable
4	16 ÷ 36	600 ÷ 700	1.5 ÷ 2.1	16 ÷ 22	6 ÷ 11	<0.1	1 ÷ 3	68 ÷ 72	-	<1	<1 ppm	flammable
5	13 ÷ 33	800 ÷ 920	2.1 ÷ 2.8	0.4 ÷ 5	45 ÷ 48	7 ÷ 9	5 ÷ 7	35 ÷ 39	-	<1	<1 ppm	flammable / toxic
6	11 ÷ 31	400 ÷ 440	2.1 ÷ 2.8	0.4 ÷ 5	51 ÷ 55	1 ÷ 3	11 ÷ 13	29 ÷ 33	-	<1	<1 ppm	flammable / toxic
7	10 ÷ 30	30 ÷ 60	1.4 ÷ 1.9	0.6 ÷ 7	73 ÷ 79	2 ÷ 4	16 ÷ 18	0.1 ÷ 0.9	-	<1	<1 ppm	flammable / toxic
8	9 ÷ 29	30 ÷ 60	0.9 ÷ 1.4	<0.1	purity up to- 5.0	<0.2	<0.2	<0.1	-	<0.2	-	flammable
9	10 ÷ 37	30 ÷ 60	<0.02	<0.1	purity up to- 5.0	<0.2	<0.2	<0.1	-	<0.2	-	flammable
10	1 ÷ 1.5	10 ÷ 40	0.5 ÷ 0.8	2 ÷ 17	21 ÷ 42	6 ÷ 10	39 ÷ 60	0.3 ÷ 3	-	<0.6	-	flammable / toxic

* All flows are in Nm^3/h relative to a production of 1 Nm^3/h of hydrogen.

Table 6 shows a comparison of components size. For large plants, usually coupled with refinery or chemical industries, the size of the reformer reactor can be more than 10 meters in height and width; moreover also the PSA sections and the surge drum typically feature large dimensions.

Table 6: *Configuration 1 - Large scale SR - Indicative relative size of relevant components*

Config. ref.	Description	Relative size
A	Desulfurization Unit	+
B	Pre-reformer	++
C	Reformer	++/+++
D	High temperature WGS	+/++
E	Pressure Swing Adsorption	+++
F	Surge drum	+++

4.1.2 Configuration 2 - Small to medium scale steam reforming of natural gas with CO-PrOx

In applications requiring low pressure syngas with high content of hydrogen the solution described in this configuration would meet the needs, and is significantly widespread in the real practice. Typical users of hydrogen in such conditions may be fuel cell types where the constrains on the composition of the reformate gas are mainly related to the content of carbon monoxide and sulphur components. For instance, in low temperature fuel cells (as in Polymer Electrolyte Membrane) the limitations for CO content are typically below 10 to 20 ppmvd.

With respect to configuration 1, the differences are due to the necessity of simplicity related to the smaller scale:

- The method to purify the produced hydrogen stream after the steam reforming and WGS section is the CO preferential oxidation (CO-PrOX).
- Natural gas desulphurization ahead the reforming section is typically carried out at low temperature.

A PrOx reactor typically consists of a catalyst bed, which is passed by the fuel gas, containing hydrogen and carbon monoxide, while introducing also a small amount of oxygen or air. Carbon oxide is then oxidized to carbon dioxide thanks to the catalyst, operating in a preferential way with respect to hydrogen. The CO content can therefore be reduced to few ppm.

In this process the two reactions:

$$CO + \frac{1}{2}O_2 \rightarrow CO_2 \qquad \Delta H^0_{298\,K} = -283\ \mathrm{kJ/mol} \qquad (5)$$

and:

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \qquad \Delta H^0_{298\,K} = -241\ \mathrm{kJ/mol} \qquad (6)$$

are in competition. Therefore, the catalyst selectivity is fundamental in order to reduce the hydrogen consumption. Metal oxides (CoO_x, CuO-CeO_2) and supported noble metal (Ru, Pt and Rh) catalysts have currently suitable characteristics. Each of this catalyst has an optimal operation temperature range that can vary from about 80 °C to more than 250 °C.

Ahead the reforming section, desulfurization is mandatory due to the sensitivity of reforming catalysts to sulphur presence in the feeding. Due to the smaller sizes, a cold desulphurization based on adsorption can be adopted; usually some activated carbon beds are cyclically operated in adsorption and regeneration mode. Operating temperature are usually close to room temperature during adsorption. The regeneration phase requires an air stream and possibly a low amount of superheated steam to enhance the stripping process.

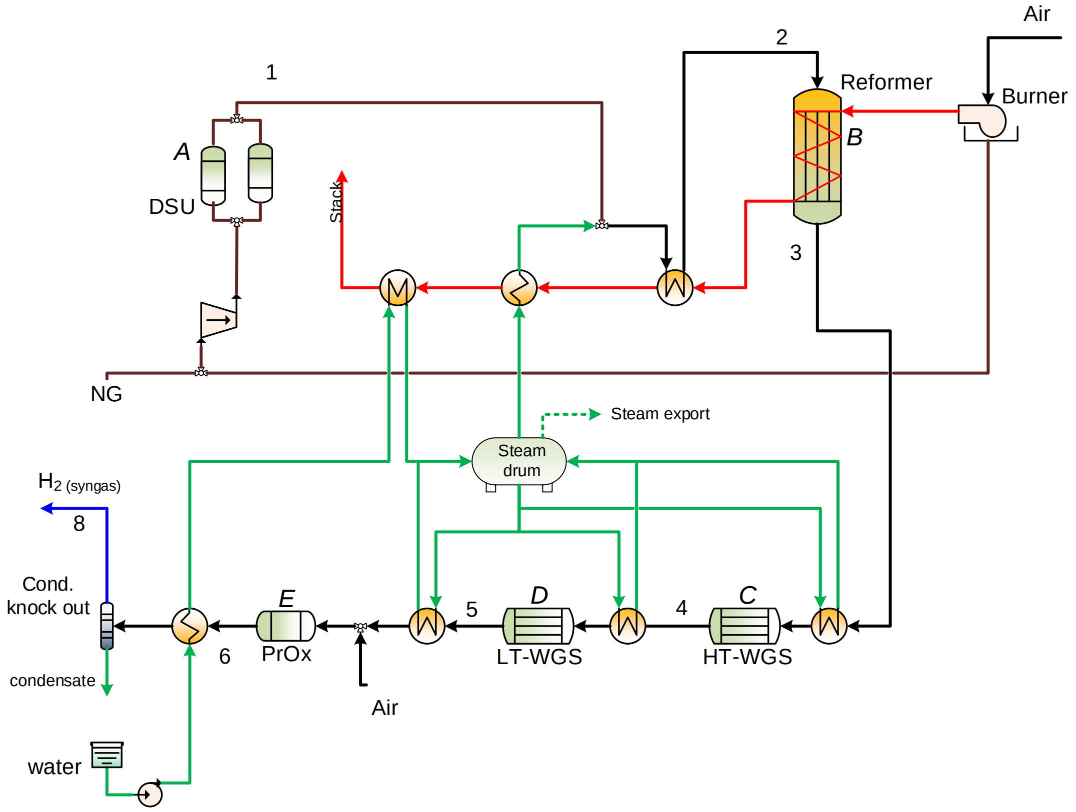

Figure 7: *Configuration 2 - Steam reforming of natural gas with CO-PrOx*

As shown in Figure 7, this layout differs from the large scale steam reforming plant just in the desulfurization and in the purification sections.

In this case only NG from the grid is burned in the reformer to sustain the reaction; the additional heat from CO oxidation is recovered by steam production.

Table 7 shows a summary of plant operating conditions, and Table 8 evidences the relative size of main components.

Table 7: *Configuration 2 - SR with PrOX - Operating conditions*

Point	P	T	F	Composition (% molar)								Notes
	[bar$_a$]	[°C]	[*]	C_xH_y	H_2	CO	CO_2	H_2O	O_2	N_2	H_2S	
1	16 ÷ 36	20 ÷ 40	0.37 ÷ 0.41	94 ÷ 100	-	-	<2	-	<0.1	<5	<1 ppm	flammable
2	16 ÷ 36	500 ÷ 700	1.4 ÷ 2	20 ÷ 28	<1	-	<1	72 ÷ 80	-	<1	<1 ppm	flammable
3	13 ÷ 33	800 ÷ 920	2.1 ÷ 2.8	0.4 ÷ 5	45 ÷ 48	7 ÷ 9	5 ÷ 7	35 ÷ 39	-	<1	<1 ppm	flammable / toxic
4	11 ÷ 31	400 ÷ 440	2.1 ÷ 2.8	0.4 ÷ 5	51 ÷ 55	1 ÷ 3	11 ÷ 13	29 ÷ 33	-	<1	<1 ppm	flammable / toxic
5	9 ÷ 29	100 ÷ 300	2.1 ÷ 2.8	0.4 ÷ 5	52 ÷ 58	<2	12 ÷ 15	26 ÷ 30	-	<1	<1 ppm	flammable / toxic
6	8 ÷ 28	80 ÷ 300	2.2 ÷ 2.9	0.2 ÷ 4	48 ÷ 54	<10 ppm	11 ÷ 16	25 ÷ 31	-	3 ÷ 4	<1 ppm	flammable
7	7 ÷ 27	30 ÷ 60	1.4 ÷ 2.1	0.5 ÷ 6	70 ÷ 76	<10 ppm	16 ÷ 21	0.1 ÷ 0.9	-	4 ÷ 5	<1 ppm	flammable

* All flows are in Nm^3/h relative to a production of 1 Nm^3/h of hydrogen.

Table 8: *Configuration 2 - SR with PrOX - Indicative relative size of relevant components*

Config. ref.	Description	Relative size
A	Desulphurization unit	+
B	Reformer	++/+++
C	High-temperature WGS	+/++
D	Low-temperature WGS	+/++
E	Preferential oxidation reactor	+

4.1.3 Configuration 3 – Small to medium scale steam reforming of natural gas with PSA

This third layout is an alternative option, very similar to the previous one and significantly diffused in practical applications. Due to the small or medium scale of the plant, the desulfurization technology adopted is again a cold one, based on adsorption. On the other hand, if the hydrogen purity requirements are not very strict, a small PSA purification system is appropriate; moreover, as mentioned in the large scale layout description, this solution allows to design the WGS section with both LT and HT reactors or with a single HT WGS, simplifying the control system and the flow scheme. The off-gas produced by hydrogen purification contains a large amount of fuel (mainly CO) and therefore it is convenient to recycle this stream in the reformer reactor burners.

The resulting layout is shown in Figure 8.

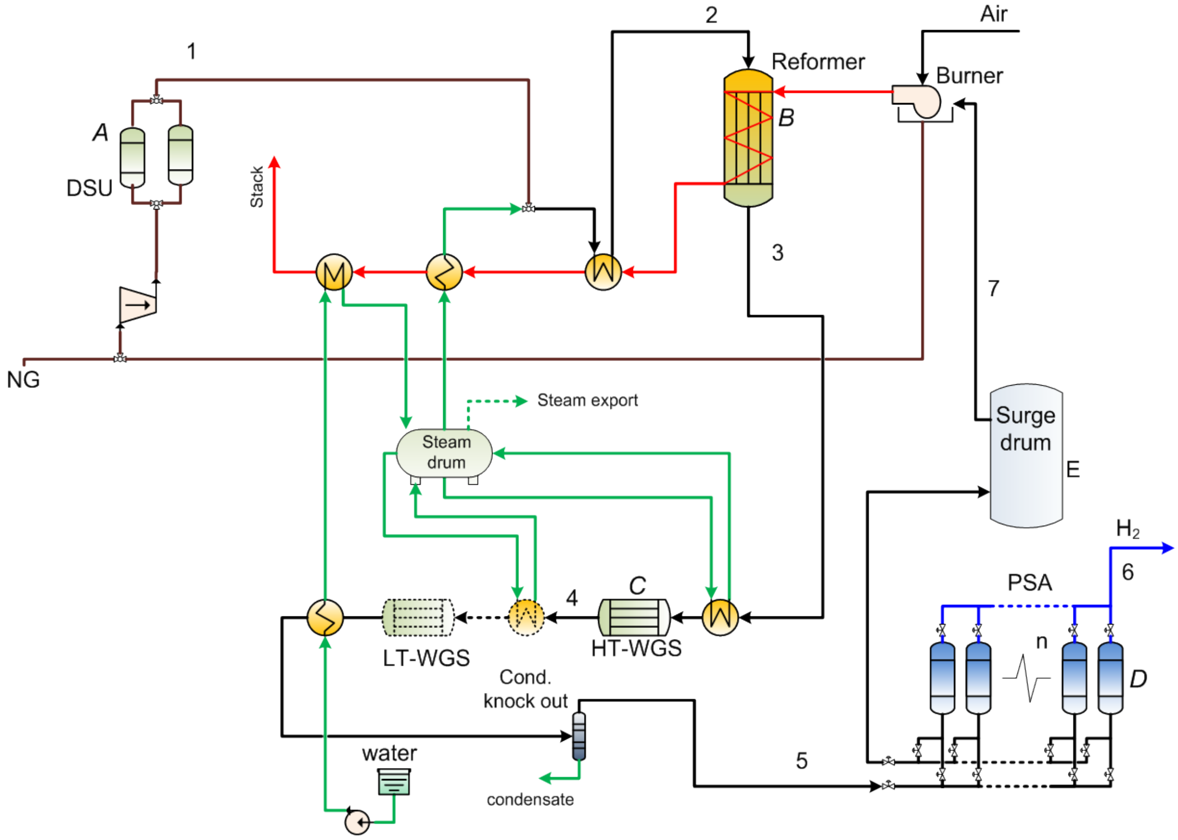

***Figure 8:** Configuration 3 - Steam reforming of natural gas with PSA*

Table 9 and Table 10 summarize common operational conditions and main components relative size for this kind of plant.

***Table 9:** Configuration 3 - SR with PSA - Operating conditions*

Point	P	T	F	Composition (% molar)								Notes
	[bar$_a$]	[°C]	[*]	C_xH_y	H_2	CO	CO_2	H_2O	O_2	N_2	H_2S	
1	16 ÷ 36	10 ÷ 40	0.37 ÷ 0.41	94 ÷ 100	-	-	<2	-	<0.1	<5	<1 ppm	flammable
2	16 ÷ 36	500 ÷ 700	1.4 ÷ 2	20 ÷ 28	<1	-	<1	72 ÷ 80	-	<1	<1 ppm	flammable
3	13 ÷ 33	800 ÷ 920	2.1 ÷ 2.8	0.4 ÷ 5	45 ÷ 48	7 ÷ 9	5 ÷ 7	35 ÷ 39	-	<1	<1 ppm	flammable / toxic
4	11 ÷ 31	400 ÷ 440	2.1 ÷ 2.8	0.4 ÷ 5	51 ÷ 55	1 ÷ 3	11 ÷ 13	29 ÷ 33	-	<1	<1 ppm	flammable / toxic
5	10 ÷ 30	30 ÷ 60	1.4 ÷ 1.9	0.6 ÷ 7	73 ÷ 79	2 ÷ 4	16 ÷ 18	0.1 ÷ 0.9	-	<1	<1 ppm	flammable / toxic
6	9 ÷ 29	30 ÷ 60	0.9 ÷ 1.4	<0.1	purity up to-5.0	<0.2	<0.2	<0.1	-	<0.2	-	flammable
7	1 ÷ 1.5	10 ÷ 40	0.5 ÷ 0.8	2 ÷ 17	21 ÷ 42	6 ÷ 10	39 ÷ 60	0.3 ÷ 3	-	<0.6	-	flammable / toxic

* All flows are in Nm^3/h relative to a production of 1 Nm^3/h of hydrogen.

***Table 10:** Configuration 3 - SR with PSA - Indicative relative size of relevant components*

Config. ref.	Description	Relative size
A	Desulphurization unit	+
B	Reformer	++/+++
C	High temperature WGS	+/++
D	Pressure Swing Adsorption	+++
E	Surge drum	+++

4.1.4 Configuration 4 – Autothermal reforming

Autothermal steam reforming (ATR) differs from the previous described process due to the adoption of another heat source for the reforming reaction, provided by the combustion of a fraction of the processed fuel.

The hydrocarbon feed is introduced in the reactor and mixed with steam and a sub-stoichiometric amount of oxygen or air. Then, the ATR reactor consists of three different sections: combustion, thermal and catalytic zone.

In the first section of the reactor (combustion zone), a turbulent flame provides heat for the subsequent endothermic reaction. In the subsequent zone (thermal zone), the steam reforming and water gas shift reaction start due to the high temperature; finally, reactions are completed in the third zone on a catalytic bed. The catalyst is usually alumina-supported Ni.

This system can work at much higher pressures (up to about 18 ÷ 70 bar) than the classical fired tubular steam reforming because of the absence of thermal and mechanical stresses in the reactor tubes. The operating temperatures are also much higher (above 1000 °C) and good conversion can be reached with lower steam to carbon ratios. Typically, the resulting H_2/CO ratio is lower than in the steam reforming process.

Air feeding is economically convenient in comparison with oxygen one, but leads to a large amount of nitrogen in the product that has to be removed (with the exception of hydrogen used for ammonia production).

The resulting plant is more compact than the tubular steam reformer, but when using an oxygen feeding it requires a rather complex air separation unit (ASU).

In the following we consider the case of a large scale application, with oxygen-fed ATR.

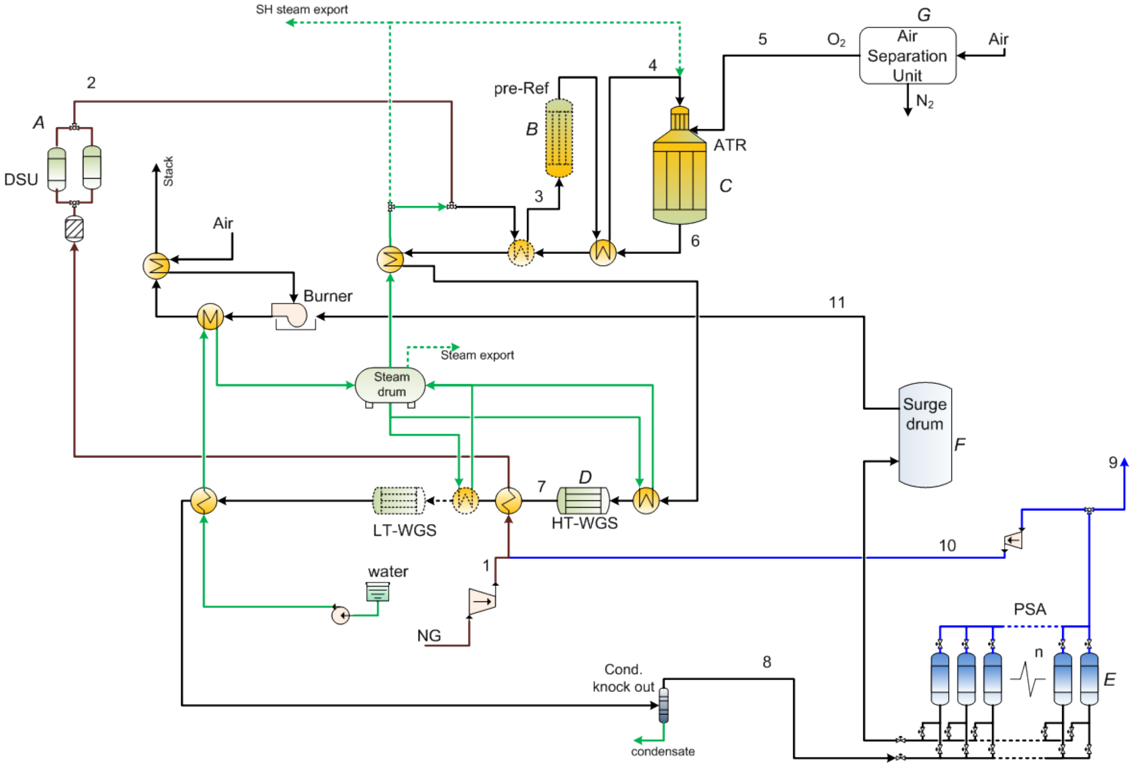

Figure 9: *Configuration 4 - Autothermal reforming of natural gas*

In Table 11 and Table 12, common operational conditions and main components relative size of this kind of plants are summarized.

Table 11: *Configuration 4 - ATR - Operating conditions*

Point	P	T	F	Composition (% molar)								Notes
	[bar$_a$]	[°C]	[*]	C_xH_y	H_2	CO	CO_2	H_2O	O_2	N_2	H_2S	
1	17 ÷ 70	120 ÷ 150	0.37 ÷ 0.41	94 ÷ 100	-	-	<2	-	<0.1	<5	<1	flammable
2	16 ÷ 69	300 ÷ 400	0.37 ÷ 0.41	94 ÷ 100	<3	-	<2	-	<0.1	<5	<1 ppm	flammable
3	16 ÷ 69	500 ÷ 600	1.4 ÷ 2.0	30 ÷ 45	<1	-	<1	51 ÷ 70	-	<1	<1 ppm	flammable
4	16 ÷ 69	600 ÷ 700	1.5 ÷ 2.1	28 ÷ 43	6 ÷ 11	<0.1	1 ÷ 3	42 ÷ 65	-	<1	<1 ppm	flammable
5	20 ÷ 75	160 ÷ 200	0.3 ÷ 0.5	-	-	-	-	-	92 ÷ 95	2 ÷ 5	-	highly reactive
6	12 ÷ 66	950 ÷ 1050	2.0 ÷ 2.8	<1	42 ÷ 45	9 ÷ 15	5 ÷ 10	30 ÷ 35	-	1 ÷ 2	<1 ppm	flammable / toxic
7	10 ÷ 64	400 ÷ 440	2.0 ÷ 2.8	<1	50 ÷ 55	2 ÷ 5	15 ÷ 20	20 ÷ 26	-	1 ÷ 2	<1 ppm	flammable / toxic
8	9 ÷ 63	30 ÷ 60	1.3 ÷ 1.8	<1	68 ÷ 75	1 ÷ 3	21 ÷ 28	0.1 ÷ 0.9	-	1 ÷ 2	<1 ppm	flammable / toxic
9	9 ÷ 29	30 ÷ 60	0.9 ÷ 1.4	<0.1	purity up to- 5.0	<0.2	<0.2	<0.1	-	<0.2	-	flammable
10	10 ÷ 37	30 ÷ 60	<0.02	<0.1	purity up to- 5.0	<0.2	<0.2	<0.1	-	<0.2	-	flammable
11	1 ÷ 1.5	10 ÷ 40	0.5 ÷ 0.8	2 ÷ 17	21 ÷ 42	6 ÷ 10	39 ÷ 60	0.3 ÷ 3	-	<0.6	-	flammable / toxic

* All flows are in Nm^3/h relative to a production of 1 Nm^3/h of hydrogen.

Table 12: *Configuration 4 - ATR - Indicative relative size of relevant components*

Config. ref.	Description	Relative size
A	Desulphurization unit	+
B	Pre-reformer	++
C	ATR reactor	++/+++
D	High-temperature WGS	+/++
E	Pressure Swing Adsorption	+++
F	Surge drum	+++
G	Air separation unit	+++

4.1.5 Configuration 5 – Partial oxidation

The partial oxidation (POx) is another major commercial route for hydrogen production. This process is based on a combined feeding of fuel and oxygen (or air), theoretically without steam addition, in proportions that grant the conversion in a mixture of H_2 and CO, according to reaction (4). However, water has to be fed in the process in order to sustain the pre-reforming and the WGS reactions if required.

The ratio of oxygen to carbon (O/C) is controlled in order to maximize the yield of CO and H_2, while maintaining an acceptable level of CO_2 and residual methane. The overall process is exothermic and can be carried out catalytically or not. This technology differs from the previous ones because of the absence of a specific burning zone; the combustion takes place in the catalytic zone together with the reforming reactions. Moreover it can be operated without steam addition.

Two solutions can be adopted: a catalytic and a non-catalytic one. The non-catalytic process (POX) operates at very high temperatures (1100÷1500 °C) and can utilize any feedstock; the catalytic process (CPO or CPOX) works at lower temperatures (600÷900 °C) and is suitable for lighter hydrocarbons. The first one has been commercially practiced for decades in refineries, in order to utilize the heavy residues (high in sulphur and heavy metals and otherwise very difficult to process). However, natural gas is the preferred feed from the technical point of view and can be used to produce hydrogen competitively in POX/CPO plants. The high-temperature stream at the reactor outlet can be a problem for the heat exchangers and has to be cooled.

In the catalytic section, a number of reactions take place (partial and complete combustion, steam reforming and water gas shift reactions) and typically reach the chemical equilibrium. An issue is the temperature control in the reactor that can locally exceed 1000 °C due to the initial very high rate of reaction of partial and complete combustion (reaction (3) and (4)). Different solution for the catalyst (materials, shape, ...) are currently under development to improve the performances and the lifetime.

Both air and oxygen feeding solutions can be adopted, where the first one reduces the investment costs but generates nitrogen diluted hydrogen.

Figure 10 shows the layout of a NG partial oxidation plant; the adopted configuration considers a pure oxygen feeding (with ASU). As evident, the conceptual layout is essentially identical to the ATR.

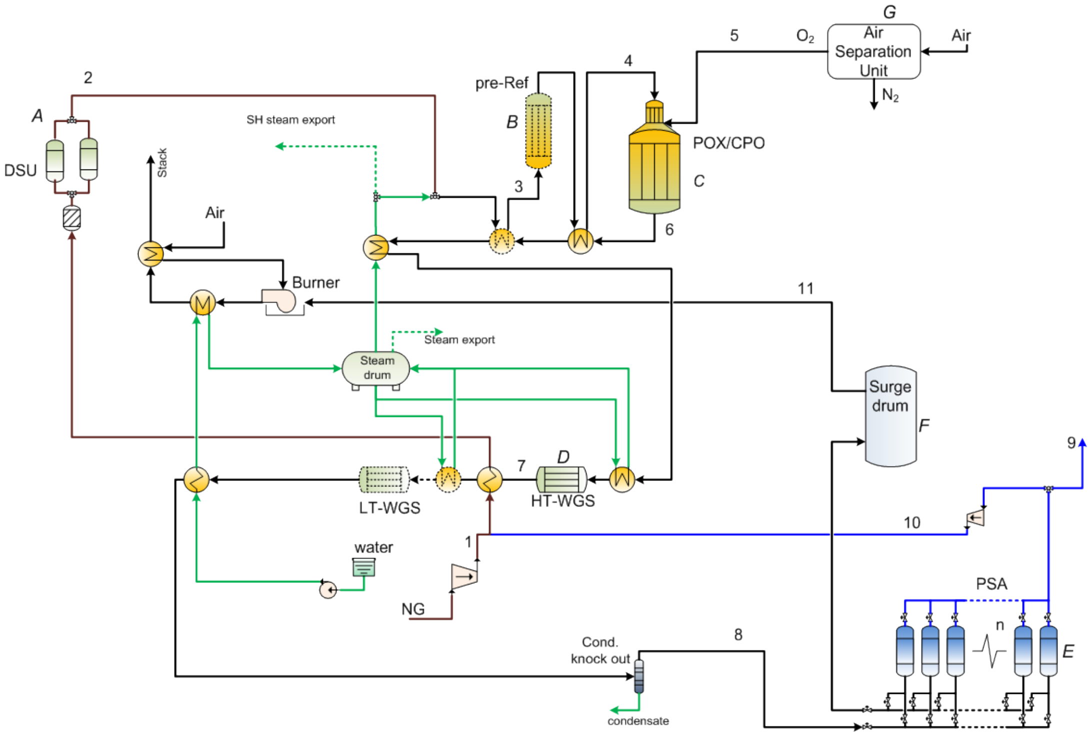

Figure 10: *Configuration 5 - Partial oxidation of natural gas*

Table 13 summarizes common operational conditions of a CPO plant. The values refer to a plant where both a pre-reforming unit and one or more WGS reactors are included, in order to process a heavier feedstock and to improve the conversion of CO to H_2.

Table 13: *Configuration 5 - POX - Operating condition*

Point	P	T	F	Composition (% molar)								Notes
	[bar$_a$]	[°C]	[*]	C_xH_y	H_2	CO	CO_2	H_2O	O_2	N_2	H_2S	
1	17 ÷ 37	120 ÷ 150	0.37 ÷ 0.41	94 ÷ 100	-	-	<2	-	<0.1	<5	<1	-
2	16 ÷ 36	300 ÷ 400	0.37 ÷ 0.41	94 ÷ 100	<3	-	<2	-	<0.1	<5	<1 ppm	-
3	16 ÷ 36	300 ÷ 500	0.61 ÷ 0.83	42 ÷ 68	<1	-	<1	33 ÷ 50	-	<3	<1 ppm	-
4	16 ÷ 36	600 ÷ 700	0.65 ÷ 0.86	20 ÷ 35	15 ÷ 40	1 ÷ 7	3 ÷ 8	20 ÷ 45	-	<3	<1 ppm	flammable
5	20 ÷ 45	160 ÷ 200	0.10 ÷ 0.14	-	-	-	-	-	92 ÷ 95	2 ÷ 5	-	highly reactive
6	12 ÷ 32	700 ÷ 1100	0.95 ÷ 1.31	<1	30 ÷ 55	10 ÷ 20	2 ÷ 6	15 ÷ 30	0	<2	<1 ppm	flammable / toxic
7	10 ÷ 30	400 ÷ 440	0.95 ÷ 2.8	<1	50 ÷ 55	2 ÷ 5	15 ÷ 20	10 ÷ 20	-	<2	<1 ppm	flammable / toxic
8	9 ÷ 29	30 ÷ 60	0.82 ÷ 2.5	<1	68 ÷ 75	1 ÷ 3	21 ÷ 28	0.1 ÷ 0.9	-	<2	<1 ppm	flammable / toxic

Point	P	T	F	Composition (% molar)								Notes
	[bar$_a$]	[°C]	[*]	C_xH_y	H_2	CO	CO_2	H_2O	O_2	N_2	H_2S	
9	5 ÷ 15	30 ÷ 60	0.9 ÷ 1.4	<0.1	purity up to-5.0	<0.2	<0.2	<0.1	-	<0.2	-	flammable
10	10 ÷ 37	30 ÷ 60	<0.02	<0.1	purity up to-5.0	<0.2	<0.2	<0.1	-	<0.2	-	flammable
11	1 ÷ 1.5	10 ÷ 40	0.5 ÷ 0.8	2 ÷ 17	21 ÷ 42	6 ÷ 10	39 ÷ 60	0.3 ÷ 3	-	<0.6	-	flammable / toxic

* All flows are in Nm^3/h relative to a production of 1 Nm^3/h of hydrogen.

In case of a plant that adopt the POX technology, no catalyst is present in the reactor; as a consequence, the temperature in the POX unit can reach values above 1300 °C that are required by the reaction as stated before. The outlet stream (6) has to be cooled with additional water before the heat exchangers in order to avoid damages. Water in stream 6 is required by the further steps of WGS and therefore fed upstream; in case of absence of CO converters, this kind of plants can be operated with a very low ratio 'H_2O to carbon' at the POX/CPO reactor inlet, nominally in the range 0÷0.15. The resulting ratio H_2/CO is lower (about 1.6÷1.9).

In all the cases, the ratio between the oxygen provided and the CH_4 in the feeding at the reactor inlet is about 0.6÷0.8 in order to grant the energy required by the endothermic reactions.

Table 14 presents a comparison of the relative size of main components.

Table 14: *Configuration 5 - POX - Indicative relative size of relevant components*

Config. ref.	Description	Relative size
A	Desulphurization unit	+
B	Pre-reformer	++
C	Partial oxidation reactor	++/+++
D	High-temperature WGS	+/++
E	Pressure Swing Adsorption	+++
F	Surge drum	+++
G	Air separation unit	+++

4.2 Production from solid fuels

Solid fuels are largely available with limited costs and therefore represent a valid alternative to more conventional hydrogen sources (i.e. natural gas for steam reforming). Coal and biomass are the most reasonable solutions from this point of view; anyway, the processes described in the following can be applied to refinery scraps and other heavy residues, which up to now represent one of the most experimented application. The product is a synthesis gas (mixture of different species, among which H_2 and CO); it could be directly used in an integrated plant for electricity generation or has to be treated in order to obtain a pure hydrogen flow. This kind of plants can be classified among the large scale ones (above 20.000 Nm^3/h) and their typical efficiencies (about 50÷75 %) are low in comparison with steam reforming technologies.

Two technologies are currently available to process solid fuels, gasification and pyrolysis, that are based on different physical principles.

Gasification involves non-catalytic partial oxidation according to a general reaction scheme in the form:

$$C_\mathrm{n}H_m + \frac{\mathrm{n}}{2}\mathrm{O}_2 \leftrightarrows \mathrm{nCO} + \frac{\mathrm{m}}{2}H_2 \qquad (7)$$

that proceeds together with other reactions that depends on the species present in the feeding (e.g. carbon complete and partial oxidation, steam reforming, water gas shift, methanation reactions, thermal decomposition). A substechiometric oxidant feed is typical of this technology, as described further below. The ratio H/C can vary in a wide range according to the specific fuel adopted and, as a consequence, influences the composition of the syngas product and the optimal operating conditions. Due to the impurities in the feeding that cannot be removed before the gasification (sulphur compounds, ash, heavy metals), the adoption of catalysts is impossible and the reactors are operated at high temperatures (above 900 °C) in order to improve the reaction rate; as a consequence, the outlet composition is very similar to the thermodynamic equilibrium one. An efficiency loss is due to carbon particles (*soot*) formation that can be improved by local conditions in the reactor; this phenomenon could be avoided by a fast and strong mixing of the feeding streams that nevertheless is not an industrial practice due to technical issues. Other unwanted products are sulphur and nitrogen compounds that has to be removed to preserve downstream catalytic units and to reduce the environmental impact.

Different reactor configurations identify the currently available technologies, among which the main ones are:

- *fixed bed*, in which the solid feed has a slow downward motion due to gravity, while the gases (oxygen and water vapour) flow counter-current. The outlet gas temperature is usually low (about 500÷600 °C) while very high temperatures can be reached in the middle section of the reactor (above 1500 °C). Operating pressures are in the range 25÷30 bar. In this case the particle size of the feeding is not an issue (up to 50 mm in diameter particles are allowed).
- *fluidized bed*, in which the feeding gas flow forms a suspension of the solid particles in the reactor; the mixing of the reactants is very strong and the heat and mass exchange improved. In order to grant a correct operation of the system, the size of the particles must be controlled (up to 10 mm) and a preliminary treatment of the solid charge could be required. In order to avoid melting and coalescence of the ashes that could cause the de-fluidization of the bed, operating temperatures are lower than the ones in fixed bed configuration (up to 1100 °C for coal, up to 950 °C for biomass). Pressures up to 30 bar are tolerated. Limestone can be added directly in the reactor in order to remove the sulphur with high efficiency.
- *entrained bed*, in which the oxidant flow and the solid are fed in co-current from the top of the reactor; the residence time is very short (few seconds) and therefore high temperatures (above 1300 °C) are required to obtain the required conversion rate. In this case the thermal conditions are uniform along the reactor. Typical operating pressures are in the range 20÷80 bar. The solid feed has to be fine-grained (hundreds of micron in diameter); in practice, also liquid or gaseous feeding could be treated with this technology.

Among the described solutions, the one typically applied in coal and biomass gasification is the entrained bed due to its higher conversion rate, fuel flexibility and control simplicity; it requires a preliminary milling of the solid feed and an efficient heat recovery from the high temperature products.

Either pure oxygen or air can be adopted as oxidant flow. In the first case, plant components are smaller and a lower thermal input (i.e. hydrocarbon feed consumption) in the reactor is required due to the absence of the large amount of nitrogen that the air solution implies. However, the production of pressurized pure hydrogen is a energy intensive process and a significant fraction of the plant consumptions; this is anyway the most common solution.

Pyrolysis differs from gasification due to the absence of any oxidant directly fed to the reactor; indeed, the solid feed is thermally decomposed. Conventional pyrolysis works at 700÷900 °C and its major products are char and syngas. It’s a process currently adopted for waste and biomass treatment. The required input of energy is typically applied indirectly, through the walls of the reactor; anyway the pyrolysis process could take place into gasification reactors, too. In fact, after the complete oxidant consumption in the first gasification section, the reaction proceeds through thermal decomposition in a oxidant-free zone of the reactor.

4.2.1 Configuration 6 - Gasification

The gasification plant scheme (Figure 11) described in this chapter is an example of the most common technology for coal gasification, but it can be applied with minor changes to any of the previously listed feedstock, including refinery residues which are probably the most frequent fuel used in nowadays existing large-scale plants.

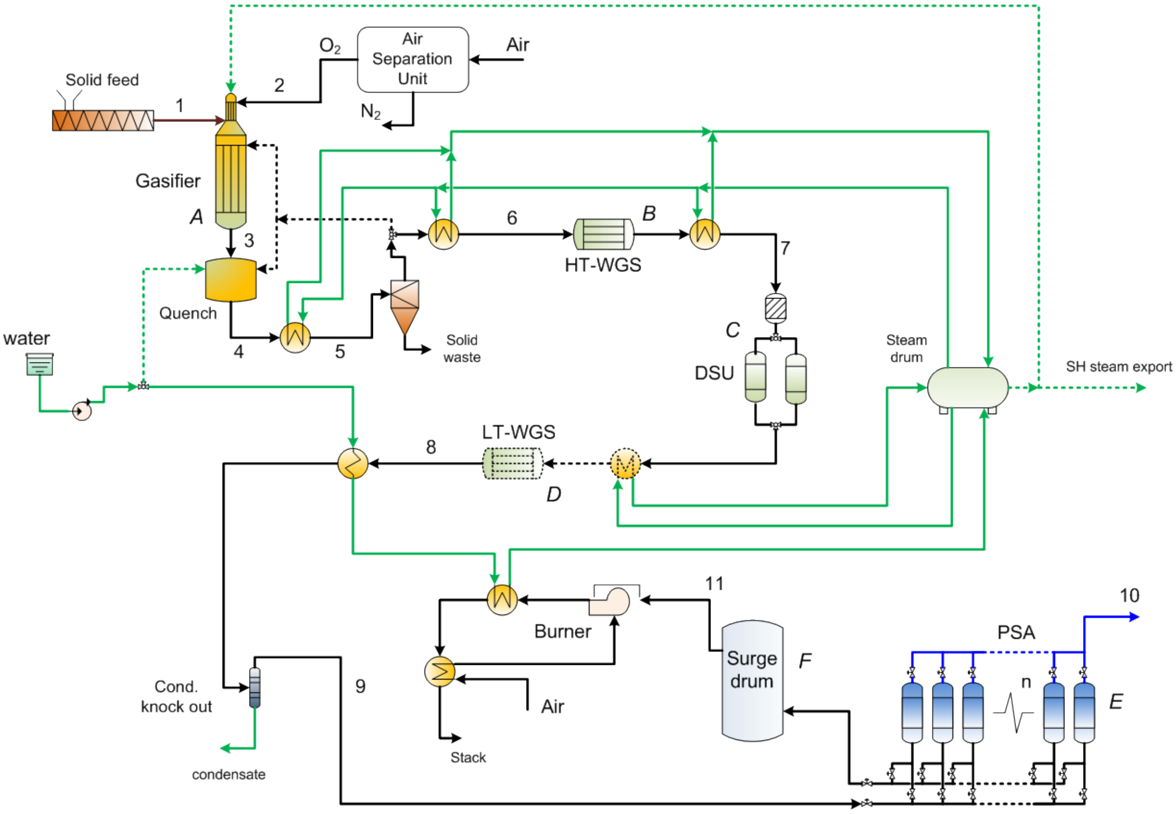

__Figure 11:__ Configuration 6 - Gasification of solid fuels.

A milling or fuel preparation section is usually included before the reactor to reach the particle size required by the gasification process. Two solutions can be adopted to feed the solid into the reactor: a discontinuous “lock-hoppers” system or a continuous “water slurry” system. In the first case the solid is put into a hopper that is pressurized with a gas (usually nitrogen) and then discharged into the reactor; the second technology feeds a mixture of pulverized solid fuel and water (“slurry”). The addition of nitrogen or water is useful for maximum temperature control.

As mentioned before, the reactor can be fed either with air or pure oxygen; Figure 11 shows the oxygen case in order to evidence the presence of the plant section required for oxygen production (ASU).

A critical plant section is the one downstream the gasification reactor, where the products are progressively cooled down. Different solutions can be adopted. First of all, the gas products can be cooled (down to about 900 °C) in a radiative heat exchanger (“syngas coolers”); the high temperature and the high sulphur content in the stream are not compatible with a traditional convective heat exchanger. A cheaper solution is to dilute the products with cold gas flow recirculated from a downstream section (“syngas quench”). Otherwise, cooling can be carried out by liquid water injection (“water quench”) up to saturation, resulting in a more effective process thanks to the high water vaporization heat, with a larger temperature drop; on the other hand, this is a drawback for the subsequent heat recovery and steam production (yielding a lower steam pressure). After this first cooling step, a second step is carried out by traditional convective heat exchangers. Heat recovery is generally very important in terms of plant global efficiency; however a detailed description of heat integration with other processes (including the applications within power plants) is very case-dependent and beyond the scope of this work.

At gasifier outlet, the stream contains solid particles (“fly ash”); most of them are separated by the water quench where adopted, but in any case a solid separator (cyclones, scrubbers or electrostatic precipitators) is included before the convective heat exchangers and the catalytic reactors (WGS), whose surfaces would be otherwise damaged by the particles.

A significant difference with respect to hydrogen production from gaseous or liquid feeding is the removal of sulphur compounds. Direct removal of sulphur compounds in the gasification reactor can be carried out only in fluidized bed gasifiers by means of limestone addition within the reactor. In the other cases, a desulphurization unit (DSU) is introduced downstream the reactor, with the same working principles described for the case of steam reforming process (section 4.1.1).

The water gas shift section converts the large amount of CO in the syngas to hydrogen; they can be separated in two reactors according to operating temperature, with the same characteristics already described for the WGS reactors in hydrogen production plants operating with gaseous fuels. The low temperature WGS catalysts are very sensitive to sulphur poisoning and therefore they are arranged downstream the DSU unit; according to the requirement of the final hydrogen purification section, WGS section can be arranged with only the high temperature reactor.

Table 15 shows indicative ranges for the plant operating conditions, that can vary significantly according to the feedstock and to each technology as described before.

Table 15: *Configuration 6 - Gasifier - Operating condition*

Point	P	T	F	Composition (% molar)								Notes
	[bar_a]	[°C]	[*]	C_xH_y	H_2	CO	CO_2	H_2O	O_2	N_2	H_2S	
1	23 ÷ 82	60 ÷ 100	**	coal + nitrogen (lock-hoppers)								
2	25 ÷ 85	160 ÷ 200	**	<1	-	-	-	-	92 ÷ 95	<5	-	highly reactive
3	20 ÷ 80	500 ÷ 1400	1.1 ÷ 3.1	<1	20 ÷ 40	40 ÷ 60	1 ÷ 20	2 ÷ 8	-	<10	<1	contains fly-ashes
4	18 ÷ 78	300÷400[a] 800÷900[b]	1.5 ÷ 4.0	<1	17 ÷ 40	35 ÷ 60	1 ÷ 20	2 ÷ 30	-	<10	<1	contains fly-ashes
5[c]	17 ÷ 77	450 ÷ 650	1.5 ÷ 4.0	<1	17 ÷ 40	35 ÷ 60	1 ÷ 20	2 ÷ 30	-	<10	<1	contains fly-ashes
6	15 ÷ 75	250 ÷ 450	1.5 ÷ 4.0	<1	17 ÷ 40	35 ÷ 60	1 ÷ 20	2 ÷ 30	-	<10	<1	flammable / toxic
7	14 ÷ 74	150 ÷ 350	1.5 ÷ 4.0	<1	37 ÷ 55	10 ÷ 40	20 ÷ 40	2 ÷ 20	-	<10	<1	flammable / toxic
8	10 ÷ 70	100 ÷ 200	1.5 ÷ 4.0	<1	40 ÷ 70	1 ÷ 10	25 ÷ 50	1 ÷ 5	-	<10	<1ppm	flammable / toxic
9	9 ÷ 69	30 ÷ 60	1.4 ÷ 3.8	<1	42 ÷ 73	1 ÷ 11	26 ÷ 52	0.1 ÷ 0.9	-	<10	<1ppm	flammable / toxic
10	5 ÷ 65	30 ÷ 60	0.9 ÷ 1.2	<0.1	purity up to- 5.0	<0.2	<0.2	<0.1	-	<0.2	-	flammable
11	1 ÷ 1.5	10 ÷ 40	0.5 ÷ 2.9	2 ÷ 5	21 ÷ 50	6 ÷ 12	39 ÷ 60	0.3 ÷ 3	-	<0.6	-	flammable / toxic

* All flows are in Nm^3/h relative to a production of 1 Nm^3/h of hydrogen.

** Inlet solid flow highly depends on the nature of the feeding and on its composition; maximum oxygen flow is about 20÷30% of the stoichiometric.

[a] Temperature in case of complete quench. The further heat exchanger can be avoided.

[b] Temperature in case of partial quench.

[c] In case of total quench, this point coincides with 4.

Table 16 presents a comparison of the relative size of main components.

Table 16: *Configuration 6 - Gasifier - Indicative relative size of relevant components*

Config. ref.	Description	Relative size
A	Entrained flow reactor	++/+++
B	High-temperature WGS	+/++
C	Desulphurization unit	+
D	Low-temperature WGS	+/++
E	Pressure Swing Adsorption	+++
F	Surge drum	+++
G	Air separation unit	+++

4.3 Production from electricity

Hydrogen production from electricity is based on the water electrolysis process, according to the water splitting reaction:

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2 \qquad (8)$$

that requires a DC electrical input. The reaction can be split in two steps (water reduction and oxidation of the intermediate ions) that take place separately on two metallic electrodes, where the two gases (hydrogen and oxygen) are generated; an electrolyte is interposed between the electrodes in order to allow the intermediate ions to flow. The nature of this electrolyte and of the ions distinguishes and classifies the different electrolysis technologies. The electrodes materials are usually studied in order to catalyse the reactions and improve the efficiency of the process.

The thermodynamics of the process is improved at higher temperature, while working with water at higher pressures requires a higher electrical input but allows obtaining an already pressurized hydrogen flow, reducing or eliminating (for low pressure applications) the necessity of compressors - typically very energy demanding - downstream the electrolyser. Therefore, a large research effort is presently made in order to solve the mechanical and practical issues that limit the operating temperature and pressure.

Two different technologies are currently available on the market, that differ for the nature of the intermediate ions and therefore of the electrolyte interposed between the electrodes. The first one is the *alkaline electrolyser* in which the electrolyte is an aqueous solution of an alkali (usually potassium or sodium); the electrolyte is liquid and circulates in the system with the feeding water. The alternative is the *PEM electrolyser* (Polymer Electrolyte Membrane or Proton Exchange Membrane) in which the electrodes are separated by a solid polymeric electrolytic layer. In the following both of them will be analyzed in detail, in order to evidence their features and the common operational conditions.

In both the cases the system is essentially composed by a stack of cells, in which the reaction takes place, and by some auxiliary devices. A typical configuration of the whole system is shown in Figure 12.

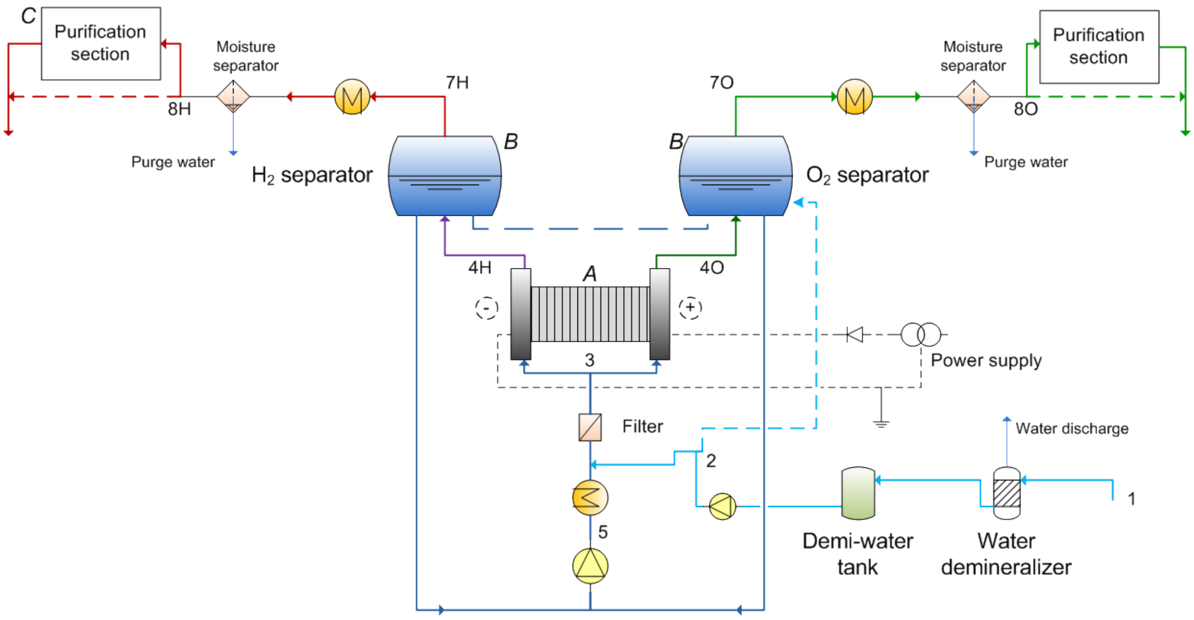

Figure 12: *Electrolysis system configuration.*

The main feedings are demineralized water and electricity. The main component is the stack (A) composed of a large number of cells; its size varies depending on the production required. For large scale plants, many stacks can be connected in parallel with common auxiliaries in order to reach the required production level. In fact, electrolysis system are completely modular and in principle the same scheme can be easily extended to any plant size.

The internal connection of the electrolysis cells in the stack can be in parallel (monopolar electrodes) or in series (bipolar electrodes). The first configuration makes each cell electrically independent from the next; as a consequence, the component is more reliable and the maintenance easier. In the bipolar configuration the single electrode is both the positive pole of a cell and the negative of the next; this leads to more compact stacks.

Depending on the customer requirements, the oxygen generated in the process can be directly vented in air; in this case the right section of the scheme (indicated by “O” in stream labels) is no more present.

The purification section can be present or not, according to the requirements on hydrogen purity. Without purification, a hydrogen purity of about 99.9 % can be reached, thanks to the absence of contaminants in the system feeding (demineralised water). The presence of the purification section can lead to very high purity (99.999 % or grade 5.0) removing residual water and oxygen traces. Figure 13 shows a typical configuration for the purification section.

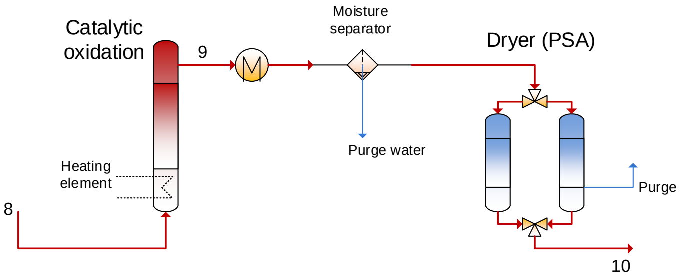

Figure 13: *Detail of "Purification section" in electrolysis systems configuration*

After an electrical heating, the hydrogen current passes through a catalytic bed that activates the combustion of the residual traces of oxygen. The current is than cooled and the condensed water removed. In order to avoid the use of sophisticated cooling systems, the residual water is removed by means of absorption beds, whose number depends on the gas flow, that are operated cyclically in absorption/regeneration. Regeneration is carried out by means of a pressure swing cycle and a flow of recirculated pure hydrogen.

The system requires an electric power input which is proportional to the plant size (in terms of hydrogen production rate). The electrical section, that basically includes a transformer (AC/AC) and a rectifier (AC/DC) to generate the DC current consumed by the electrolysis stack, can assume a significant role in the balance of plant. Usually power electronic components are located in a separate cabinet in order to guarantee safety.

4.3.1 Configuration 7 - Alkaline electrolyser

Alkaline electrolysers represent a very mature technology that is the current standard for large-scale electrolysis, due to the large number of installed units in operation (the first is reported to have entered service in 1902 [7]) and due to the proved performances in terms of durability, reliability and safety [8]. Thanks to the modularity of the electrolysis technology, hydrogen production plants based on alkaline electrolysers are available from low to high hydrogen outputs (e.g. >10.000 Nm^3/h for large installations coupled with hydroelectric plants). Larger systems are currently operated at atmospheric pressure, while in case of medium scale systems, also pressurized units (up to 30 bar) are available on the market. The single electrolysis stack is usually rated for some hundreds of Nm3/h at atmospheric pressure, while pressurized units are currently smaller (at most 10÷15 Nm^3/h); nevertheless, a large number of them can be put in parallel to reach higher production. Alkaline electrolysers usually operate with efficiencies in the range of 40 ÷ 80 %[1] [8]. A list of main manufacturers and available systems can be found in [8] and [9].

In this systems, the anode and cathode materials are typically nickel-plated steel and steel respectively. The electrolyte is a liquid based on a highly caustic KOH solution in water, or more rarely a NaOH solution. The concentration of the alkali usually ranges between 25 $\%_w$ and 30 $\%_w$ in order to minimize the ohmic resistance of the electrolytic and in order to improve the performances. The charge carrier is the hydroxide ion (OH^-) that is exchanged between the electrodes through the electrolyte.

With reference to the previous scheme (Figure 12 and Figure 13), the operational conditions of an alkaline electrolyser are listed in Table 17.

Table 17: *Configuration 7 - Operational condition of alkaline electrolyser*

Point	**P**	**T**	**Vol. Flow**	**Mass Flow**	**Composition (% molar)**				**Notes**
	[bar_a]	**[°C]**	**[Nm^3/h]**	**[kg/h]**	**H_2O**	**KOH**	**O_2**	**H_2**	
1	1	15	-	1.2 ÷ 2	100	-	-	-	-
2	1 ÷ 40	15	-	0.8 ÷ 1.2	100	-	-	-	-
3	1 ÷ 40	20 ÷ 50	-	20 ÷ 40	balance	10 ÷ 15	-	-	caustic / corrosive
4H	1 ÷ 40	70 ÷ 90	-	10 ÷ 20	78 ÷ 85	10 ÷ 15	-	4 ÷ 7	caustic / corrosive
4O	1 ÷ 40	70 ÷ 90	-	10 ÷ 20	80 ÷ 88	10 ÷ 15	2 ÷ 4	-	caustic / corrosive
5	1 ÷ 40	70 ÷ 90	-	20 ÷ 40	balance	10 ÷ 15	-	-	caustic / corrosive
6	1 ÷ 40	20 ÷ 50	-	20 ÷ 40	balance	10 ÷ 15	-	-	caustic / corrosive
7H	1 ÷ 40	70 ÷ 90	1.0	-	saturation	-	traces	balance	flammable
8H	1 ÷ 40	20 ÷ 40	1.0	-	saturation	-	<0.5	purity 2.5-3.0	flammable
9H	1 ÷ 40	50 ÷ 200	1.0	-	saturation	-	0 ÷ 0.001	purity 4.5-5.0	flammable
10H	1 ÷ 40	20 ÷ 40	1.0	-	<1ppm	-	0 ÷ 0.001	purity 4.5-5.0	flammable
7O	1 ÷ 40	70 ÷ 90	0.5	-	saturation	-	balance	traces	highly reactive
8O	1 ÷ 40	20 ÷ 40	0.5	-	saturation	-	99 ÷ 99.9	<1	highly reactive
9O	1 ÷ 40	50 ÷ 200	0.5	-	saturation	-	99.99 ÷ 99.995	<0.01	highly reactive
10O	1 ÷ 40	20 ÷ 40	0.5	-	<1ppm	-	99.99 ÷ 99.995	<0.01	highly reactive

* All flows relative to a production of 1 Nm^3/h of hydrogen

In addition, a membrane (*diaphragm*) is always interposed in the gap between the electrodes, in order to avoid dangerous mixing of the gas products in this narrow space, separating the gases evolving at the electrodes. However the OH^- ions must permeate through the diaphragm to reach the electrodes and keep the reaction on; therefore this

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[1] Efficiency defined as ratio between the produced hydrogen LHV and the electrical energy input

component is critical both for safety and for performances. To preserve its integrity it is very important to keep a correct pressure balance between the hydrogen and the oxygen side. The production rate is usually limited to 20 % ÷ 100 % of the nominal range, in order to prevent conditions that could potentially lead to the formation of flammable mixtures.

This system works at low temperatures due to the electrolyte nature (a water solution) and to materials requirements; in fact, the structure of the stack must resist at high pressure in a corrosive environment. R&D activities are made on materials improvement, also in order to rise the operating temperature, with advantages in terms of lower electrolyte resistance and higher efficiency.

One of the main safety issues is the presence of a large amount of caustic electrolytic solution circulating in the system (as a rule of thumb, about 100 litres in a 10 Nm^3/h system). In case of pressurized electrolysers a particular attention must be paid to the presence of this large inventory of pressurized liquid.

In Table 18, the sizes of the main components are compared.

Table 18: *Configuration 7 - Relative size of components (alkaline electrolyser)*

Config. ref.	Description	Relative size
A	Electrolytic cells stack	++/+++
B	Separation tanks	+/++
C	Purification section	+

Among the main components, the size of the electrical conditioning system is relevant; however, it’s usually separated from the electrolysis system in a different cabinet.

The water fed to the system has to be relatively pure (below 5 *μS/cm*) in order to preserve membrane from ions such as Cl or Ca which reduce its durability.

4.3.2 Configuration 8 - PEM electrolyser

PEM electrolyser technology is more recent than alkali electrolysis, and is originated from the R&D developed in the 1950s for compact and reliable space applications. Nowadays, electrolysers based on this technology are commercially available, usually for small and medium scale applications, although few manufacturing companies are on the market. Specific investment costs tend to be higher than for the alkaline technology due to the limited production capacity and still not solved lifetime issues. Production rate for a single stack is currently in the order of 30 Nm^3/h with efficiency in the order of 40 ÷ 60 %[2] [8]. Some companies are working on much higher sizes (about 1 MW).

In this case the electrolyte is a thin (below 0.2 mm, zero-gap configuration) polymeric membrane with a strongly acid character; this material, once properly wetted with water, can transport protons (H^+) through a ionic exchange mechanism. As for PEM fuel cells, the most commonly used membrane is the Nafion™ (*DuPont* trademark).

The electrodes are assembled on two layers: a support on which are built water feeding and gas removing channels, and a thin porous catalytic layer (platinum or iridium based). For this technology, the bipolar configuration is almost always adopted.

With reference to the previous scheme (Figure 12 and Figure 13), in Table 19 are listed common operational conditions of PEM electrolyser.

Table 19: *Configuration 8 - Operational condition of PEM electrolyser*

Point	P	T	Vol. Flow	Mass Flow	Composition (% molar)			Notes
	[bar$_a$]	[°C]	[Nm^3/h]	[kg/h]	H_2O	O_2	H_2	
1	1	15	-	1.2 ÷ 2	100	-	-	-
2	1 ÷ 85	15	-	0.8 ÷ 1	100	-	-	-
3	1 ÷ 85	20 ÷ 50	-	1.5 ÷ 10	100	-	-	-
4H	1 ÷ 85	50 ÷ 80	-	0.1 ÷ 5	0.1 ÷ 85	traces	4 ÷ 99.9	flammable
4O	1 ÷ 85	50 ÷ 80	-	1 ÷ 5	80 ÷ 88	2 ÷ 4	-	-
5	1 ÷ 85	50 ÷ 80	-	1.5÷ 10	100	-	-	-
6	1 ÷ 85	20 ÷ 50	-	1.5 ÷ 10	100	-	-	-
7H	1 ÷ 85	50 ÷ 80	1.0	-	saturation or traces	traces	balance	flammable
8H	1 ÷ 85	20 ÷ 40	1.0	-	saturation or traces	traces	purity 3.0-5.0	flammable
9H	1 ÷ 85	50 ÷ 200	1.0	-	saturation or traces	0 ÷ 0.001	purity 4.5-5.0	flammable
10H	1 ÷ 85	20 ÷ 40	1.0	-	<1ppm	0 ÷ 0.001	purity 4.5-5.0	flammable
7O	1 ÷ 85	50 ÷ 80	0.5	-	saturation	balance	-	highly reactive
8O	1 ÷ 85	20 ÷ 40	0.5	-	saturation	99 ÷ 99.9	<1	highly reactive
9O	1 ÷ 85	50 ÷ 200	0.5	-	saturation	99.99 ÷ 99.995	<0.01	highly reactive
10O	1 ÷ 85	20 ÷ 40	0.5	-	<1ppm	99.99 ÷ 99.995	<0.01	highly reactive

* All flows relative to a production of 1 Nm^3/h of hydrogen

Thanks to the internal structure of the cell (zero-gap) and to the small sizes allowed by operating at higher current densities with respect to the alkaline electrolysers, PEM electrolysers are very compact and could reach higher pressures (currently up to 85 bar);

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[2] Efficiency defined as ratio between the produced hydrogen LHV and the electrical energy input

nevertheless commercial models are designed for lower pressures (below about 30 bar) because of a lack of large-scale plant operational experience. The structural properties allow a differential pressure between the hydrogen and the oxygen side, although few models are designed for both hydrogen and oxygen recovery. On the other hand, the presence of the polymeric membrane limits the temperatures at about 80° C.

Due to the reduced permeability of the membrane to gases, this technology can be operated in the whole regulation range and can tolerate a current 20 % over the nominal for short time periods. In fact, the risk of formation of flammable mixtures in the cell is low. Moreover, the system shows a lower inertia than the alkaline one; fast changes in power regulation are therefore allowed.

In Table 20, the sizes of the main components are compared.

Table 20: *Configuration 8 - Relative size of components (PEM electrolyser)*

Config. ref.	Description	Relative size
A	Electrolytic cells stack	++
B	Separation tanks	+/++
C	Purification section	+

With respect to the alkaline electrolyser, the stack is more compact; however the size of power electronics devices is the same, while a higher purity of the feeding water is required (about 1 *μS/cm*).

4.4 Other non-conventional technologies

This part will provide a short list of non-conventional technologies, briefly addressing their principles and possible external references for in-depth analysis. The list could include the technologies (e.g. plasma reforming, thermolysis, photocatalytic water splitting, sulfur-iodine cycle), which are not considered in the previous sections.

Main sources for this section are “Hydrogen Fuel” [2] and “Hydrogen Technology” [3].

4.4.1 Carbon dioxide reforming of methane

An alternative to methane oxidation through water is the reaction with carbon dioxide (*dry reforming*)

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad \Delta \mathrm{H}^0_{298\,\mathrm{K}} = 247\ \mathrm{kJ/mol} \qquad (9)$$

whose equilibrium lead to a predominance of CO and H_2 at temperatures above 800 °C. The process is highly endothermic and produces a syngas with high CO/H_2 ratio (1:1). Practical implementation faces several economical and technical challenges. First of all, the pressure of common hydrogen production plants (20÷40 bar and higher) induces a non complete conversion of the reactants. Moreover, iron-, cobalt- and nickel-based catalyst, adopted in order to activate and promote the reaction, are sensible to carbon deposition, that is thermodynamically favoured by the operating conditions of this process.

The process requires a large amount of pressurized pure CO_2; in case of pure hydrogen production, a subsequent WGS section is required, with conversion of CO and steam into CO_2 and additional hydrogen. By this point of view the process finally releases all the CO_2 initially used in (8), thus not implying a reduction in global CO_2 emissions.

4.4.2 Steam-iron process

Steam-iron process is one of the oldest commercial methods for H_2 production, mainly adopted in small scale supply unit for industrial processes. In the last decades, it has been drop in favour of the more economical SMR process, but some interest is still present due to the intrinsic simplicity and flexibility for small-scale applications. It is based in principle on two subsequent reactions: (i) the reduction of iron oxide (Fe_3O_4) to wustite (FeO) by a reducing gas (i.e. hydrocarbons and syngas), followed by (ii) regeneration of iron oxide with steam. The real reaction scheme is much more complicated due to the large number of intermediate and parasitic reactions occurring at the high temperatures (600÷800 °C) featured by the process. Reactors can be either cyclic or continuous (fluidized bed) and usually pressurized (up to 70 bar). This process is an alternative considered for H_2 production from heavy hydrocarbons residues or from solid feedstock, when the fluidized bed solution is adopted.

4.4.3 Plasma reforming

This technology is based on electricity-assisted generation of syngas and hydrogen, and can be classified as thermal or non-thermal, oxidative or oxygen-free. This system is currently investigated to develop a supporting technique (e.g. as heat source for other downstream processes) for traditional systems (SMR, ATR, POX) or for mobile applications, due to its compactness and modularity and to the absence of catalysts. Anyway, the size of these systems is currently limited to laboratory scale.

Thermal oxidative plasma reforming consists of an electric arc that ionizes a high speed gaseous feedstock, thanks to the high temperatures (about 5000 °C). The presence of highly reactive species (active radicals and ionized species) catalyses the reactions that produce hydrogen. Against the rapid response, low feedstock consumption and absence of catalysts advantages, this technology require a large energy input and electrode cooling, in addition to some difficulties in high-pressure operation. The non-thermal alternative is based on particular configurations of the reactors designed in order to generate gliding electrical arcs; they produce local non-equilibrium conditions (highly reactive species), while the average temperature of the reactor is limited (400÷800 °C, depending on the reactor configuration and the contemporary processes).

Non oxidative processes can be assimilated to thermal decomposition described later in this section, where heat used to decompose the hydrocarbon molecules is provided by a high temperature plasma. A non-thermal process is considered also in this case, according to the principle of gliding electrical arcs; the high-temperature ionization is spatially limited to a small zone (around the arc), while the average temperature of the reactor is much lower. The absence of high-temperature oxygen prevents the oxidation of the electrodes, that consequently can be uncooled.

4.4.4 Photoproduction of Hydrogen from hydrocarbons

This technology targets the direct use of photons energy to break the chemical bounds of hydrocarbons and separate hydrogen. Due to the high dissociation energy of H-C bonds, an high energy UV radiation would be required; however, the equivalent wavelengths are not present neither in the solar spectrum nor in the artificial light from common UV lamps. Therefore, the dissociation has to be promoted with appropriate photocatalysts (Pt-, Ti-, Zn-, Cd-, Cu-based or organic compounds). Anyway, the useful range of wavelengths in common lights (solar and UV) spectrum remains very small (about 4÷5 %).

This technology is still mainly at a speculative stage or basic research (focusing on materials) stage. Promising applications can be found in the treatment of waste waters (organic contaminants decomposition) or complex structure hydrocarbons (aliphatic or aromatic chains).

Photobiological methods are also proposed, that take advantage of the photosynthesis carried on by algae or bacteria in order to split water, where the energy input is provided by the solar radiation.

4.4.5 Thermal decomposition of methane

Hydrocarbons thermally decompose at high temperature according to the general reaction:

$$C_nH_m \rightarrow nC + \frac{m}{2}H_2 \tag{10}$$

whose energy contribution depends on the nature of the hydrocarbon (higher energy required by saturated hydrocarbons). In the case of methane, one of the most stable molecules, the required energy is among the highest of all organic compounds. The process is favoured at low pressure, and the asymptotic maximum conversion at equilibrium is reached at temperatures above 800 °C. However, the process must be carried out at higher temperatures (> 1500÷2000 °C) in order to achieve an acceptable reaction rate.

When carried out in heterogeneous conditions (i.e. catalytic), the reaction shows a much lower activation energy and therefore seems to be more attractive. Literature data refer to nickel, iron, carbon or other transition metals (Co, Pd, Pt, Cr, Ru, Mo, W) as feasible catalysts. In this case the process can be carried out at temperatures in the order of 700÷1000 °C. Moreover, some molten metals (Pb or Sn) act like catalysts and could promote the decomposition reaction through gas bubbling.

This technology could be usefully applied with energy sources making available large amounts of heat (nuclear plants, solar concentrators, ...). Some demonstrations were set up, but this technology is nowadays far from a large commercial diffusion.

4.4.6 SOEC electrolysis

Due to thermodynamics of the process, electrical energy consumption for electrolytic water splitting at high temperatures is considerably much lower than the consumption at low temperature (which is the current state-of-art for alkaline and PEM electrolysers), while the fraction of energy required in form of heat increases. A typical technology, based on the results of high temperature fuel cells, is the SOEC (Solid-Oxide Electrolysis Cell) that works in the range of temperatures between 700 and 1000 °C. The principle is very much similar to the one presented before in the section about PEM electrolysis. However, some significant differences can be evidenced in addition to the higher temperatures. Water must be fed as steam, leading to auxiliary consumptions and to some complications in heat management. The ions that have to migrate through the electrolyte are oxygen ions (O^{2-}); as a consequence, the transfer mechanism is based on vacancies in the lattice structure of the oxide adopted as electrolyte (e.g. a zirconium oxide with appropriate dopants).

This kind of electrolytic cell is widely studied, but some issues related to reliability and lifetime, together with difficulties in control strategies, make them still not mature for commercialization.

4.4.7 Thermochemical water splitting

Thermochemical waters splitting consists in utilizing high temperature heat, together with a chemical substance catalysing the reaction, to split water into hydrogen and oxygen. It involves intermediate reaction steps using different possible chemical substances (for instance based on mixed iron oxides, zinc oxides, sulphur- and iodine-based acids) and water, where hydrogen and oxygen are finally separated from the water molecule ([10], [11]).

The energy required by this kind of processes must be supplied by high-temperature (about 700÷1000 °C) heat sources; these systems stem from research on heat recovery from high temperature nuclear plants (HTGR). Anyway, some applications could be found in coupling with concentration solar plants (CSP) or other low cost heat sources.

Among the proposed alternatives, the more developed concept is the sulphur-iodine process based on hydrogen iodine (HI), following a reaction pathway that includes sulphuric acid (H_2SO_4), iodine and sulphur dioxide; the central reaction works at about 850°C and is globally strongly endothermic.

The system consists of different reactors that take up the reaction steps in a closed loop. A rough estimation of the potential conversion efficiency is about 50% (in terms of hydrogen LHV vs. heat input), whereas the realization of these systems presents some practical issues linked to the highly corrosive nature of the involved substances and the separation of the reactants through the different reaction steps (fractional distillation), in addition to the high costs. Due to that, the technology seems to be very far from a real-scale demonstration stage.

Alternatively from thermochemical water splitting, the thermal water splitting process carried out by simple heating (thermal hydrolysis) without contribution of chemical reactions is also theoretically possible; nevertheless some technological issues make it almost unfeasible. First of all, the required temperatures are in the order of 2500 K, bringing about issues for materials selection and system management. Moreover, the product gases (oxygen and hydrogen) tend towards a fast recombination to form steam and therefore have to undergo a very fast cooling (in the order of hundreds of Kelvin in few milliseconds) or a high-temperature mechanical separation (through microporous ceramic membranes, centrifugal devices, ...), with many practical issues still to be solved.

5 Hydrogen transport and storage

At normal conditions (1 bar, 298.15 K), the density of gaseous hydrogen is 0.08238 kg/m^3 that in terms of volumetric energy content yields about 2.75 kWh/m^3. At the same conditions, gasoline density is about 720 kg/m^3 and volumetric energy content 8770 kWh/m^3. Therefore it is clear that for an efficient storage, hydrogen density should be increased; this aim can be addressed according to three basic strategies: increasing the pressure, decreasing the temperature or reducing the repulsion interaction between hydrogen molecules by means of bindings with other materials. The technical solutions and processes that will be discussed in the following sections are classified in Figure 14 and include:

- Hydrogen compression
- Compressed hydrogen storage (bottles and tanks) and transport
- Pipeline transport
- Hydrogen liquefaction
- Liquefied hydrogen storage and transport
- Solid storage in metal hydrides

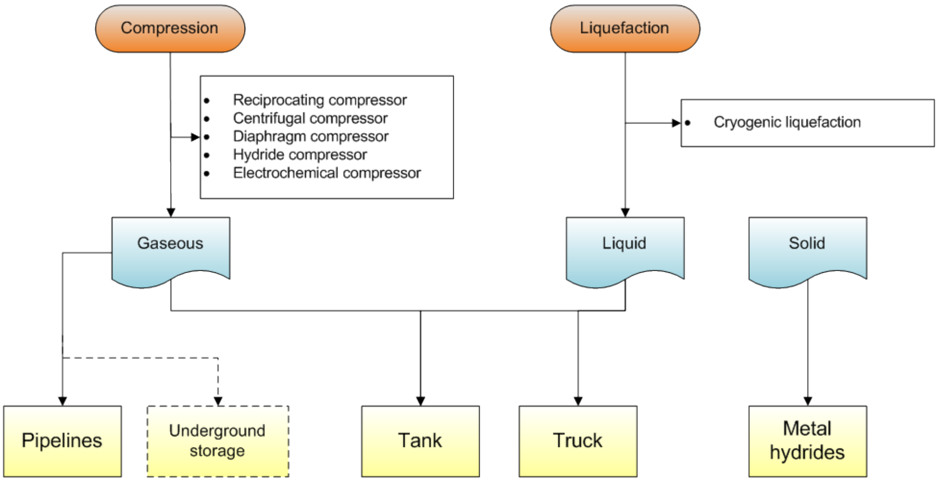

Figure 14: *Classification of the considered storage and transport technologies.*

High-pressure gas cylinders are the most common storage systems; they can be stationary tanks (i.e. for industrial applications) or packages of cylinders on trucks for transport. Recently developed cylinders can tolerate pressures up to 700 bar. At such high gas pressure, leakage by diffusion and the cyclic stability and fatigue-life of the cylinders are important drawbacks; nevertheless, this technology is relatively simple, cheap and rather well-established. As an alternative to tanks, gaseous hydrogen can be transported by means of pressurized pipelines at pressures up to 70-100 bar; currently, this solution is adopted in industrial areas and commonly covers only relatively short distances.

Liquid hydrogen is stored in cryogenic tanks at about 21 K at ambient pressure. The challenges for liquid hydrogen production and storage are improving the energy efficiency of the liquefaction process and the thermal insulation of the cryogenic storage vessels, in order to reduce the rate of hydrogen boil-off. As a consequence, this technology can be currently adopted in applications where costs are not the primary issue (e.g. space applications) and in which hydrogen is consumed within a rather short period of time after storage. Cryogenic tanks can be either stationary or wheel-mounted for transport.

Hydrogen can be adsorbed by different materials by means of Van der Waals interactions; the simultaneous presence of attractive and repulsive forces leads to a minimum energy equilibrium position for the hydrogen molecule in the adsorbent structure. This physical bond is very weak, therefore this phenomena is significant only at low temperatures (< 273 K). Materials with a large specific surface area like activated or nanostructured carbon and carbon nanotubes are possible substrates for physiorption; beside carbon-based structures, other nanoporous materials have been investigated for hydrogen adsorption (i.e. zeolites). The rather small gravimetric and volumetric hydrogen densities on carbon, together with the low temperatures required, are very significant drawbacks of this technology.

Hydrogen can be also bound with many metals, intermetallic compounds and alloys where in general it reacts to form mainly solid metal-hydrogen compounds; in these cases the chemical bond can be ionic, polymeric covalent, volatile covalent and metallic, according to the nature of the substances. Metal hydrides are very effective for storing large amount of hydrogen in a safe and compact way; nevertheless, in many cases their physical properties have still to be investigated in order to verify their realistic performances (i.e. stability, energy consumption and operating conditions).

A special case of gaseous hydrogen storage is the use of large underground cavities, similar to those now used to store natural gas. This technology has a large potential in terms of quantities of energy stored for extended periods. Two methods that are suitable are the use of salt caverns and empty aquifers. In Tees Valley (Texas, UK) a salt dome is used to store about 1000 tons of hydrogen for industrial uses [12].

In Table 21, the performances of common storage technologies in terms of specific storage capabilities are summarized.

Table 21: *Performances of typical storage technologies* [13]

	Gravimetric hydrogen density ***kg H_2 / kg system***	**Volumetric hydrogen density** ***kg H_2 / m^3 system***
pressure cylinder (500 bar, 25°C)	0.04	27
liquid hydrogen (1 bar, 20 K)	0.03 (1)*	40 (71)
physisorbed hydrogen (70 bar, 73 K)	0.02 (0.04)*	30
metal hydrides (1 bar, 25 °C)	0.012 (0.019)*	50 (110)
complex hydrides (1 bar, 150 °C)	0.04 (0.135)*	50 (120)
water (1 bar, 25 °C)	0.11	11

* in parenthesis is indicated the theoretical limit for the given material / technology.

Compression and liquefaction systems that are required to reach the operating conditions featured by each storage technology are described in the following sections.

5.1 Hydrogen compression

The compression of a fuel gas like hydrogen has in principle some similarities with the compression of another well-known fuel, which is natural gas. However, while natural gas compressors are a well-established technology, hydrogen compressors create significant challenges due to the smaller and lighter molecule, coupled with the higher specific volumes of hydrogen [2], which bring about issues related to leakages, larger compressor sizes and higher energy consumption.

The most important commercially available compression technologies are based on piston (or reciprocating) and rotary compressors, briefly described in the following paragraphs. These devices are similar to those adopted in natural gas compression, with some modifications in design and materials. Other solutions (centrifugal, diaphragm, hydride and electrochemical) are also addressed. In order to improve efficiency, the gas is usually cooled down between consecutive compression stages.

Figure 15 shows common operating ranges (capacity and pressure) of prevailing compressor technologies. The characteristics of each compressor are a function of the flow rate and pressure.

In comparison with natural gas compressors, issues related to sealing are complicated by the small size of the molecule and the low viscosity, requiring very specialized designs (special seals and very refined tolerances).

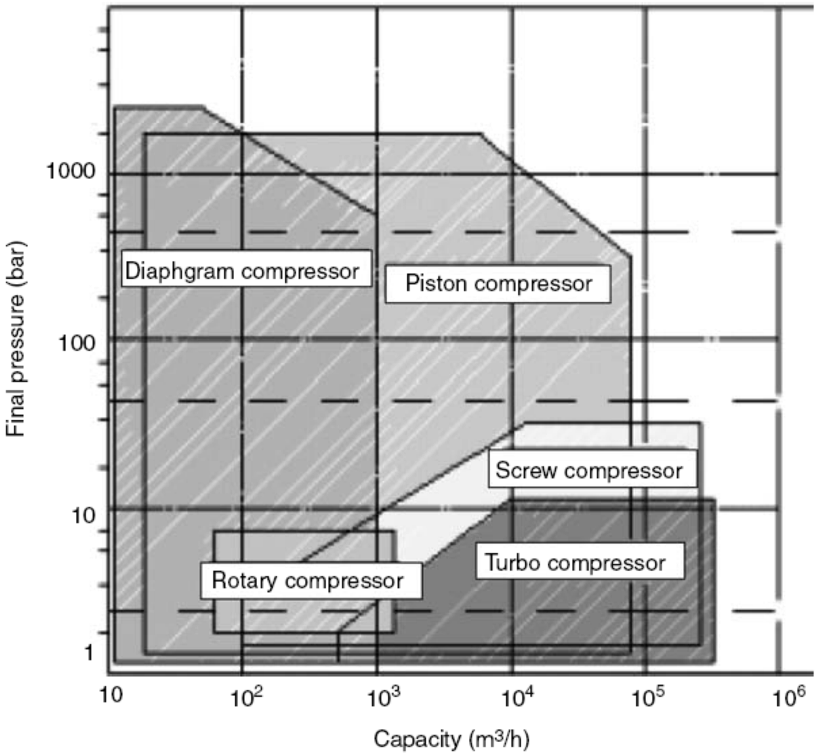

Figure 15: *Operating characteristics of various compressors* [14]

5.1.1 Mechanical compressors

This category includes different kinds of compressors:

- *Volumetric compressors*, based on the mechanical variation of the volume of a finite chamber containing the gas; among them piston and rotary compressors are the most diffused, but screw compressors are also available.

- *Continuous flow compressors* (turbo compressors), based on a variation of the angular momentum caused by a deviation of the gas flow; they could take advantage of a variation of the radial position of the flow (centrifugal compressor) or not (axial compressors). The first class is suitable for lower mass flow rates and high pressure ratios, whereas the axial compressors are the best solution for large flow rates. However, when compared with natural gas turbo-compressors, the low molecular mass of hydrogen makes necessary to have a larger number of stages for the same pressure ratio. The larger number of stages makes more difficult to keep internal sealing, which requires improved refinement of tolerances and materials.

Oiled and oil-less lubrication types are available, the first with advantages in terms of hydrogen containment, the second with lower risks of contamination of the compressed flow. As typical for compressors working with a flammable fluid, mechanical compressors are usually driven by an electrical motor through a magnetic transmission.

5.1.2 Diaphragm compressors

Diaphragm compressors are a particular solution of piston compressors; the piston is isolated from the process fluid by a set of metal diaphragms. The piston moves a column of hydraulic fluid acting on the diaphragm that, as a consequence, displaces the process gas.

This system allows a higher compression ratio per stage in comparison with piston compressors and is compatible with all types of gases. The diaphragm prevents any contamination of the hydrogen and leakages into the atmosphere. Currently this solution is available for limited flows (up to about 2000 Nm^3/h); a single stage diaphragm compressor can pressurize hydrogen from 18 bar up to 400 bar. Careful design is mandatory to control deflection and inherent stresses of the metal diaphragm.

5.1.3 Hydride compressors

The metal hydride compressors are thermally powered systems that use the properties of reversible metal hydride alloys to compress hydrogen without contaminations. Operating conditions (i.e. temperature and pressure) in reaction beds during absorption and desorption are different (Figure 16) and can be used to obtain a compression effect. Due to the exponential dependence of the pressure on temperature, a large pressure increase can be obtained with moderate temperature increases.

Metal hydride compressors operate cyclically between two temperatures and therefore heating and cooling resources are required. Heat recovery from industrial processes increases the electrical efficiency which is otherwise very low in case of electrical heating. The low temperature heat source can be the ambient or water from a cooling system.

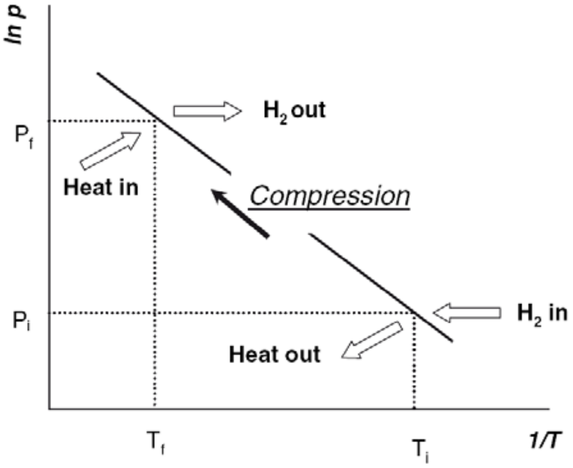

Figure 16: *Operation principle of a single-stage hydride compressor [3]*

For instance, a mixed metal alloy (usually AB_x where A is a rare earth or an alkaline earth metal, B is a transition metal) can take hydrogen up to 100 bar at 95 °C from a 20 bar and 20 °C gas input. Single-stage hydride compressors currently available present a maximum temperature limit of about 100 °C, above which the thermal degradation of the alloy leads to decreasing performances. Moreover, waste heat is usually available at low temperatures; as a consequence, higher temperature systems which could have higher efficiencies would be less effective in the exploitation of heat recovery sources. A series of compression modules can be adopted to reach high pressures, each one designed for a specific pressure range [3]. Outlet pressures up to 400 bar were demonstrated for particular hydride compressor operation [15], while more common commercial units typically compress hydrogen up to 200 bar.

Advantages of this technology are the absence of moving parts and the relatively limited sizes allowed by the high volumetric density of the alloys. Moreover, this solution is particularly attractive for high purity hydrogen because of the absence of sources of contaminations. They are compact, silent and require very little maintenance. However, they are a rather recent technology and are not proved on large scale systems. Another drawback is the high cost in comparison with traditional compressors.

5.1.4 Electrochemical compressors

This class of compressors is used for applications where a low mass flow rate has to be compressed to high pressures, due to the better performances in comparison with mechanical systems. The working principle is based on an electrochemical cell, composed of an anode, a membrane electrode assembly (MEA) based on wet polymeric membranes and a cathode ([16], [17]) as shown in Figure 17. The structure is similar to PEM fuel cells.

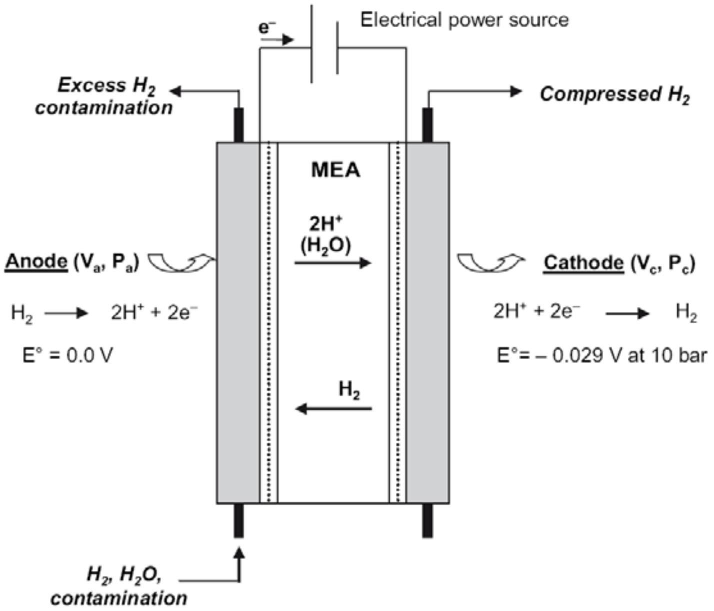

Figure 17: *Operation principle of a single-stage electrochemical compressor [3]*

A potential difference applied between the electrodes generates the oxidation of hydrogen on the anode to protons H^+ and their movement towards the cathode; on the cathode they are reduced to H_2 at higher pressure, if the cathode chamber is initially hermetically sealed and then maintained at high pressure. A multi-stage compression increase pressure from stage to stage, leading to the required final pressure. The humidification of the membrane is mandatory to maintain the ionic flow and therefore the efficiency of the system.

This system is selective to hydrogen and can be used in order to separate contaminants from the hydrogen flow. The absence of moving parts reduces wear, noise and energy intensity of the system; moreover, this system is very compact. The scale-up of this technology to large mass flows rates have still to be addressed in practical applications.

5.2 Compressed hydrogen storage (bottles and tanks) and transport

Hydrogen, as an industrial gas, is stored either as a compressed gas or as refrigerated liquefied gas. This last option is addressed further in section 5.5.

Gaseous hydrogen is usually stored in cylindrical or spherical geometry high pressure vessels. Four classes of pressurized vessels can be currently identified [18], whose main characteristics are summarized in Table 22:

- Type I, metallic vessels
- Type II, thick metallic liner hoop wrapped with a fiber-resin composite
- Type III, metallic liner fully-wrapped with a fiber-resin composite
- Type IV, polymeric liner fully-wrapped with a fiber-resin composite

All of these classes can be actually adopted for gaseous storage, according to pressure requirements and to a compromise between technical performances and costs. Type I vessels are the state-of-the-art for industrial gas storage, where weight and pressure are not limiting issues, but costs are relevant. In fact, this vessels are the cheapest and usually chosen for operating pressures around 200÷300 bar. Type II are the common solution for stationary applications at higher pressure. Type III and type IV are intended for portable applications, for which the weight is a relevant parameter. Recently, they have also begun to be used for hydrogen trailers.

Table 22: *Classification and characteristics of high-pressure vessels for gaseous hydrogen storage [18]*

	Type I	**Type II**	**Type III**	**Type IV**
Max pressure *[bar]*	up to 500	not limited	up to 350	up to 700
Cost performance	++	+	-	-
Weight performance	--	-	+	+
Mature technology	yes	yes	difficulties in pressure cycling tests for 700 bar	350 bar mature; 700 bar under development

A schematic of a typical high-pressure Type IV, C-fibre wrapped H_2 storage is shown in Figure 18.

Performances of the vessels are generally compared according to some indexes:

- weight performances (C_m), defined as the mass of H_2 stored divided by the mass of the vessel (%wt);
- volume performances (C_v), defined as the mass of H_2 divided by the external volume of the vessel (g/l);
- costs, for instance expressed with respect to the quantity of stored hydrogen (€/kg).

A first cause of failure of metallic vessels is the embrittlement of the steel: hydrogen atoms dissolution and trap in the material can lead to a premature crack and to the burst of the tank. Actually, a large effort in last decades was made in order to understand and prevent this phenomena and prevention rules for 200 bar steel vessels were defined.

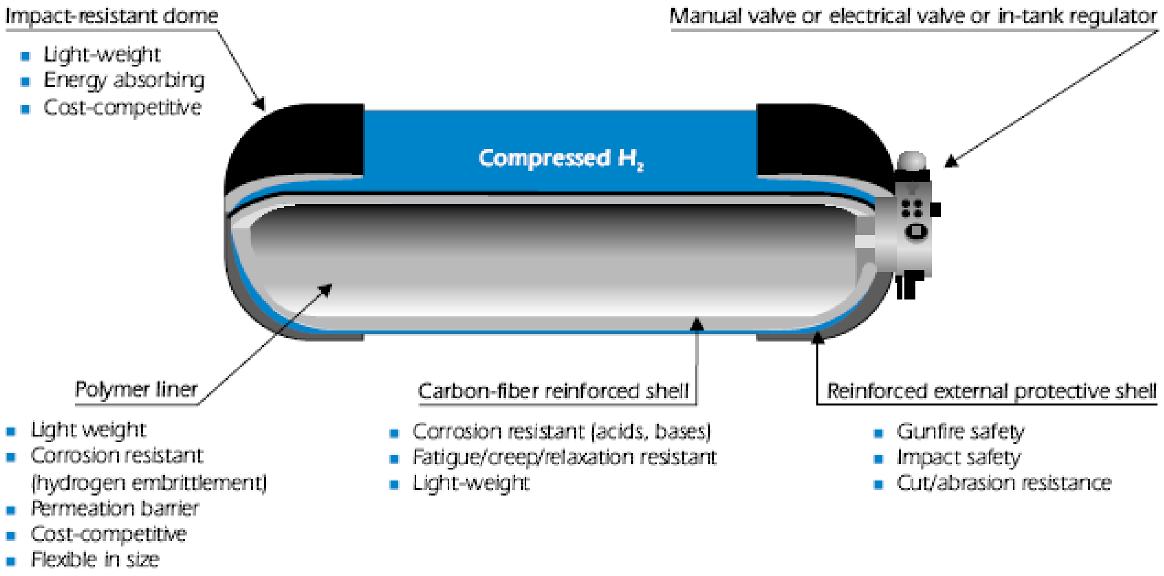

Figure 18: *Schematic of a Type IV vessel structure [19]*

An issue specific of Type IV vessel is the permeation of hydrogen through the polymeric liner; gas dissolution and diffusion in the polymeric matrix is an issue common to many gases, but they are enhanced by the small dimension of the hydrogen molecule. For safety reasons, the permeation shall be kept below fixed limits in order to avoid the presence of trapped hydrogen between the polymeric liner and the composite covering, which can cause the liner blistering or collapse.

For Type I, II and III both steel and aluminium alloys can be adopted; in case of Type IV tanks common fibres are glass, aramidic or carbon ones, where these last are favoured for very high pressures due to their mechanical properties. In the same way, various resins are available (polyester, epoxy, phenolic, ...), but the most used is epoxy resin due to its good mechanical properties and stability.

Due to these issues, specific case by case embrittlement and permeation tests shall be performed before the introduction of new designs or materials.

5.3 *Pipeline transport of gaseous hydrogen*

Currently, there is a quite significant amount of hydrogen pipelines mainly in Europe and USA. These ones include systems in the North Europe (mainly in The Netherlands, northern France and Belgium), Germany (Ruhr and Leipzig areas), UK (Teesside) and in North America (Gulf of Mexico, Texas-Louisiana, California); in all, total extension of the network is about 1500 km in Europe and 900 km in USA. Pipelines network predominantly serves petroleum refineries and chemical plants; therefore they are not subject to the technical issues related with the coupling of centralized and large-volume production with widespread distribution (variable flow and pressure). Currently adopted pipes materials are low to medium strength carbon steels and pressures are generally below 100 bar [20].

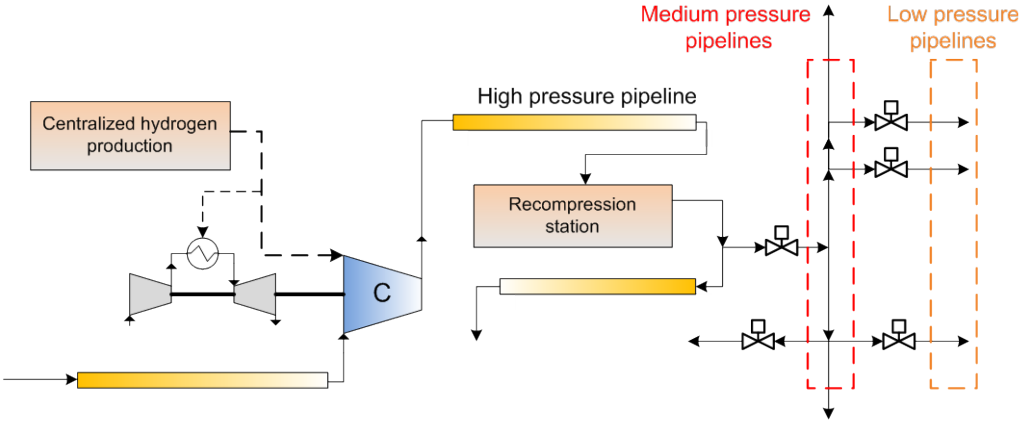

Figure 19: *Concept of hydrogen distribution pipeline infrastructure*

With respect to natural gas pipelines, seals, valves and fittings present more design troubles in order to avoid leakages. As a consequence, accurate materials choice and robust design have to be coupled with monitoring systems based on a large number of sensors.

Material challenges are linked with the embrittlement phenomena of steel pipelines that is currently extensively studied but not completely understood. High strength steel types with high manganese and carbon content are particularly vulnerable to cracking due to this phenomenon; a solution could be the use of thicker low strength steel and limit gas humidity (< 60 %). Moreover, at high pressure (> 100 bar) and temperatures (> 200 °C), H_2 could react with carbon and cause chemical steel erosion [20]. By contrast, at low pressures the choice of pipeline material is more flexible.

An indication of best practices in hydrogen pipelines design is provided by European Industrial Gases Association [21], based upon the combined knowledge, experience and practices of the major producers in Western Europe and North America adopting conservative criteria. This study considers the range of operating pressures 10 ÷ 210 bar as feasible for transport and distribution infrastructure.

Different approaches can be adopted to define the pipeline design in the case of a long-distance distribution grid comparable to the one of natural gas. In order to distribute an amount of energy comparable with current natural gas pipelines, without changes in standard diameters of pipes, an increase of the pressure to about 100÷150 bar would be required due to the different energy density of hydrogen [22]. Nevertheless, from an economical point of view, given an operating pressure and a pipe diameter, an optimum mass flow exists that minimizes the transport cost. Results given by this approach are presented in [23] and summarized in Table 23 for a reference pressure and reasonable pipe diameters.

Table 23: *Optimal mass flow rates in hydrogen and natural gas pipelines over a long distance distribution [23].*

Specie	**Medium diameter pipe**		**Large diameter pipe**	
	H_2	**NG**	**H_2**	**NG**
Inlet pressure	75 bar			
Distance	5000 km			
Tube diameter *[cm]*	59.2 (24”)		138.4 (56”)	
Compression stations	18		8	
Optimal mass flow *[kg/s]*	~ 14	~ 60	~ 85	~ 380
Energy (LHV) *[GW]*	~ 1.7	~ 3	~ 10.2	~ 19

According to the economical optimum, a dedicated hydrogen pipeline transports about 22÷24 % of the natural gas mass flow rate in similar conditions and therefore about 54÷57 % of the transported power (LHV basis).

As an alternative to the developing of a new dedicated hydrogen pipeline infrastructure, the upgrading of existing natural gas pipelines could be a feasible pathway; economical barriers to the development of a dedicated infrastructure (i.e. very high initial investment cost) are the justification to this approach. Some projects are currently investigating the consequences of injections of hydrogen in the natural gas grid in order to evaluate the effects on pipelines and on the final users; a volumetric concentration up to about 20 % hydrogen may require only modest modifications to the pipeline [24], while converting the network to deliver pure hydrogen would require more substantial modifications. The main issues raised by this approach are [25]:

- the durability of the transmission and distribution pipeline systems and of the end user infrastructure (diffusion into materials changes the mechanical properties);
- the gas quality management issues related to the gas delivery;
- the performances of end user applications;
- the effectiveness of current standards and regulations.

These aspects are diffusely addressed in the framework of the EU NaturalHy project [26].

5.4 Hydrogen liquefaction

In the early 1880s Wroblewski and Olszewski established the first low temperature laboratory, the Cracow University Laboratory in Poland, and succeeded in liquefying oxygen and nitrogen in a sufficient quantity to investigate their properties. However, when they attempted to liquefy hydrogen in 1884, they obtained only a mist of liquid droplets. It was Dewar, the inventor of the vacuum-insulated vessel, who obtained liquid hydrogen as a bulk at the Royal Institute of London in 1898. Through the years until the late 1940s, hydrogen liquefiers for continuous production became more and more common in laboratories but they never reached large scales and high efficiencies. The drive for the construction of industrial-size systems came in the early 1950s from the increasing demand of liquid hydrogen requested by the aerospace sector, for airplane and rocket propulsion, and by the nuclear sector, for deuterium production by cryogenic distillation.

Currently, hydrogen is utilized mostly in the gaseous form by the petrochemical, pharmaceutical, metallurgical, electronic and food industries, whereas in a lesser extent in the liquid form by the aerospace agencies. However, hydrogen transportation as a liquid is the most economical manner when large quantities are involved. Typically, large liquefiers are rated at 5-20 tpd per train (tons per day, the custom unit in the sector). Globally, the world capacity is 250-300 tpd.

The liquefaction of cryogenic fluids is commonly obtained exploiting an expansion based on the Joule-Thomson effect in a throttling valve.

The Joule-Thomson coefficient, μ_{J-T} [K/Pa], is defined as:

$$\mu_{J-T} = \left(\frac{\partial T}{\partial P}\right)_h$$

When μ_{J-T} is positive, an isenthalpic expansion produces a reduction in temperature and if the inlet temperature at the valve is low enough, after the expansion part of the fluid will be in liquid phase. The coefficient μ_{J-T} at ambient temperature for hydrogen is negative and turns positive only below 205 K (the maximum inversion temperature). Therefore, a precooling stage by liquid nitrogen (LN_2) is commonly used to chill hydrogen below that temperature. Nitrogen is the typical choice because it is cheap, available in large quantity, and not flammable.

Given this situation, there are two physical ways to cool hydrogen: (i) expansion without mechanical work extraction, i.e. simple throttling, and (ii) expansion with mechanical work extraction coupled with throttling [27].

The simplest way to liquefy hydrogen according to the first option is the Linde cycle with liquid nitrogen precooling (Figure 20a): the feed gas at ambient conditions is compressed and cooled by nitrogen, then expanded in the throttling valve; the liquid phase is the product, while the gas is recirculated to the compression section.

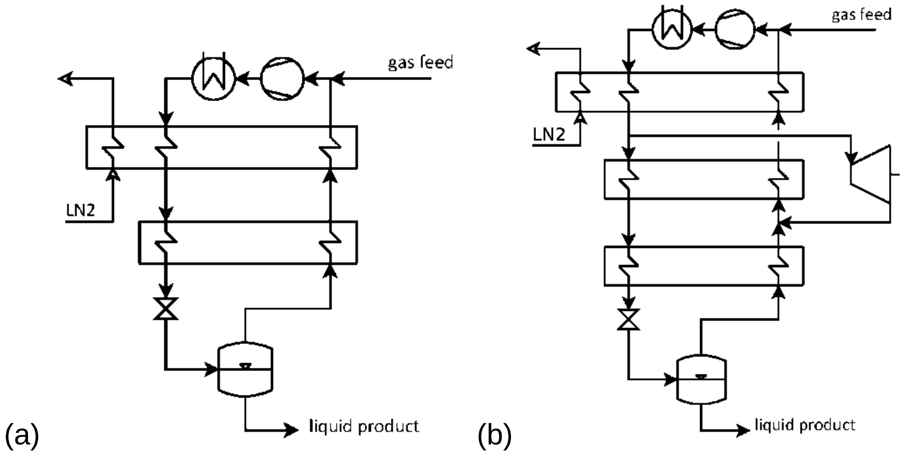

***Figure 20:** (a) Linde cycle with liquid nitrogen precooling; (b) Claude cycle with liquid nitrogen precooling.*

The second approach relies on the addition of an isentropic expansion (adiabatic process) with mechanical extraction of useful work from the gas stream. Since it is technically unfeasible to expand the fluid in a mechanical expander covering all the transformation from the gas phase to the liquid phase, the mechanical expander and the throttling valve are coupled in the liquefaction process named Claude cycle (Figure 20b). In the Claude cycle the feed gas is compressed, cooled in the first heat exchanger by the low pressure stream and then split in two streams: one is directly expanded by a machine (turbine or volumetric expander); the other is cooled in the second and third heat exchangers, then expanded in the throttling valve. The liquid is the product, the gas is recovered through the third heat exchanger, mixed with the cold stream from the expander and warmed up to the compression section.

The efficiency of the Claude cycle is higher than the Linde cycle thanks to energy extraction in the expander (in other terms, the process is more reversible than pure throttling), since only a portion of the stream passes through the valve. On the other hand, due to this last feature, the liquid yield after the valve is lower in Claude cycle. Maximum operating pressures are typically lower than in Linde cycle. Considering the whole liquefaction process, the specific production energy is about 1 kWh/l corresponding to a second law efficiency of about 20 % with reference to a reversible process.

Another issue in hydrogen liquefaction is connected to the fact that there are two forms of the hydrogen molecule H_2, which differ by the relative orientation of the spin of the nuclei ([28], [29]). Ortho-hydrogen has parallel spin, while para-hydrogen has anti-parallel spin. They have similar volumetric behavior and physical properties (critical temperature and pressure, density, saturation curve), but very different specific heat at constant pressure in ideal gas state, as explained by quantum mechanics, and thermal conductivity. At ambient temperature and above, the equilibrium composition is 75% orthohydrogen and 25% parahydrogen. This composition is named normal-hydrogen. At lower temperature, the composition shifts in favor of parahydrogen, the form with lower energy content, up to 100% parahydrogen when approaching the absolute zero, as shown in Figure 21.

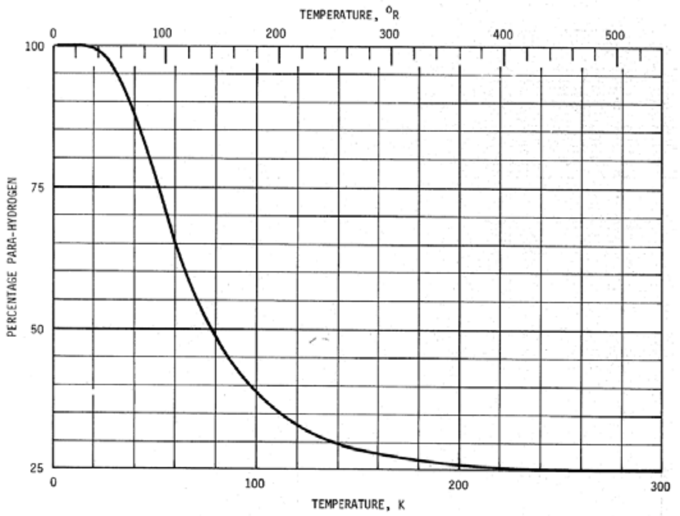

Figure 21: *Equilibrium percentage of parahydrogen [29]*

The ortho- to parahydrogen conversion is exothermic and the lower the temperature the higher the heat of conversion, as depicted in Figure 22.

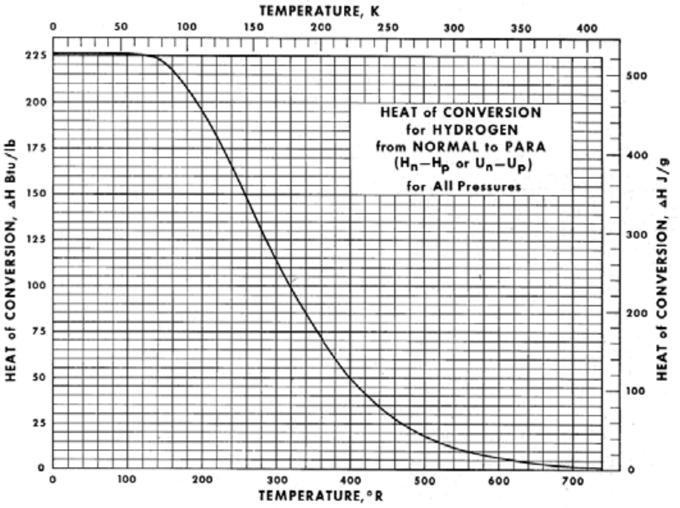

Figure 22: *Enthalpy (or heat) of conversion from normal- to parahydrogen [29]*

The ortho- to para-hydrogen conversion is very slow. Spontaneously it would take place in the storage tank with a relevant rate of evaporation of hydrogen due the large heat of conversion (527 kJ/kg to convert normal-hydrogen in parahydrogen) compared with the heat of vaporization (443 kJ/kg at Normal Boiling Point). To limit the evaporation losses, the conversion must be promoted by a catalyst during the liquefaction process. The catalyst can be a substance with magnetic properties like $Fe(OH)_3$, which is effective and inexpensive. The conversion can take place in three ways, as described in the following.

- Isothermal conversion: the reactor with the catalyst inside is immersed in a cryogenic fluid that takes out the heat of reaction by evaporation at constant temperature. The auxiliary fluids are typically liquid nitrogen for conversion at high temperature (around 80 K) and liquid hydrogen for conversion at low temperature (around 20 K).
- Adiabatic conversion: hydrogen flows in the reactor and warms up due the heat of conversion, then must be re-cooled in a heat exchanger.
- Continuous conversion: the catalyst is put inside the heat exchangers and the ortho-para composition is narrow to equilibrium conditions; the cold fluid takes away both sensible and reaction heat. This is the most efficient process because heat is removed at temperatures as high as possible [30].

5.4.1 Conventional liquefier configuration

A typical large-scale hydrogen liquefier is depicted in Figure 23 and related common operational conditions are summarized in Table 24.

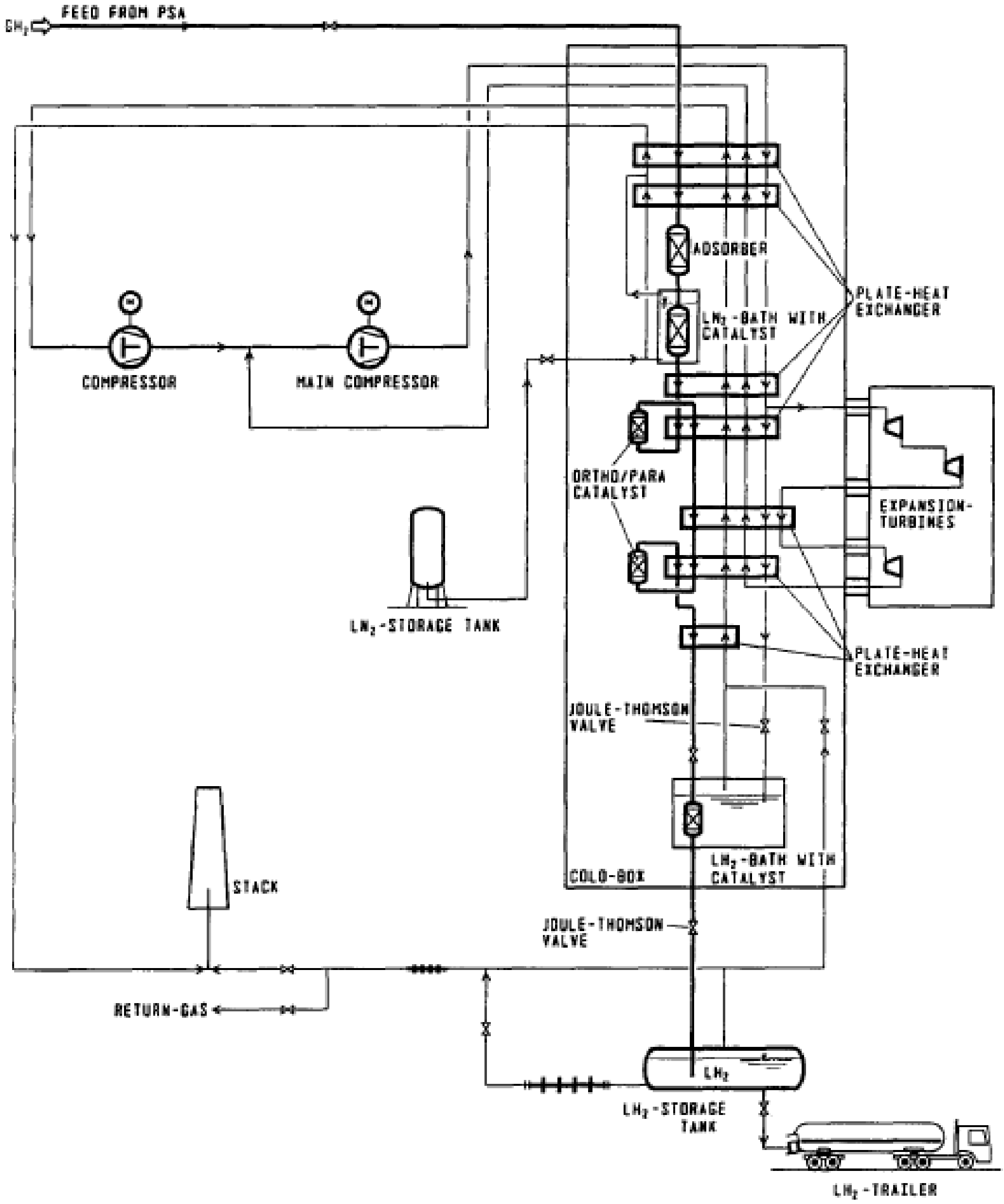

Figure 23: *Flow-scheme of Linde plant in Ingolstadt [31]*

The feed gas is high-purity normal-hydrogen at ambient temperature and about 20 bar. The operative pressure is supercritical (critical pressure = 12.96 MPa) to avoid the isothermal condensation at very low temperature that would require great power consumption at constant temperature to remove the condensation heat.

Table 24: *Technical data of the liquefier [31]*

Section	P [bar_a]	T [K]	Impurities
Feed gas	20	< 308	max 4 ppm
LH_2 product	1.3	21	< 1 ppm
Compression stages	1 ÷ 3 3 ÷ 22	n.a.	n.a.
Expansion - turbines	22 ÷ 3	80 ÷ 30	n.a.
Joule-Thompson valve	21 ÷ 1.2	30 ÷ 20	n.a.
LN_2 section	1.4	80 ÷ 300	n.a.

The core equipment of the plant is the “cold box”, a big cylinder with a vacuum annulus, similarly to a Dewar bottle, and multi-layer insulation to limit heat entrance from the environment. Within the cold box, there are the main heat exchangers and reactors. All the heat exchangers are vacuum-brazed aluminum plate-fin type; spiral-wound bath type heat exchangers are used only for isothermal steps.

The gas of the main stream enters the “cold box” and passes through a series of heat exchangers and reactors (two isothermal and two adiabatic in the example of Figure 23) before reaching the throttling valve. The liquid is then available after the valve at a pressure slightly higher than ambient (1.3 bar, at the corresponding saturation temperature, about 21 K) and with a high para-hydrogen content (>95%).

The liquefaction process can be divided in three stages:

- 300-80 K: liquid nitrogen precooling;
- 80-30 K: refrigeration by turbines in the Claude cycle;
- 30-20 K refrigeration and liquefaction by Joule-Thomson valves, both in the main stream and in the Claude cycle.

The liquid nitrogen bath has a twofold function: precooling the hydrogen while reducing the duty of the bottoming Claude cycle and removing the heat of the ortho-to-para conversion in the first isothermal reactor (80 K). The large quantity of liquid nitrogen (the mass ratio to the product is nearly 10) required is stored in a tank (1.5 bar) and after the heat exchange into the “cold box” the gaseous nitrogen is vented to the atmosphere. To enhance the purity of hydrogen below 1 ppm of contaminants there is an adsorber operating at the bath temperature.

The main cooling load is met by the Claude cycle, which uses hydrogen at a very high para-hydrogen content as working fluid. The ratio between the main line mass flow rate and Claude mass flow rate is around eight to ten. The aim of the Claude cycle is not to obtain LH_2 as product, but to produce the refrigeration needed to liquefy the hydrogen of the main stream. In the Claude cycle, from the maximum pressure (22 bar), after the nitrogen precooling, the stream is split into two flows. One flow (about 40%) is expanded (to 3 bar) by a series of turbines and then warmed up to ambient temperature while cooling the main stream and the other flow. The power obtained from turbines is small and thus simply dissipated by brakes. The other flow (the remaining 60%) is cooled down by the expanded hydrogen and then throttled (to 1.2 bar) to supply the liquid hydrogen bath, where it is immersed the final reactor of conversion operating on the main stream. The gas evaporated from the bath is mixed with the flash gas generated through the isenthalpic expansion on the main stream and recuperatively returns to ambient temperature. It is compressed, mixed with the stream from the turbines and compressed to the maximum pressure. The minimum pressures after the expansion by turbines or by throttling valve is variable to allow a good performance of the plant also during partial load operation.

Some variations can be found in other plants, where the Claude cycle may have two branches with different turbines, the working fluid is normal-hydrogen, completely separated from the feed hydrogen; on the main line the catalyst can be integrated in the heat exchangers.

Compressors and turbines, vacuum pumps, electrical motors and brakes are located in a dedicate building. Reciprocating machines with oil-free lubricating system are used in gas compression to avoid oil contamination. Turbines are located in satellite “cold boxes”, connected to the main cold box by flexible vacuum insulated lines. At current liquefaction plant sizes, they have a typical rotation speed of around 70000 rpm and use an oil system for the lubrication of the bearings. In cryogenic expanders also magnetic or gas (static or dynamic) bearings are used.

In the plant there are also PSA system and storage tanks for the cryogenic liquids, nitrogen and hydrogen. The liquid hydrogen tank has a vacuum insulation able to limit in current industrial plants at around 0.3% per day the evaporation losses. Thanks to its large volume, the tank acts as a buffer between the production rate and the market demand. Near the storage tank there are the stations to fill trailers, which are used to deliver the product to the customers.

Table 25 shows the indicative relative size of the components, classified according to the methodology previously described for hydrogen production technologies.

Table 25: *Liquefier - Relative size of components*

Plant section	Relative size
PSA	++
LN_2 tank	++/+++
LH_2 tank	++/+++
Cold box	++
Compression section	+/++
Expansion section	+/++

5.5 Liquefied hydrogen storage and transport

Cryogenic vessels have been commonly used for more than 40 years for storage and transportation of industrial and medical gases. In comparison with high pressure gaseous storage, the higher gas density at low pressure is a clear advantage, together with the reduction in walls thickness and vessels weight. On the other hand, cryogenic liquid hydrogen storage shall use high efficiency insulated vessels in order to maintain very low temperatures inside the tank, due to the fact that hydrogen has a low boiling point (about 20 K) at atmospheric pressure in comparison with other industrial gases (i.e. carbon dioxide, nitrogen). Insulated vessels are generally composed by an inner pressure vessel and an external protective jacket (Figure 24).

A perfect insulation is impossible, due also to the retaining structure and the pipe connections (filling and safety valves); a little amount of product is therefore always lost by vaporization (boil off) and has to be vented in order to maintain constant the pressure inside the vessel (pressure relief device). With state-of-the-art industrial insulation, typically around 0.4 % a day is lost from a 50 m^3 vessel, decreasing to about 0.2 % a day from a 100 m^3 storage thanks to the more favourable surface to volume ratio featured by larger tanks.

Currently, liquid hydrogen is transported on roads using trucks which can exceed a capacity of 60 m^3. The intercontinental transport of hydrogen could be carried out in liquid form using ships to some extent comparable to LNG vessels, although specialized with appropriate tanks and port facilities; nevertheless, realization of these concepts could take place only if the trade in liquid hydrogen would reach a very large scale.

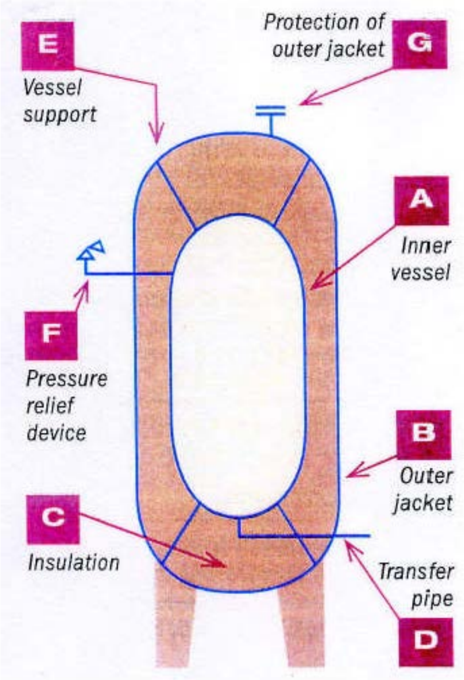

Figure 24: *Concept of insulated cryogenic vessels*

5.6 Solid storage in metal hydrides

Storage of hydrogen in solid materials has large potential due to the high volumetric density at low pressures (up to 30 bar), as shown in Figure 25. However, the gravimetric density is usually low and therefore this solution is suitable for small storages or for applications where the weight is not an issue. Among the solid storage techniques mentioned in the introduction of this chapter, metal hydrides seems to be the most promising in the near future.

In the simplest cases metal hydrides are ternary systems AB_xH_y where the element proportion can be adjusted in order to reach the desired properties. Some examples of this compounds are shown in Figure 25. The element A is usually a rare earth or an alkaline earth metal, while B is a transition metal; some well defined ratios *x* (B:A = 0.5, 1, 2, 5) lead to hydrogen to metal ratios up to 2 [32].

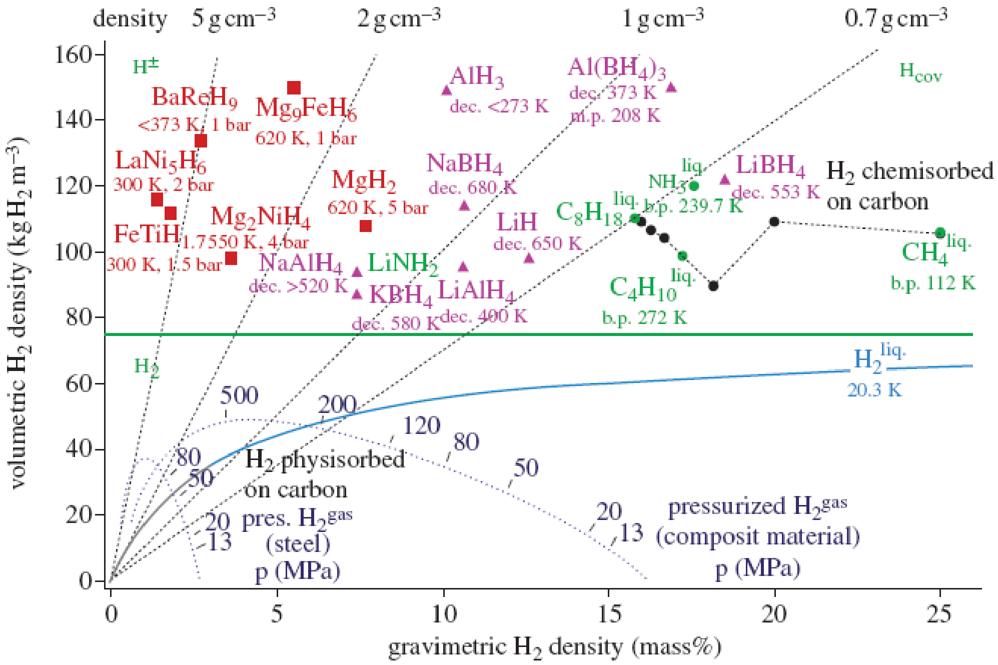

Figure 25: *Performances comparison of different classes of solid storage (metal hydrides, chemisorption and physisorption), conventional liquid and gaseous storage [13]*

A summary of the most important families of hydride intermetallic compounds is shown in Table 26.

Table 26: *Summary of most important families of intermetallic hydride compounds* [32]

Structure	Prototype materials
AB_5	$LaNi_5$
AB_2	ZrV_2, $ZrMn_2$, $TiMn_2$
AB_3	$CeNi_3$, YFe_3
A_2B_7	Y_2Ni_7, Th_2Fe_7
A_6B_{23}	Y_6Fe_{23}
AB	TiFe, ZrNi
A_2B	Mg_2Ni, Ti_2Ni

Metal hydrides can absorb large amount of hydrogen (hydrogen to metal ratios up to 2) without increasing their operating pressure thanks to a solid phase transition. The metal hydride formation is a strongly exothermal reaction that involves a significant heat evolution during hydrogen absorption; the same amount of heat has to be provided to the hydride in order to desorb hydrogen. This amount of heat is strongly related with the stability and the formation enthalpy of each compound.

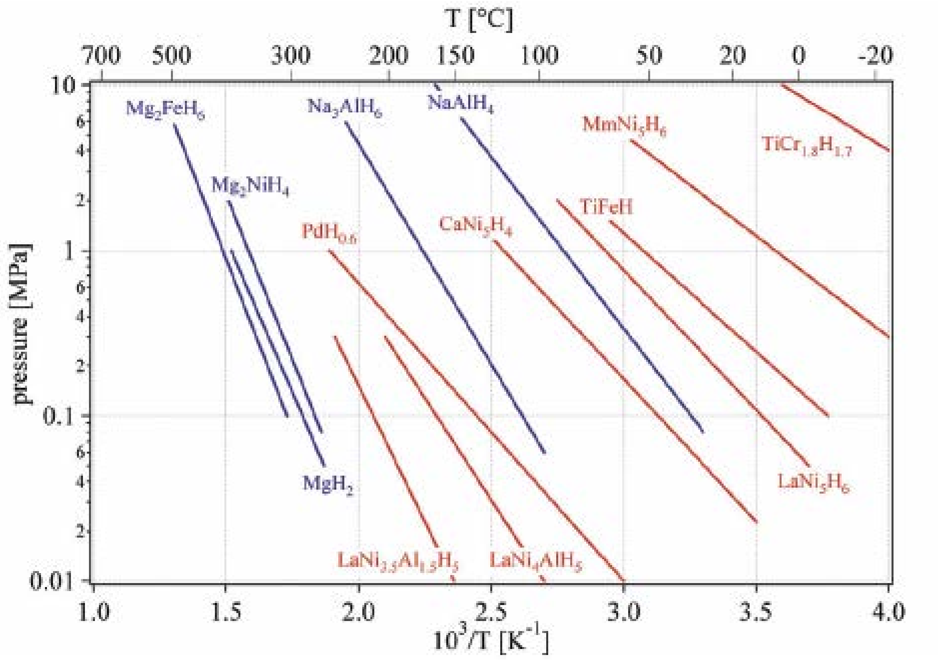

Figure 26: *Equilibrium curves of some metal hydrides (Van't Hoff plots) [13]*

Lightweight metal hydrides (i.e. Al, Li, K compounds) performances have still to be assessed; they are interesting because of the improvement in gravimetric density, which is otherwise typically very low and represents a strong drawback of the other metal compounds. They are addressed as complex hydrides and differs from metal hydrides in the nature of the chemical bond between hydrogen and metal. They can reach greater hydrogen-to-metal ratios (above 4); however, the desorption process could require temperatures in the range 80÷600 °C [12].

Hydride formation and decomposition can be limited by reaction kinetics, and various physical and chemical pre-treatment can be adopted to improve performances. Moreover, the kinetics can be improved by some catalysts. Impurities in the hydrogen stream can cause poisoning or retardation of the kinetic with consequent lowering of the storage capability.

The large amounts of heat involved in absorption and desorption steps call for efficient solutions in heat management, a relevant issue especially for portable applications.

Chemical bonds avoids safety concerns about leakages. However, thermal cycling cause fracturing and lead to a fragmentation of the hydride into very small particles (10÷100 μm) [32], whose entrainment in the outlet gas flow must be avoided.

Large research effort has been made in last years in order to improve hydride H_2 storage capacity, thermal properties, kinetics, toxicity, cycling behaviour and cost. Mg-based hydrides are promising due to the high gravimetric density; however, the high desorption temperatures (about 300 °C) and relatively slow kinetics reduce their effectiveness for portable applications. Complex hydrides have theoretically high capacities, but in practice the current technology gives lower results; improvement are required in order to avoid degradation with cycling. An extended review of the compounds studied for solid hydrogen storage can be found in [33], where detailed operational conditions for each substance are specified.

5.7 Final user distribution

Distribution of hydrogen to final users may be carried out in different ways according to the requirements, including the set up of high pressure gaseous hydrogen dispensers as well as of liquid hydrogen dispensers.

A possible artistic view of a complete hydrogen fuelling station is shown in Figure 27. It may include local gaseous hydrogen production (e.g. from hydrocarbons through reforming, as well as in principle with any of the other processes described in the section dedicated to hydrogen production), compression (with a selected compressor technology) and distribution with high pressure dispensers; moreover it includes liquid hydrogen delivery from trailers (liquefaction is generally considered to be carried out in centralized plants), storage in a LH2 tank and feeding of liquid hydrogen dispensers.

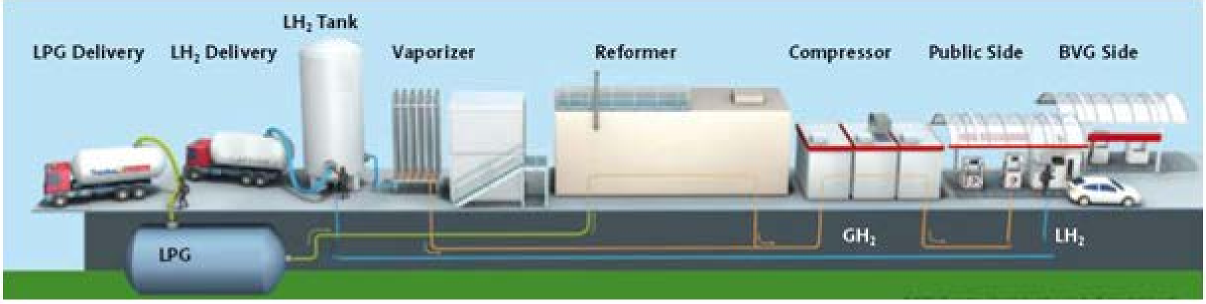

Figure 27: *Example of integrated refuelling station as proposed in projects related to hydrogen use for transport [34]. Both LH_2 delivery and in loco production from LPG are addresed.*

6 Nomenclature

Acronyms

ATR	Auto-Thermal Reforming
CO-PrOX	CO Preferential Oxidation
CPO	Catalytic Partial Oxidation
DSU	De-Sulphurization Unit
FTR	Fired tubular reformer
NG	Natural gas
PEM	Polymeric Electrolyte Membrane (Proton Exchange Membrane)
POX	Partial OXidation
SR	Steam Reforming
WGS	Water Gas Shift

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