



OVERVIEW OF HYDROGEN PRODUCTION METHODS

Doc 251/24

EUROPEAN INDUSTRIAL GASES ASSOCIATION AISBL

AVENUE DE L'ASTRONOMIE 30 • B-1210 BRUSSELS

Tel: +32 2 217 70 98

E-mail: info@eiga.eu • Internet: www.eiga.eu





OVERVIEW OF HYDROGEN PRODUCTION METHODS

Prepared by WG-14 – Hydrogen Production

Disclaimer

All technical publications of EIGA or under EIGA's name, including Codes of practice, Safety procedures and any other technical information contained in such publications were obtained from sources believed to be reliable and are based on technical information and experience currently available from members of EIGA and others at the date of their issuance.

While EIGA recommends reference to or use of its publications by its members, such reference to or use of EIGA's publications by its members or third parties are purely voluntary and not binding.

Therefore, EIGA or its members make no guarantee of the results and assume no liability or responsibility in connection with the reference to or use of information or suggestions contained in EIGA's publications.

EIGA has no control whatsoever as regards, performance or non performance, misinterpretation, proper or improper use of any information or suggestions contained in EIGA's publications by any person or entity (including EIGA members) and EIGA expressly disclaims any liability in connection thereto.

EIGA's publications are subject to periodic review and users are cautioned to obtain the latest edition.

© EIGA grants permission to reproduce this publication provided the Association is acknowledged as the source



Table of Contents

1	Introduction	1
2	Scope and purpose	1
2.1	Scope	1
2.2	Purpose	1
3	Definitions	1
3.1	Publication terminology	1
3.2	Technical definitions	1
4	Direct H ₂ Production	2
4.1	Steam Methane Reforming (SMR)	2
4.2	Partial Oxidation (POX)	3
4.3	Autothermal Reforming (ATR)	6
4.4	Electrolysers	8
4.5	Methanol Cracking	12
5	H ₂ Purification	13
5.1	Pressure Swing Adsorption	13
5.2	Membrane Separation	14
6	Carbon Capture	15
6.1	Amine Wash and Other CO ₂ Removal Processes	16
6.2	Physical Absorption Processes	17
6.3	Chemical Absorption Processes	18
6.4	Typical basic process configuration for an amine-based CO ₂ removal system	19
7	Hydrogen Liquefaction	20
8	Cryogenic Separation of Syngas	21
8.1	Syngas Coldbox	21
9	Hydrogen Production, Carbon Intensity and Environmental Attributes	22
9.1	Carbon Intensity and Environmental Attributes	22
9.2	Hydrogen Production Colours	24
10	References	24

1 Introduction

There has been a recent increase in interest in the topic of hydrogen production, from many sectors, as hydrogen users shift from traditional operators such as refineries or industrial gas companies using conventional carbon feedstock based hydrogen production processes to clean energy users needing hydrogen with low or zero carbon footprint. There is an urgent need to decarbonise energy production, with increasing demand for hydrogen as a feedstock and for energy uses. Many new hydrogen production facilities are forecast to be needed to fulfil this increasing demand. There was a gap in existing texts, with no simple comparative overview available of all commercial scale hydrogen production methods, so this EIGA document was produced to fill that gap.

2 Scope and purpose

2.1 Scope

This publication covers current commercially available industrial hydrogen production methods.

2.2 Purpose

The purpose of this document is to provide an accessible overview of current commercially available industrial hydrogen production methods.

3 Definitions

For the purpose of this publication, the following definitions apply.

3.1 Publication terminology

3.1.1 Shall

Indicates that the procedure is mandatory. It is used wherever the criterion for conformance to specific recommendations allows no deviation.

3.1.2 Should

Indicates that a procedure is recommended.

3.1.3 May

Indicates that the procedure is optional.

3.1.4 Will

Is used only to indicate the future, not a degree of requirement.

3.1.5 Can

Indicates a possibility or ability.

3.2 Technical definitions

AEL – Alkaline Electrolysis
ATR – Auto Thermal Reforming
DIW – De Ionised Water
GHG – Green House Gas
HyCO – Hydrogen & Carbon Monoxide Production Plant
LCA – Life Cycle Assessment
LHy – Liquid Hydrogen

aMDEA – Activated Methyldiethanolamine
MDEA – Methyldiethanolamine
LPG – Liquefied Petroleum Gas
POX – Partial Oxidation
PCF – Production Carbon Footprint
PEM – Proton Exchange Membrane Electrolysis
PSA – Pressure Swing Adsorber
SMR – Steam Methane Reforming
Syngas – Synthesis Gas

3.2.1 Pressure

In this publication bar shall indicate gauge pressure unless otherwise noted i.e. (bar, abs) for absolute pressure and (bar, dif) for differential pressure.

4 Direct H₂ Production

4.1 Steam Methane Reforming (SMR)

Steam methane reforming (SMR) is a well-established, industrial process for the large-scale production of hydrogen. The SMR process involves the conversion of a hydrocarbon feedstock with steam to hydrogen through catalytic reactions. Most commonly methane is used as a feedstock but alternatively heavier hydrocarbons up to naphtha can serve.

Typically in a traditional SMR process, all the carbon within the feedstock and fuel is ultimately emitted to the atmosphere as carbon dioxide hence hydrogen from a SMR is usually considered to be “[Grey Hydrogen](#)”; however there is a drive towards using SMR process technologies where this carbon is captured from within the process for sequestration, thus becoming “[Blue Hydrogen](#)”, see [Section 6 for Carbon Capture Technologies](#) and see [Section 9 on Carbon Intensity](#).

Until recently SMR has been the dominant technology for hydrogen production, given the competitive production cost as well as the widespread availability of natural gas and higher hydrocarbons as a feedstock, and it continues to play a role in meeting the demand for hydrogen across industrial sectors.

The steam methane reforming process can be broken down into the following steps:

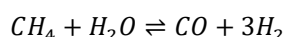
Feed purification and pre-heat

Prior to the main steam methane reforming process, the feedstock must be initially purified to eliminate harmful contaminants, particularly sulphur and chloride compounds. Usually this is achieved by passing the feedstock through a hydrogenator reactor then absorbers, where impurities are hydrogenated then absorbed. Alongside this, water is purified in preparation for raising steam for the reactions. Steam is injected to the feed gas downstream of the feed purification section at an optimal ratio.

Reforming reaction

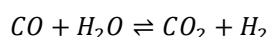
If the feedstock includes heavier hydrocarbons, it can be preferable to include a pre-reforming step, this reduces the duty in the main reformer leading to lower operating costs and can extend the life of the main reformer catalyst. The pre-reforming reaction occurs in a fixed bed reactor where the heavy hydrocarbons react to form methane. If using a natural gas feedstock this step can be omitted.

The methane and steam mix pass to the main reformer where, promoted by the catalyst, it undergoes a strongly endothermic reaction resulting in a synthesis gas mixture comprising mainly hydrogen and carbon monoxide. The main reaction can be represented by the equation:



Water Gas Shift Reaction

To improve the yield of hydrogen, the residual steam and carbon monoxide present in the gas mixture from the reforming step can undergo an additional reaction known as the water gas shift reaction. This reaction is employed to further enhance the hydrogen content in the final product. The main water gas shift reaction is represented by the equation:



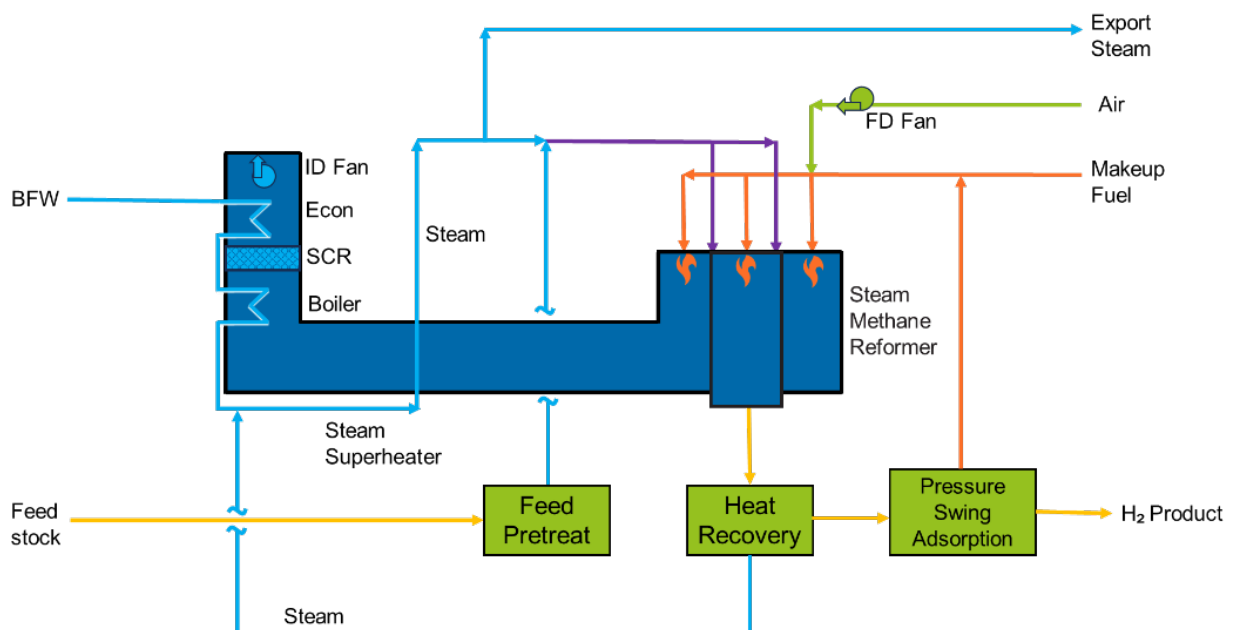
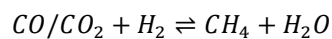
Heat Recovery

The upstream reactions yield a saturated syngas mixture comprising mainly hydrogen, carbon monoxide, steam/water, residual amounts of methane and trace quantities of other substances such as carbon dioxide, plus inert gases such as nitrogen and argon if these were present in the feed. This syngas stream is cooled in stages, with heat being recovered to raise steam for the reaction, and pre-heat the various feed and reformer fuel and combustion air streams. Residual water in the syngas condenses and is collected for recycling back to the main process steam system.

Product purification

To ensure the high purity of the hydrogen product gas the syngas stream further undergoes a further purification process, typically in a multi-bed PSA ([see section 5.1 for more on PSA's](#)), this removes many residual impurities, including carbon monoxide, carbon dioxide, nitrogen, methane, and water. The impurities are removed as a low-pressure off-gas stream which is returned to the main reformer, where it meets most of the process requirements for fuel.

For further removal of low ppm levels of carbon oxides in the product hydrogen, for example to produce fuel cell specification hydrogen, an additional methanation step can be beneficial. The methanation reaction is represented by the equation:

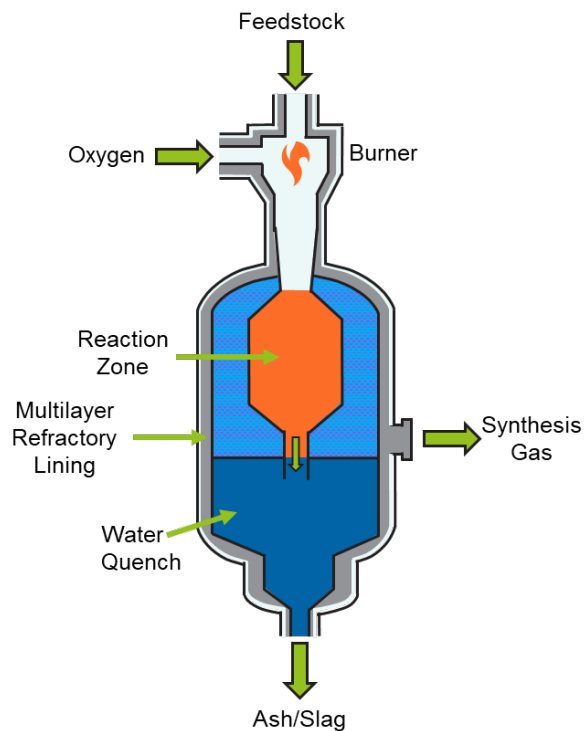


[Figure 1 – Schematic of a typical SMR plant]

See also EIGA Doc 242, [1] “Safety of Hydrogen, HYCO Production and Carbon Capture”, EIGA Doc 246 [2] “Guideline for Small Scale Hydrogen Production”, EIGA Doc 155 [3] “Best Available Techniques for Hydrogen Production by Steam Methane Reforming” and EIGA Doc 230 [4] “Safe Catalyst Handling in HyCO Plants.”

4.2 Partial Oxidation (POX)

For many decades Partial Oxidation (POX) represents a matured and well-known industrial process for a broad range of syngas production applications. Due to its required substantial capital investment, it is usually applied for medium to large scale syngas applications.



[Figure 2 Schematic overview of POX reactor]

Hydrocarbon feedstock is fed via a burner/feed injector into a reaction chamber within a refractory lined vessel. Across the reaction zone, the hydrocarbon feedstock reacts in under-stoichiometric conditions with a co-injected oxidant (typically pure oxygen) and forms syngas, a mixture consisting mainly of hydrogen and carbon monoxide. The typical operating pressure of POX units covers a range of 40 to 100 barg.

The overall POX process is called auto-thermal and proceeds exothermally, hence there is no need for an external heat supply. Feedstock and Oxygen are typically preheated before injection.

The different reactions, that occur simultaneously within the reaction zone, can be clustered as follows:

Hydrocarbon conversion



Combustion reactions



Homogeneous gas phase reactions



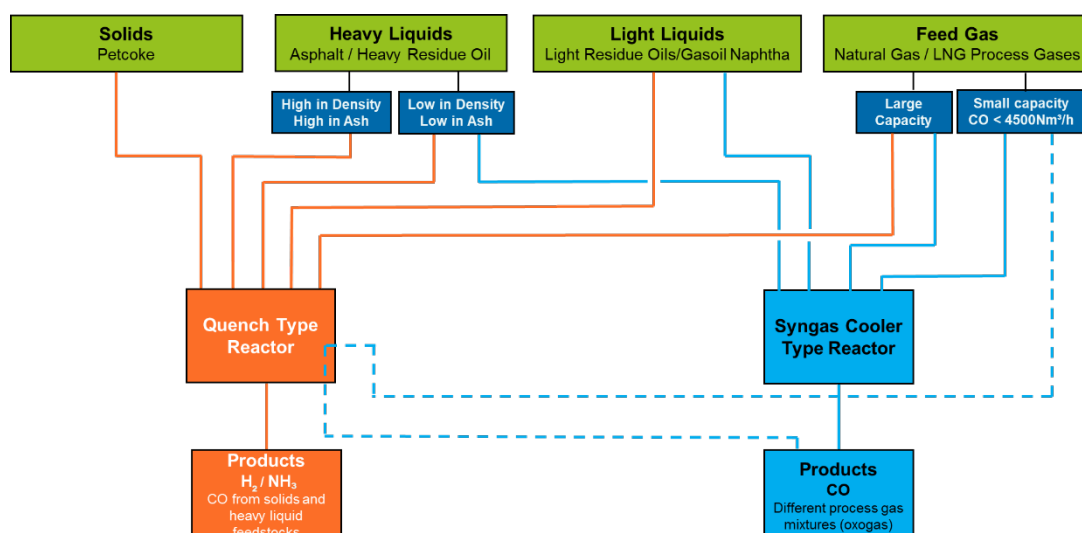
Heterogenous gas-solid reactions



Equation (1) shows the desired reaction where hydrocarbons are partially oxidated towards hydrogen (H_2) and carbon monoxide (CO). The exothermic combustion reactions **(2)**, **(3)** and **(4)** are providing the heat for the POX reactor by full oxidation of contained methane, hydrogen, and carbon monoxide to carbon dioxide (CO_2) and steam (H_2O). **Equation (5)** is representing the water-gas shift reaction, which shows the equilibrium for shifting carbon monoxide by steam towards carbon dioxide and hydrogen. For higher temperatures the equilibrium of water-gas shift reaction is favouring the carbon monoxide production. **Equation (6)** represents the hydrocarbon steam reforming equation, which converts hydrocarbons by steam to hydrogen and carbon monoxide. Especially the equilibrium of the heterogenous gas-solid reactions, i.e. the soot formation, is dependent on the feedstock used for the process.

Due to the absence of catalyst, syngas production via Partial Oxidation is quite robust and flexible regarding feedstock type and quality. Typical applications cover the processing of coal, liquid feedstocks such as oil or heavy hydrocarbon residues and lean gaseous feeds like natural gas. But partial oxidation strictly requires a proper mixing of the reactants and high reaction temperature (approx. 1400 °C) to ensure complete carbon conversion and to reduce soot formation especially for heavy feedstocks. Sometimes steam addition as moderating agent is required to suppress carbon formation.

The hot syngas leaving the POX reactor must be cooled in a further process step. The selection of syngas cooling concept is critical and depending on feedstock and project specifics. Below **Figure 3** gives an overview about the syngas cooling selection and some typical feedstocks used for syngas generation via POX:



[Figure 3 Syngas cooling depending on feedstock and its tendency of soot formation]

Since there is no external fired heater or similar required, there are no direct gaseous emissions related to the operation of such a device. Depending on the finally required syngas composition, there might be direct emissions (if they can be used: co-products) like carbon dioxide leaving a downstream CO_2 capture unit in case this is applied. Another effluent leaving the process is the ash/slag solution, again highly depending on the feedstock, its tendency for soot formation and on the applied syngas cooling concept.

Benefits

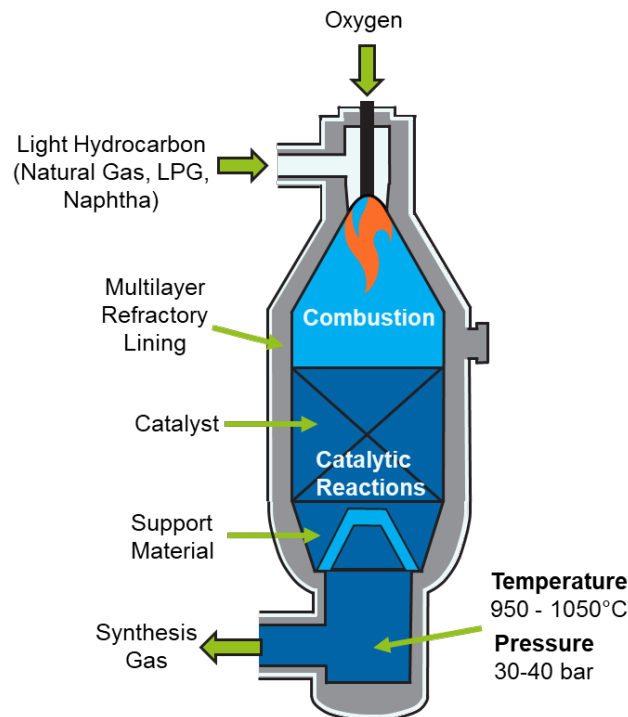
- Carbon capture is easier as CO_2 is completely contained within the process stream, (no separate flue gas as exists as in the SMR process).
- A very wide range of feedstocks can be processed, including heavy (high carbon content).

Challenges

- A high purity oxygen stream is needed for the oxidation process, typically a cryogenic air separation unit is needed.
- The main reactor cost is high as it must be rated for high pressure and temperature.

4.3 Autothermal Reforming (ATR)

Autothermal Reforming (ATR) is a process for producing syngas, composed of hydrogen and carbon monoxide, by partially oxidizing a hydrocarbon feed with oxygen and steam and subsequent catalytic reforming. Process safety and emissions for ATR are similar in many ways to POX.



[Figure 4: Schematic diagram of the ATR reactor]

The feedstock for ATR can be natural gas, refinery offgas, pre-reformed gas, Fischer-Tropsch tail-gas, Liquefied Petroleum Gas (LPG) or naphtha.

After desulfurization (optional, depending on feed gas composition), the feed gas is pre-heated and optionally pre-reformed before entering the ATR reactor at 30 to 100 barg via the burner.

In the first reaction step, the feed gas reacts with oxygen (partial combustion) and steam to produce syngas.

Combustion reaction



Catalytic reactions

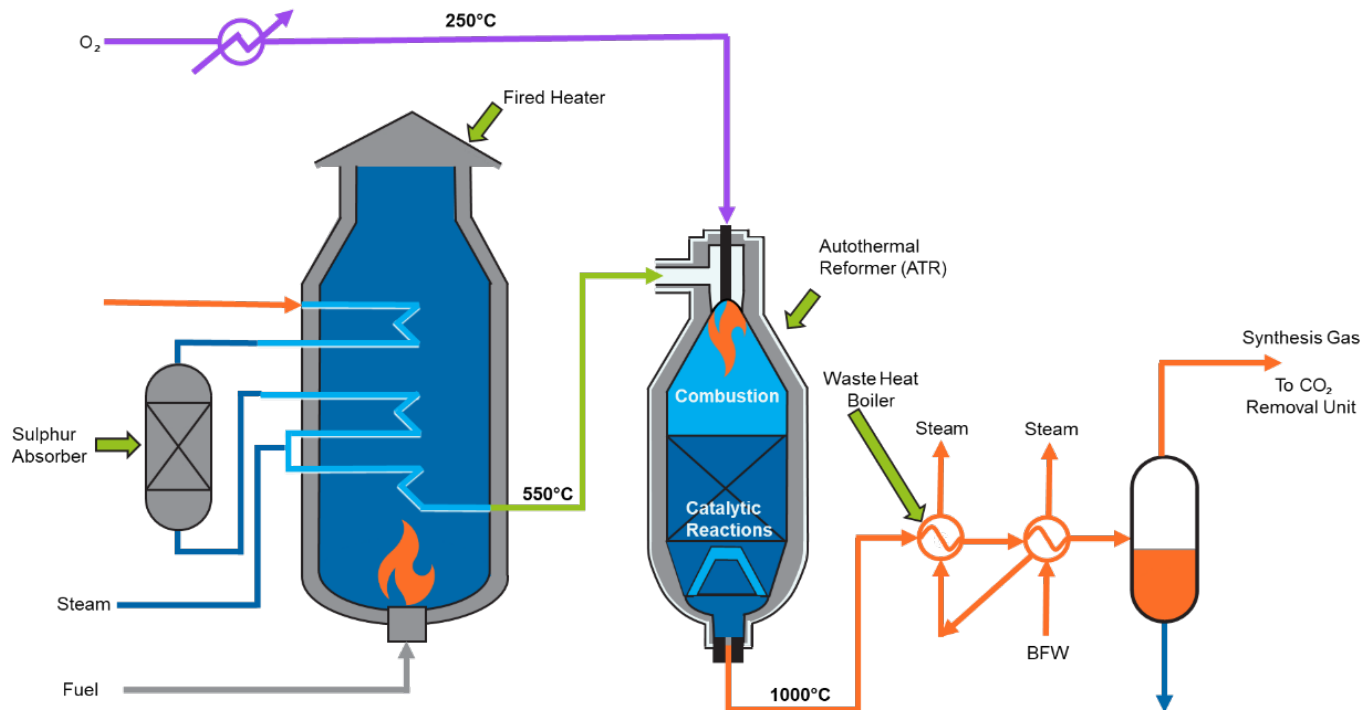


This gas mixture enters then, inside the same reactor, a catalyst bed for further reforming in order to achieve a high yield reaching thermodynamic equilibrium.

Finally, the syngas stream is cooled in a process gas boiler, generating high-pressure steam which can be exported for heating or used for power generation.

The syngas can be used as feedstock for various synthesis processes, mainly methanol and Fischer-Tropsch synthesis.

Alternatively, syngas components can be separated into pure hydrogen, carbon monoxide and carbon dioxide.



[Figure 5: Schematic diagram of ATR process flow]

Benefits:

- Referenced technology for large syngas plant sizes using natural gas.
- Easier carbon capture as the single burner is within the process and there are no other burners needed to produce the heat for the endothermic part of the reactions.
- As a standalone technology or as Combined Reforming (with Steam Methane Reformer) to adjust syngas ratio best fit for downstream wide field of application.
- High-pressure steam can be generated.

Challenges

- A high purity oxygen stream is needed for the oxidation process, typically a cryogenic air separation unit is needed.
- The main reactor cost is high as it must be rated for high pressure and temperature.

Key figures:

- Typical capacity of up to 300 kNm³/h (dry)

- Yield: 2.5 to 4.0 Nm³ syngas / Nm³ natural gas (including fuel for fired heater)
- Oxygen consumption: 0.15 to 0.25 kilograms of oxygen / Nm³ syngas

4.4 Electrolysers

Hydrogen can be produced through the electrolysis of water. In this process, electrical energy is used to separate water into its constituents, hydrogen, and oxygen. By passing an electric current between two metal surfaces ('electrodes') through a conductive media ('electrolyte'), hydrogen gas is formed at the negative electrode (cathode) and oxygen at the positive electrode (anode). The electrolyte is a chemical substance which contains free ions and carries electric current. (e.g. a proton-exchange membrane (PEM) or an alkaline solution).

Solid oxide electrolysis (SOEC) can be coupled with heat-producing technologies for a higher system efficiency, as the electrolysis of water is increasingly endothermic with increasing temperature. Therefore for SOEC, energy demand is rapidly reduced.

Anion exchange membrane electrolysis of water (AEM) are a new generation of water electrolysis which aims to combine the benefits of alkaline electrolysis (AEL), such as stability of the cheap catalyst and advantages of proton-exchange membrane systems (PEM), like the ability to operate at differential pressure, fast dynamic response, low energy losses, and higher current density.

Despite considerable research efforts in recent years, the performance of AEM electrolysis is still lower than what can be achieved with conventional technologies and the stability of AEM membranes require further investigation for industrial long-term use.

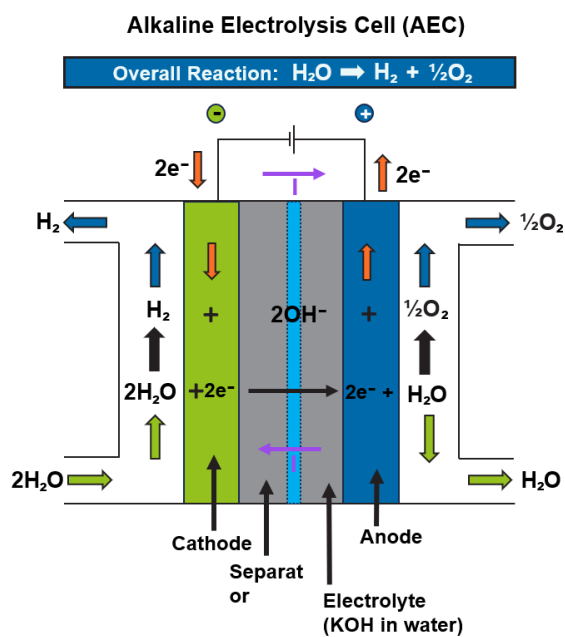
Generating hydrogen by water electrolysis has a long history. Due to its substantial high operational costs for power (about 5 kWh/Nm³H₂) but low investment costs, it has been usually applied for small scale hydrogen production. In the respect of decarbonizing the industry, "[Green Hydrogen](#)" production by electrolysis will play an important role and there is currently a strong development to medium and large-scale electrolyser applications.

Table 1 shows a general comparison of electrolysis technologies as of today.

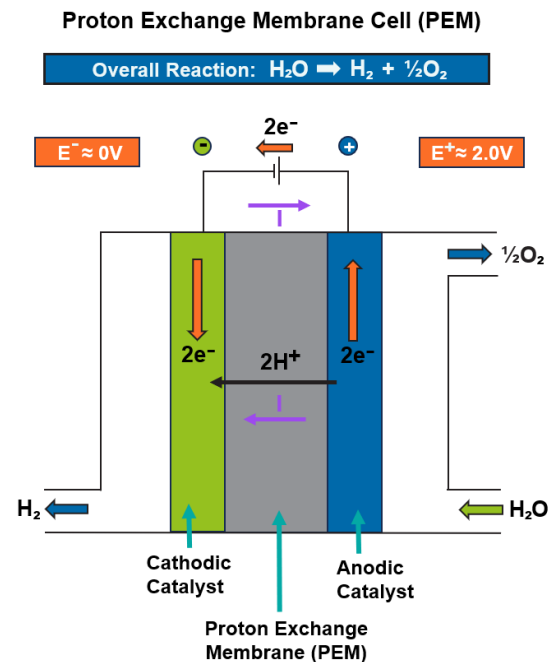
	Proton Exchange Membrane water electrolysis (PEM)	Alkaline Water Electrolysis (AEL)	Anion-Exchange membrane water electrolysis (AEM)	Solid Oxide Electrolysis Cell (SOEC)
Electrolyte	Solid (membrane PFSA)	Liquid (20-30% KOH solution)	Solid (Membrane)	Solid (solid oxide, YZS)
Electrode (Catalyst)	Platinum Group Metal Catalysts (e.g. Platinum, Iridium)	Non noble catalysts, Nickel coated perforated steel	Nickel and Ni-alloys	Nickel on solid oxide, rare earth compounds
Operational Temperature	50-80°C	70-90°C	40-60°C	500-850°C
CAPEX General	Cell stacks expensive Cheaper installation due to compact stack design	Cell stacks cheaper installation cost higher due to larger footprint		Cell stacks very expensive demanding steam treatment system
Typical Stack Efficiency	47-66 kWh/kg Hydrogen	47-66 kWh/kg Hydrogen	47-66 kWh/kg Hydrogen	35-50 kWh/kg Hydrogen
Technology status	Mature for small scale	Most mature technology	Demonstration for small scale	Demonstration
Advantages	Compact Design, ideal for containerized solutions, high dynamic operation	Low-cost materials, large stacks available for plant scale up	Low-cost materials, Potential high dynamic operation capability	High efficiency with thermal integration
Challenges/ Disadvantages	High costs of stacks Larger PEM stacks not yet available	Larger footprint Corrosive liquid electrolyte (lye handling)	Lifetime and scale-up need to be improved	Lifetimes need to be improved. High quality steam required

[Table 1 Electrolysis technology comparison table]

The operating principles of a Proton-Exchange-Membrane (PEM) water electrolysis is shown in **Figure 6** and for an Alkaline-Electrolysis in **Figure 7**



[Figure 6]



[Figure 7]

Process Description of PEM Electrolysis:

High-purity deionized water (DIW) is required for the electrolysis process. Therefore, the feed water enters a water treatment system. Depending on the incoming water quality it consists of, e.g. a reverse osmosis unit, and/or ion exchangers as well as downstream polisher beds and a deionised water tank.

Before the DIW enters the electrolysis stacks, it is led into an $\text{O}_2/\text{H}_2\text{O}$ separation. Here, the DIW and the returning water/ O_2 mixture of the anode side of the electrolysis system are both introduced into an $\text{O}_2/\text{H}_2\text{O}$ Separator. The water is pumped through a heat exchanger for cooling prior entering the electrolysis stacks with the desired operating temperature.

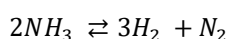
The electrolysis stack split the incoming water into hydrogen and oxygen. Both hydrogen and oxygen outlet streams contain water, and hydrogen contains traces of oxygen and vice versa, thus need to be post-processed.

The downstream $\text{H}_2/\text{H}_2\text{O}$ separator separates the water from the hydrogen gas. The water is recycled back to the DIW water tank, where it will again enter the electrolysis loop.

In the last stage the hydrogen passes a H_2 purification system, which removes any remaining impurities (e.g. moisture and oxygen) to achieve the desired hydrogen purity.

Direct electric current (DC) is required to drive the electrolysis process. For that, a rectifier and a transformer are used to convert the alternating current (AC) from the power grid to the required direct current to power the electrolysis stacks.

To solve the problem of transporting such a light gas, liquid ammonia could be used (NH_3) as a hydrogen carrier, and nearer to the point of use have an ammonia dissociation process (also known as ammonia cracking or decomposition) that splits the H_2 from NH_3 in a catalysed reaction according to equation 1:



This is the reverse of the ammonia production process, and the dissociation reaction is endothermic, with hydrogen production favoured at high temperatures and low pressures, with nitrogen as a main reaction by-product.

A typical ammonia dissociation process will first vaporise then further pre-heat the ammonia feed before the main cracking reaction occurs over a catalyst. The resulting gas mixture containing hydrogen, nitrogen and some residual ammonia will undergo separation to yield an impure hydrogen stream that can be further purified, for example in a PSA, to the desired quality. Off-gases from purification can typically be used as fuel to provide the necessary heat within this process.

At the time of release of this document this process is not yet fully developed for industrial use in large volume productions and in addition, due to its energy intensity, elevates the hydrogen production cost.

4.5 Methanol Cracking

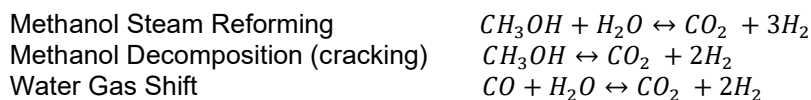
Hydrogen Production through Methanol Cracking

A Methanol Cracker plant produces hydrogen by the catalytic reforming and cracking of methanol and water vapor at elevated temperatures in a reactor heat exchanger. The methanol cracking process as shown in **Figure 8** consists of three basic steps: feed mixing, reaction, and product purification. Like the SMR process, hydrogen product purification is generally done by pressure swing adsorption.

High purity feed water is mixed with liquid methanol at ambient temperatures and pumped to high pressure, typically 18-20 barg. Usually there is no requirement for feed purification as the liquid methanol does not contain catalyst poisons. However, lower quality methanol could contain substances which may damage the catalyst and as consequence may require pre-treatment or purification.

The mixed liquid feed is heated to ~260-280°C and vaporized before entering the reactor. The vaporized, preheated feed passes catalyst filled tubes and a syngas stream (i.e. mixture of H₂, CO, CO₂ and unreacted components) is produced.

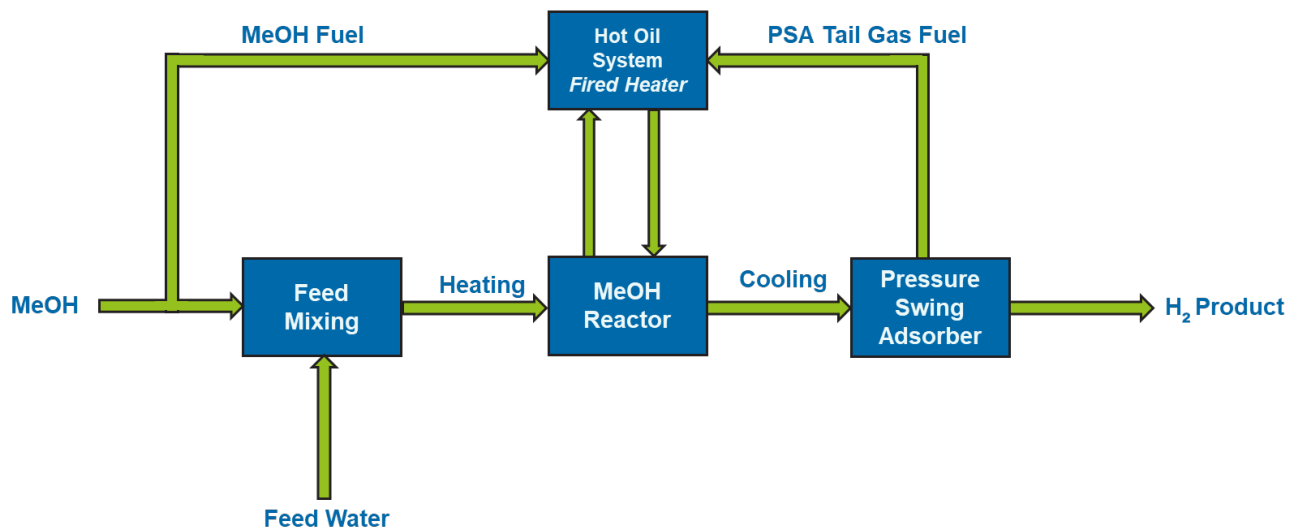
The conversion chemistry within the reactor is complex and similar to the SMR process comprises various equilibrium reactions but can be represented by the following three reactions:



Downstream the reactor the syngas stream is cooled, and the steam condensate is removed in a separator after which the syngas enters the purification unit, typically a PSA adsorption system, to produce high purity hydrogen.

The heat required for the vaporization of the mixed liquid feed and the reforming reaction is provided by a fired heater. The fired heater is mainly fuelled by low pressure purge gases from the PSA (also called "PSA tail gas"). The remainder of heat required is provided by make-up fuel, typically Methanol or LPG. As practical, the excess heat is recovered in the process. The primary methods of heat recovery from the fired heater are to either heat a circulating oil stream that provides the heat for the reactor, or to utilize the fired heater flue gases to provide the heat for the reactor directly.

MeOH Cracking Process



[Figure 8 – A block diagram representing MeOH cracking process]

5 H₂ Purification

5.1 Pressure Swing Adsorption

Pressure Swing Adsorption (PSA) is a purification method for produced Hydrogen where process contaminants are removed in a set of minimum 3 pressure vessels, up to 16 vessels and beyond is possible, filled with adsorbent materials. In addition, there will be a low-pressure off-gas vessel for collection of the tail gas (sometimes called purge gas).

Adsorbent materials are specific for each contaminant to be removed, so typical filling of vessels is made of different layers, sometimes separated by a metal mesh.

Typical adsorbent material currently used in a PSA are molecular sieve, activated alumina, activated carbon.

Typical design is to have the first (in the direction of the feed flow) layer of the PSA filled with weaker adsorbent for the easily adsorbed contaminants and the last layer filled with stronger adsorbent for the hard to remove contaminants.

Easily adsorbed components are water and heavy hydrocarbons, hard to remove contaminants are inert gases like N₂.

Adsorption is enhanced by pressure, so that contaminants adsorption is effective when the vessel is operating at high pressure during the so-called "Adsorption step".

While one vessel is operating in its "Adsorption step" the other vessels of the battery are operating in one of the other following steps, to complete one full cycle of adsorption process:

Depressurization step: The vessel gas is collected in a low-pressure system which for example can be used in a combustion process, prior to the purging step; since adsorption is enhanced by pressure, when operating at low pressure, contaminants adsorbed in the adsorption (high pressure) step are released.

Purging step: The vessel is flushed with pure product to remove the remaining desorbed contaminants, which are collected in a low-pressure system which for example can be used as fuel in a combustion process.

Equalization + re-pressurization step: product is transferred from one vessel to another to equalize the pressure inside the two. At the end of equalization, re-pressurization brings back the vessel to high pressure, ready for the next adsorption step.

The percentage of “H₂ Product Flow” vs “H₂ in the Feed Flow” is usually defined as “Recovery”; the recovery of a PSA is typically above 80% for a PSA downstream of a reformer.

The longer the Adsorption time the higher the H₂ recovery, so usually the PSA is operated at the maximum allowable adsorption time, while preserving the H₂ product quality spec.

See also EIGA Doc 210 [5] Hydrogen Pressure Swing Adsorber (PSA) Mechanical Integrity Requirements.

5.2 Membrane Separation

Membranes for Hydrogen Recovery Applications

Membrane technologies for hydrogen recovery are a simple, compact, and efficient addition to refineries, petrochemical plants, or gas processing facilities. Refinery streams include hydrotreating or hydrocracking purge, catalytic reformer offgas, fluid catalytic cracker offgas, and fuel gas. Petrochemical process streams include ammonia-synthesis purge, methanol-synthesis purge, and ethylene offgas. Synthesis gases include those generated from steam reforming or from partial oxidation. Integration with renewable energy sources and [“Green Hydrogen”](#) production methods can enhance the environmental benefits of membrane-based hydrogen recovery.

Several materials can be used to fabricate membranes, but polymeric membranes are commonly used for hydrogen applications. Various polymeric materials are used for hydrogen recovery, including polysulfone, polyimide, polyetherimide, and polymeric blends. These materials exhibit good hydrogen selectivity due to their size and shape-based permeation characteristics. Polymer modifications such as incorporating functional groups or nanoparticles, can enhance selectivity and permeability.

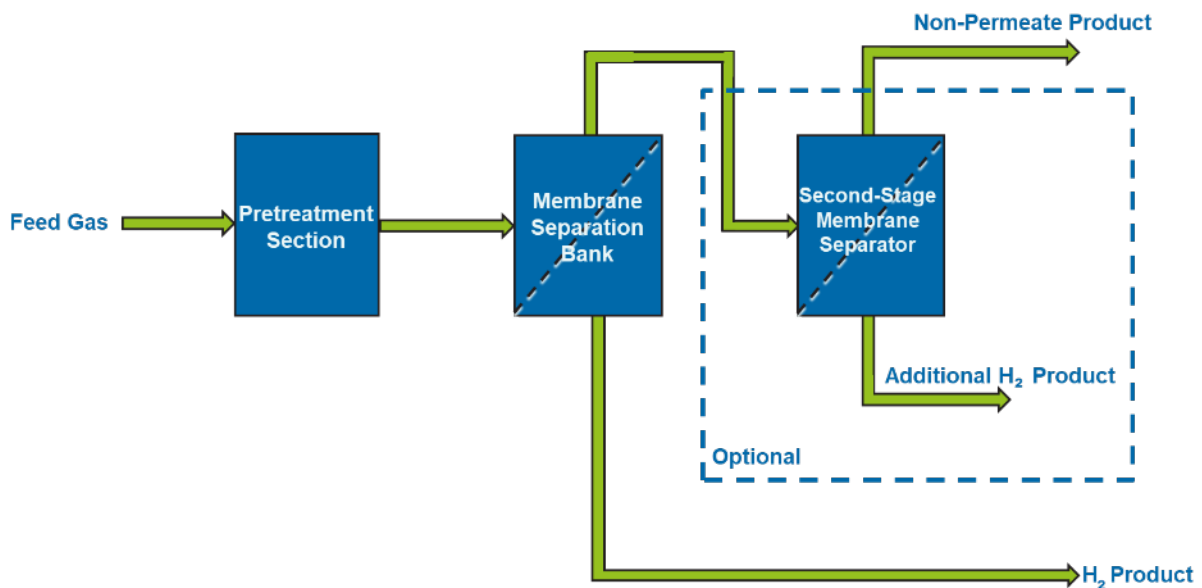
Several factors influence the efficiency of membrane-based hydrogen separation. The selectivity and permeability of the membrane material are critical, as higher selectivity enables better separation efficiency, and higher permeability reduces the required membrane area. Other factors include temperature, pressure, feed gas composition, and membrane configuration. Understanding and optimizing these factors are crucial for designing effective hydrogen recovery processes. Typical hydrogen purities obtained with a polymeric membrane range from 80% to 99.9%. Typical hydrogen recoveries are in the range of 80% to 95%. Higher recoveries are possible, but a cost benefit analysis will determine the viability of using membranes in those cases.

The membrane system design varies by application (see the process flow diagram in the **Figure 9** below), but typical installations consist of a pretreatment section, which heats the gas and removes entrained liquids, followed by a membrane separator bank. A second-stage membrane separator may be added. Ammonia synthesis purge gas pretreatment includes a water scrubber to recover ammonia. Each hydrogen membrane separator is constructed from thousands of hollow fibre membranes, which allow hydrogen molecules to permeate the hollow fibre and exit the separator at lower pressure. The remaining hydrocarbon-rich gases flow through the process at high pressure for use as fuel gas or to the secondary treatment step. In a synthesis gas application, the membranes adjust the ratio of hydrogen to carbon monoxide, with the non-permeate flow becoming the final synthesis gas.

Hydrogen membrane separator systems are reliable, easy to operate, and affordable. The modular design facilitates scalability by adding or removing separators as production requirements demand. The system is delivered on a fully contained skid with all necessary assemblies and connections for easy installation. In general, each skid system is factory-tested to provide safe and reliable commissioning.

[6]

Membranes for Hydrogen Recovery Applications



[Figure 9 -Process flow diagram membrane system for hydrogen recovery]
MembraneSolutions.com [6]

(see also EIGA Doc 155 [3] Best Available Techniques for Hydrogen Production by Steam Methane Reforming).

6 Carbon Capture

Electrolyser technologies are developing over the next years to meet industrial scale hydrogen capacities for the production of carbon free - so called "Green Hydrogen".

Currently around 99% of the global hydrogen production is based on non-renewable, carbon containing feedstocks. The enormous amount of installed conventional hydrogen production facilities and capacities require a transition period where reducing the carbon footprint is a key task. Hydrogen with a reduced carbon footprint is called "Blue Hydrogen" and generally is produced from conventional syngas processes based on non-renewable feedstocks and integrated installations to capture the CO₂ byproduct ("carbon capture").

The principal process options to capture CO₂ in conventional hydrogen production facilities based on SMR, ATR or POX technologies are shown in attached Options 1, 2 and 3.

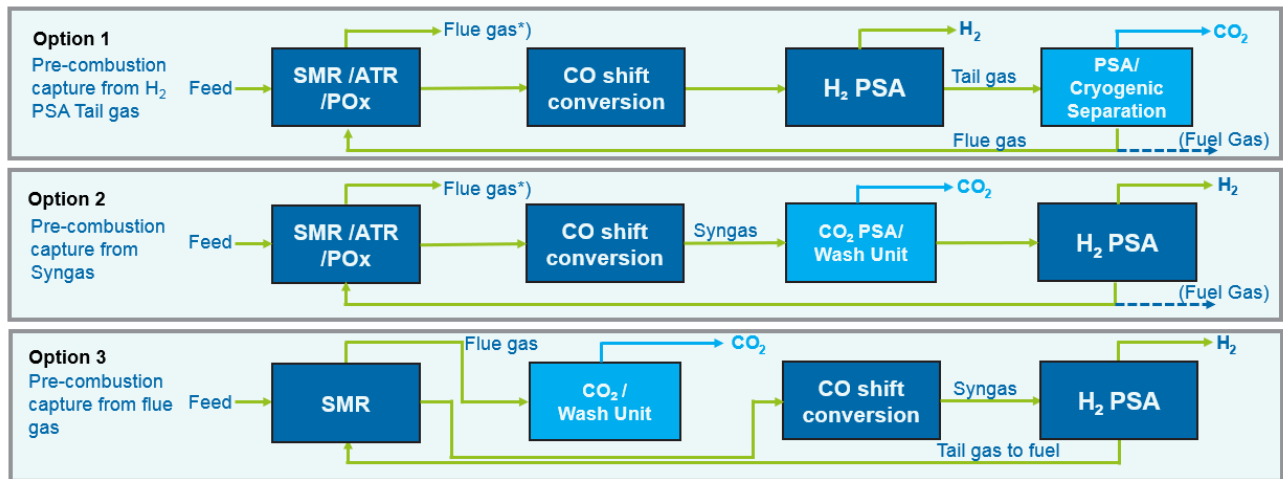
Option 1 describes the Pre-combustion capture. In such setup the CO₂ is removed from the tail gas of the hydrogen product purification unit (PSA unit) by means of a CO₂ PSA or a cryogenic separation process. The tail gas of the H₂ PSA has a low pressure and as such the CO₂ capture process is more energy intense compared to option 2. Option 1 can be relatively easy retrofitted in an existing process.

Option 2 describes an alternative Pre-combustion capture. In such setup the CO₂ is removed from the syngas downstream the shift reactor by means of a CO₂ PSA or a wash unit. The CO₂ removal takes place downstream the shift reactor and under process pressures and has the benefit of a lower energy consumption while retrofitting into an existing H₂ plant is more difficult compared to option 1.

Options 1 and 2 allow for SMR based processes CO₂ capture rates of up to 85% while ATR or POX processes enable CO₂ capture rates of 95% and above. The difference is caused by the fuel gas generated by the SMR process.

Option 3 shows the Post combustion capture. This option is specific to H₂ production processes like SMR which require a combustion to generate the heat for the syngas reaction. The combustion generates pressure less flue gas with high CO₂ concentrations. Option 3 also allows capture rates of up to 95% and can be retrofitted into existing H₂ production plants. However, investment and energy demand for this option are very high.

It is to emphasize that there is no “one-fits all” solution available. Design and site-specific aspects are decisive for the selection of the most adequate carbon capture option.



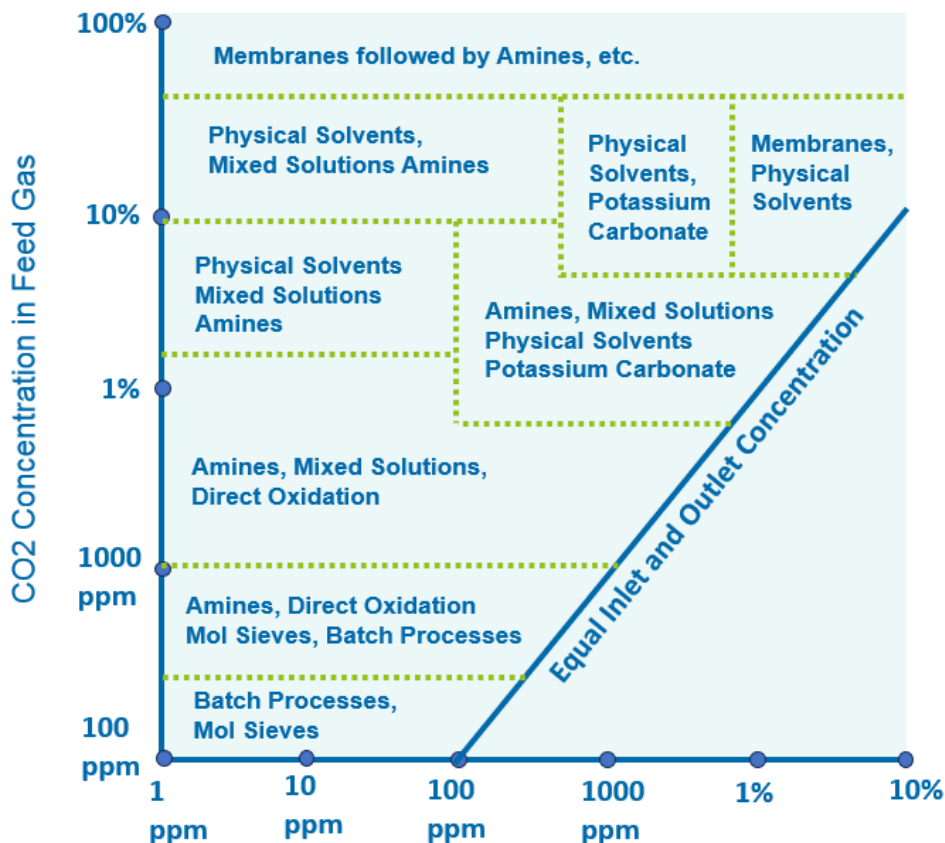
[Figure 10 -Process flow diagram membrane system for hydrogen recovery]

6.1 Amine Wash and Other CO₂ Removal Processes

Most CO₂ removal processes are based on *physical* or *chemical* absorption of CO₂ in a solvent – for the principle see the **Figure 11** below. A large number of processes have been applied so far; the present survey will only deal with the most important ones i.e. chemical absorption. Apart from the absorption processes, some *adsorption* processes (PSA) and *membrane* separation techniques have been applied successfully and will not be discussed here in absorption processes.

Syngas and a specific solvent are brought into contact counter-currently. Solvent removes one or more compounds from syngas, more or less selectively. Absorption is an exothermic phenomenon which increases the temperature of the solution. Current industrial plant operation comprises an absorption step followed by a solution regeneration step. Regeneration purpose is to remove completely or partially absorbed gas from the solution. Regeneration process depends on solvent type as well as objective of gas treating. Flashing stripping are used, alone or in combination. Stripping vapor may be generated by a reboiler or by injection of inert as nitrogen.

Typical Applications



[Figure 11: Process Selection chart]

Best technology to apply to a given feed gas depends on many factors. Apart temperature, pressure, composition, the key point is the CO₂ specification in treated gas compared to the amount of CO₂ in feed gas. **Figure 11** shows an example of a process selection chart.

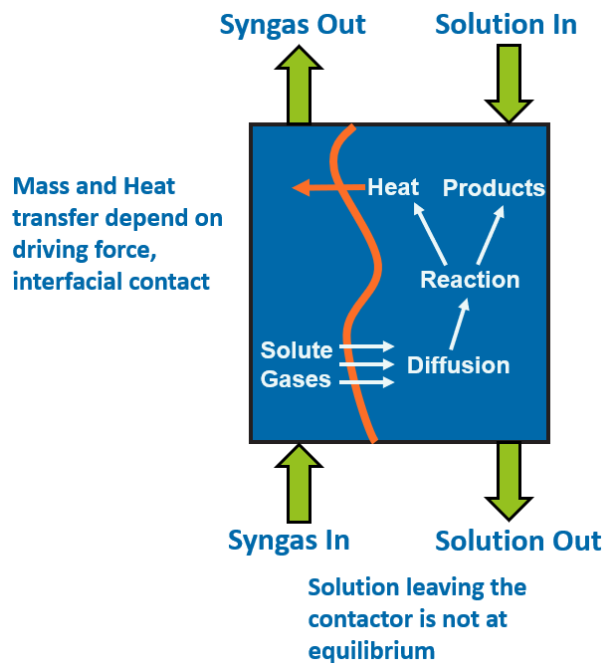
6.2 Physical Absorption Processes

Physical absorption processes generally use an organic solvent which absorbs (dissolves) carbon dioxide as a function of its partial pressure. In general, the higher the CO₂ partial pressure the better the absorption. Physical solvents absorb CO₂ without forming any chemical compounds. In general, physical processes have three major disadvantages:

- Co-absorption (and then loss) of CO, H₂, CH₄ may be significant.
- Solvents are expensive.
- Loading (mole of CO₂ per mole of total amine) is low at lower partial pressure of CO₂, leading to high solution circulation flow rate.

For physical processes, we may list RECTISOL™ and SELEXOL™.

6.3 Chemical Absorption Processes



[Figure 12]

Three main groups of chemical absorption processes can be distinguished:

- Alkanolamines solvent**, made of primary amines as MEA, secondary amine as DEA and tertiary amines as TEA....
 MDEA is a tertiary amine and has several properties which make it well suited for bulk CO₂ removal in syngas and ammonia plants as well. These include easy maintenance of solutions at high concentration (up to 40 to 50%wt) high CO₂ loading, low corrosion even at high loadings, low vapor pressure and hence minimum solution loss.
 The primary disadvantages of MDEA are a slow reaction rate with CO₂ and a tendency to cause foaming.

The CO₂ reaction occurs after it dissolves in water to form bicarbonate ion. The bicarbonate then undergoes an acid-base reaction with the amine to yield the overall CO₂ reaction.

The bicarbonate formation is a slow reaction (CO₂ and water) and takes place in the liquid phase. Thus, for effective use of MDEA, the liquid residence time must be sufficiently long for the CO₂ reaction to take place. In order to accelerate the absorption rate, some tertiary amine supplying companies have developed an activated MDEA process. The activator is a secondary di-amine.

Absorption Driving Force

CO₂ absorption occurs in response to a partial pressure driving force from gas to liquid.

In the gas phase, the acid gas partial pressure is the total pressure multiplied by the acid gas mole fraction. In the liquid phase, absorbed acid gas will exert an increasing acid gas "vapor" pressure.

The net driving force for absorption is the difference between the acid gas partial pressure and the solution acid gas vapor pressure.

At equilibrium, the two become equal, hence the net driving force becomes zero and no further absorption is possible.

Acid gas partial pressure is fixed within the feed gas. But solution acid gas vapor pressure at given loading and temperature is a function of amine reactivity. The bigger an amine's reactivity, the lower will be the acid gas vapor pressure, so the higher will be the driving force.

It is the molecular concentration of an amine that determines its capacity, not its weight concentration.

Thermal effect during Absorption

Absorber in which CO₂ is transferred from gas to liquid acts as reactor and heat exchanger. Absorption is an exothermic phenomenon. The heat of reaction is generated in the liquid phase, which raises the liquid temperature and causes further heat transfer to the gas. Feed gas temperature increases from bottom to top of the column. In the same way solution temperature increases from top to bottom. Consequence of temperature increase is that it decreases the CO₂ loading i.e. the amount of CO₂ picked up by the solution.

Stripping Column – Heat Load on the Reboiler

Heat load on the reboiler includes:

- The sensible heat required to raise the temperature of the feed rich solution to that of the regenerated solution leaving the reboiler.
- The heat of reaction required for the dissolution of the acid gases from the amine, to force the reaction (R1) to proceed toward left.
- And the heat of vaporization of the water leaving the stripping section of the column as vapor with acid gases.

Temperatures in stripper will be governed by the operating pressure. The recommended maximum allowable temperature is 114°C for aMDEA regeneration, depending on operating pressure.

A rich solution temperature of approximately 100°C is recommended. Top column temperature will be approximately 95°C, depending on the operating pressure.

The reflux ratio for the stripper is defined as the ratio of the moles of water in the acid gases from the stripping column to the moles of acid gas stripped. Reflux ratio of 1.2 is adequate.

The lean solution purity obtained from the stripper will be a function of the quantity of stripping vapor.

Other Processes

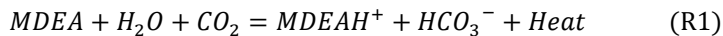
- **Hot potassium carbonates.** It is based on hot K₂CO₃ solvent. It is used for absorption of CO₂ because of its low cost, easy availability, and the readily dissociating characteristics of the bicarbonate. It has a low rate of absorption, due to slow chemical reaction between CO₂, water and generation of hydroxyl and carbonate ions in solution. Several additives have been used to accelerate this reaction. These plants are more and more converted to aMDEA process.

6.4 Typical basic process configuration for an amine-based CO₂ removal system

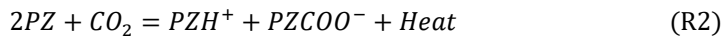
- One stage amine unit is a commonly used configuration for syngas plants. It is the lowest capital cost plant but has the highest energy to operate. If the heat below 160°C is of high value, consider other configurations.
- This arrangement including heat-regeneration stripper allows extremely low CO₂ content into the treated gas, currently, it is expected less than 50ppmv of CO₂ into treated gas. In turn, a flash regeneration alone does not permit a so low CO₂ slip.
- At higher pressures in the absorber column, H₂ dissolved in the solution will affect the CO₂ quality. To improve the CO₂ quality, consider rich solution flash tank to flash the solution to about a pressure slightly higher than CO₂ partial pressure in feed gas.

In this configuration, syngas (30 to 40°C) from reformer's cooling system enters the absorber from the bottom while the lean amine solution flows down from the top. The amine contacts the gas counter currently with CO₂ transferring into the solution. During CO₂ absorption by solution, lean solution temperature increases and becomes progressively rich in CO₂.

Thermodynamic model describing CO₂ absorption by solvent made of water, MDEA, Piperazine is very complex, so it is out of our scope. Reader may refer to reference 1 for further information. The overall reactions occurring during the CO₂ absorption may be described by the following equations:

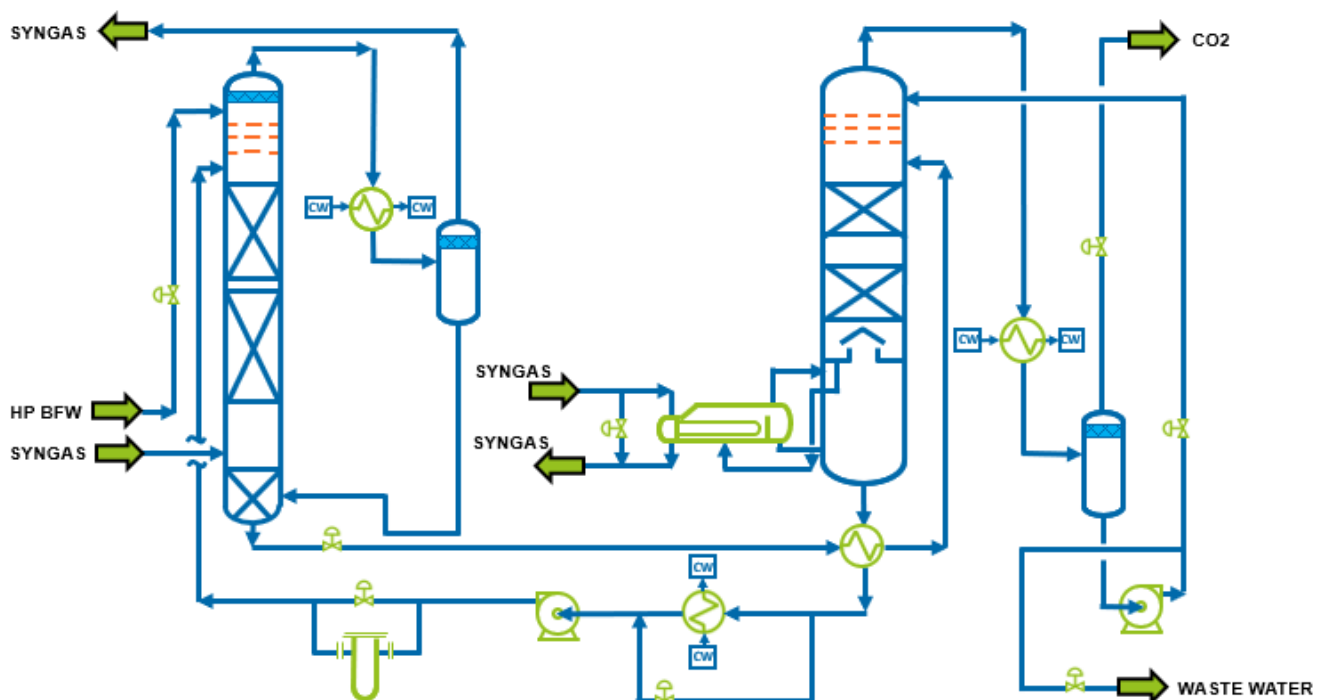


Equation R1 describes the reaction for a tertiary amine (MDEA), giving as product protonated amine and bicarbonate and heat.



Equation R2 describes the reaction for a secondary amine (piperazine), the products are protonated amine and piperazine mono-carbamate and heat. Although the reaction with PZ is fast, it is not fast enough to be considered instantaneous.

These above reactions are kinetically controlled i.e. rate of reaction depends on actual conditions of pH, temperature and composition.



[Figure 13: Typical One Stage Absorber with regeneration in stripper]

After the loaded solution, (named rich solution) leaves the bottom of the absorber, it is heated in the Lean-Rich solution heat exchanger and fed into the top of the stripper where it contacts steam produced in the reboiler at reduced pressure and high temperature.

The energy supplied by the steam reverses the reaction of the gas with the amine, increasing the partial pressure of the gas and thereby stripping it from solution.

The lean solution is sent to Lean-Rich solution heat exchanger where the temperature is reduced before it is sent to Lean solution cooler for final temperature adjustment. Lean solution is then pumped through Lean solution pump before it is returned to the absorber.

A small portion of approximated 10% pumped lean solution is diverted to the mechanical filter to remove any particles which would be present.

7 Hydrogen Liquefaction

Liquid hydrogen (LH₂ or LHy) is used in a variety of applications, including as rocket fuel, and as an energy carrier due to its high energy density. As gaseous hydrogen has such a relatively low density, liquefying it reduces its volume by a factor of approximately 800, increasing efficiency in its storage and transport.

Liquid hydrogen is produced by cryogenic liquefaction, which is an energy intensive process using multiple compression and expansion steps to cool gaseous hydrogen to below -253°C , where it exists as a liquid.

The main liquefaction process steps are as follows:

Purification: Hydrogen obtained from sources like steam methane reforming or electrolysis of water, must already have been purified to remove trace contaminants such as CO , N_2 , O_2 , CH_4 , H_2O and CO_2 , which would solidify at the extremely cold temperatures within the hydrogen liquefier. This purification can be achieved in several ways for example using PSAs. It is particularly important to remove trace oxygen as that will accumulate within the extremely cold process as a solid, where it poses a combustion hazard.

Compression, cooling, and expansion: Like in a standard refrigeration cycle, gaseous hydrogen is compressed then pre-cooled in a heat exchanger. After pre-cooling, the hydrogen gas is further cooled by expansion, typically through let-down valves.

Ortho to Para conversion: To minimise boil-off into gaseous form, the LHy undergoes catalytic Ortho to Para conversion in fixed bed reactors, as the Para form of LHy is more stable and less inclined to vaporise.

Heat integration: To further minimise energy use, heat is exchanged within the process rather than rejected from it, for example by cooling warmer streams against the increasingly cold exhaust gas from the various expansion stages. Any heat leak into the process causes inefficiency. The entire liquefaction process is typically located inside a cryogenic cold-box structure where it is well insulated.

Subcooling: It is possible to sub-cool the liquid product via heat exchange of the product against a flashing LHy stream, this provides further product stability for storage.

Storage: It is essential to maintain the low temperature of liquid hydrogen at or below its very low boiling point, which is close to absolute zero. Liquid hydrogen is stored in cryogenic tanks or shipping containers that are rated for cryogenic temperatures. These vessels are well-insulated to minimize heat leak and maintain the low temperature required to minimise boil-off. In an optimally insulated storage tank liquefied hydrogen can be stored for extended periods, allowing for efficient energy storage and long-distance shipping. This is particularly useful in renewable energy production where surplus energy generated during peak production can be stored as liquid hydrogen and used to balance off-peak shortages, enabling a more reliable and flexible energy supply.

8 Cryogenic Separation of Syngas

8.1 Syngas Coldbox

CO Coldbox is a purification system achieved by cryogenics separation/distillation process. The process recovers high purity carbon monoxide (CO) and hydrogen (H_2) from the syngas originated from steam reforming and/or partial oxidation.

The feed gas to the cold box typically comes from the acid gas removal unit which is typically an aqueous amine or other type of solvent wash unit. It is saturated with water (from MDEA removal unit) and containing traces of CO_2 (from all acid gas removal unit typically).

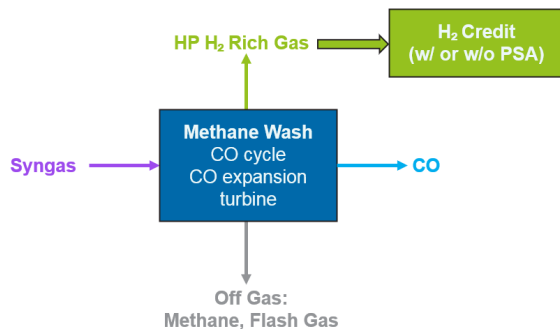
To avoid freezing in the cold box, it is pre-treated with a front-end purification dryer unit with a two-bed adsorption system to remove water and carbon dioxide and obtain a cryogenic grade syngas (dry gas with less than 0.1 ppm of CO_2).

The main components of the synthesis gas are then separated using technology that focuses on differences in their boiling points. The economics of the process can vary significantly depending on the type and quality of feedstock and the required CO product specifications.

Two main cycles for the cryogenics CO coldbox purification process:

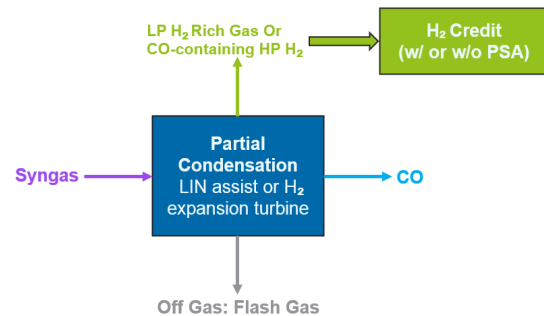
Methane Wash Process

→ If Syngas contains Methane, e.g Syngas produced from SMR



Partial Condensation Process

→ If Syngas does not (or few) contain Methane (typically <2%mol), e.g. Syngas produced from POX, ATR



[Figure 14]

- Requires methane to allow process working (>2%)
- High pressure raw H₂ product
- More complex, relatively higher Capex
- Typically, lower pressures can be used
- Higher CO recovery than partial condensation

[Figure 15]

- Typical feed gas has high CO, low CH₄
- Low pressure raw H₂ product (~ 1 barg)
- Relatively simple, relatively lower Capex
- Typically, high pressure (> 25 bar)
- Lower CO recovery than methane wash

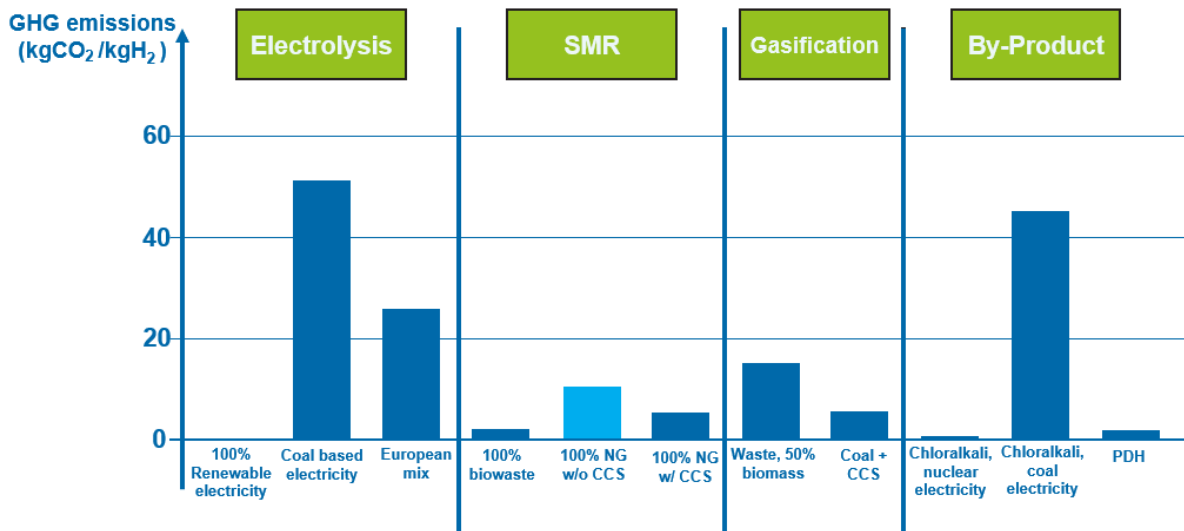
	Partial Condensation	Methane Wash
CO purity (except Nitrogen)	Up to 99.9 mol%	Up to 99.9 mol%
CO recovery	75% (single stage) 88% (multi-stage)	95-98%
Methane content in Hydrogen	A few ppmv	1 – 2.5 mol%
CO content in Hydrogen	2-10 mol%	10 ppmv – 0.4mol%
Hydrogen recovery	>97%	>97%
Hydrogen pressure	low	high
CO cycle	low	high
Turbo expander	Min. 2	Min. 1
Methane pumps	no	yes

[Table 2: Typical Comparison of the different process of Cold Box]

9 Hydrogen Production, Carbon Intensity and Environmental Attributes

9.1 Carbon Intensity and Environmental Attributes

One of the key environmental benefits of Hydrogen is that it does not emit GHG when used. However, its production and the corresponding sourcing of the energy and feedstock does. The Product Carbon Footprint (PCF) of hydrogen vary a lot depending on the production technology but even more depending on the inputs (feedstock and energy) to the production process. The graph below shows the PCF of Hydrogen for several production pathways as evaluated during the CertifHy project [7], using ISO 14067 standard [8].



[Figure 16]- GHG Emissions for different Hydrogen Production

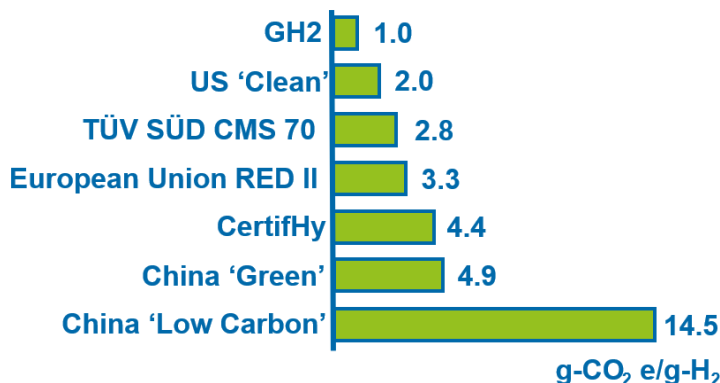
Life Cycle Assessment (LCA) methodologies must be used to determine the Product Carbon Footprint of hydrogen.

The existing ISO 14067 [8] “Carbon footprint of products — Requirements and guidelines for quantification” and the ISO 19870 [9] are providing a robust framework to do so. The Green House Gas Protocol “Product Life Cycle Accounting and Reporting Standard [10]” is nearly equivalent to these ISO standards. The boundaries and lifecycle stages to be considered must be selected according to the goal of the LCA.

These boundaries are used to establish the inventory of GHG emissions to be allocated to the hydrogen and its potential co-products. EIGA Doc 167 [11] “Methodology to establish a Product Carbon Footprint” provides more information on the way to proceed in the case of industrial gasses and for Hydrogen in particular.

“Low Carbon Hydrogen” is commonly used for hydrogen with a PCF below a certain threshold. However, the criteria to be met are defined by public authorities to serve the goals of their specific energy policies.

Labels often based on PCF thresholds (e.g. “Low Carbon Hydrogen”) and other sustainability criteria are defined by public authorities (or by the user of hydrogen) to serve the goals of their energy policies. As a result, thresholds to define LC Hydrogen vary depending on geographies and policies. Below are some examples of thresholds set by different public policies or organizations attempting to define their own labels.



[Figure 17]- Well to Tank GHG Emissions for different Hydrogen Production Pathways
H₂ emission thresholds - Source Bloomberg Energy [12]

It is a common misconception to consider that such labels should be standardised when they are the result of political decisions.

Harmonizing labels and thresholds, if possible, can only be made through negotiation between governments.

9.2 Hydrogen Production Colours

Colours have been used to categorize hydrogen according to the way it has been produced. The most commonly used are:

- Blue Hydrogen, to refer to non-renewable hydrogen produced with a low carbon footprint. As mentioned above thresholds to define “Low Carbon hydrogen” are defined.
- Grey Hydrogen, to refer to hydrogen produced from conventional resources such as Hydrogen produced by SMR using natural gas.
- Green Hydrogen, which is being used to refer either:
 - o Hydrogen produced from renewable energy and feedstock with a low carbon footprint (e.g. CertifHy [8])
 - o Hydrogen produced exclusively by electrolysis using renewable electricity.

Colours are de facto labels, for which there are no commonly agreed criteria.

In addition to Grey, Blue and Green, which are implying some specific environmental attributes, several other colours have been introduced designating specific technologies and production pathways without consideration for their actual environmental impacts.

10 References

Unless otherwise specified, the latest edition shall apply.

- [1] EIGA Doc 242, *Safety of Hydrogen, HYCO Production and Carbon Capture*, European Industrial Gases Association, Inc. www.eiga.eu
- [2] EIGA Doc 246, *Guideline for Small Scale Hydrogen Production*, European Industrial Gases Association, Inc. www.eiga.eu
- [3] EIGA Doc 155, *Best Available Techniques for Hydrogen Production by Steam Methane Reforming*, European Industrial Gases Association, Inc. www.eiga.eu
- [4] EIGA Doc 230, *Safe Catalyst Handling in HyCO Plants*, European Industrial Gases Association, Inc. www.eiga.eu
- [5] EIGA Doc 210, *Hydrogen Pressure Swing Adsorber (PSA) Mechanical Integrity Requirements*, European Industrial Gases Association, Inc. www.eiga.eu
- [6] Air Products, *Membrane Solutions*, www.membranesolutions.com
- [7] *CertifHy project*, www.CertifHy.eu
- [8] ISO 14067, *Greenhouse Gases -Standard for Carbon Footprint of Products*, International Organization for Standardization, www.iso.org
- [9] ISO 19870, *Greenhouse Gases -Standard for Carbon Footprint of Products*, International Organization for Standardization, www.iso.org
- [10] *Product Life Cycle Accounting and Reporting Standard*, Greenhouse Gas Protocol, www.ghgprotocol.org
- [11] EIGA Doc 167, *Methodology to establish a Product Carbon Footprint*, European Industrial Gases Association, Inc. www.eiga.eu

[12] *H2 Emission Thresholds*, Bloomberg Energy, www.bloomberg.com