International PtX Hub

AMMONIA, NITROGEN, AND GREEN HYDROGEN PRODUCTION & PURIFICATION

#1

Renewable Electricity

H_2

ELECTROLYSIS

Hydrogen H_2

H_2O

WATER PROCESSING

Water

Ambient Air

DAC / Swing Adsorption

Nitrogen N_2

PTX-SYNTHESIS

Ammonia NH_3

IMPRINT

OVERVIEW

Paper #1 comprehensively explores the complex processes involved in the production of green hydrogen, nitrogen separation, and ammonia synthesis. It includes a detailed examination of each key aspect, providing valuable insights into the technologies, methods, and comparisons within these areas.

The paper delves into the production of hydrogen from different electrical energy sources, emphasising electrolyser technology and its integration with renewable energy generation systems. Additionally, it explores alternative pathways such as biomass for hydrogen production, offering a comparative analysis of various hydrogen production technologies.

The nitrogen separation section dissects prevalent methods including cryogenic distillation, Pressure Swing Adsorption (PSA), and membrane permeation. A thorough comparison of nitrogen separation alternatives is presented, accompanied by considerations of oxygen volumes and achievable purity levels.

The paper investigates the traditional Haber-Bosch process for ammonia production and extends its focus to variations such as low-pressure Haber-Bosch, absorbent/adsorbent-enhanced Haber-Bosch, electrochemical synthesis, and thermocyclic production. The edition also provides insights into other emerging technologies for ammonia production, concluding with a comparison of these alternatives and ammonia quality considerations.

Through a systematic exploration of these topics, the paper aims to contribute to a detailed understanding of the technical complexities, advancements, and choices within green hydrogen production, nitrogen separation, and ammonia synthesis. This holistic overview sets the stage for a comprehensive exploration of sustainable and efficient practices in the field of clean energy and chemical production.

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UNITS

°C	Degree Celsius		**mg**	Milligram
µm	Micrometer		**mm**	Millimeter
A/cm²	Ampere per square centimeter		**mV**	Mmedium voltage
cm²	Square centimeter		**MW**	Megawatt
g	Gram		**mWh**	Megawatt hour
GJ	Gigajoule		**mΩ**	Milliohm
K	Kelvin		**Nm³**	Standard cubic meter
kJ	Kilojoule		**ppb**	Parts per billion
kW	Kilowatt		**ppm**	Parts per million
kWh	Kilowatt hour		**W**	Watt
m	Meter		**wt%**	Weight percent
m²	Square meter			

ABBREVIATIONS

AC	Alternating Current		**NiAl**	Nickel aluminite
ASU	Air Separation Unit		**Ni-YSZ**	Nickel-yttria stabilized zirconia
AWE	Atmospheric Water Electrolysis		**NiZn**	Nickel-zinc
CB	Conduction Band		**NRR**	Nitrogen Reduction Reaction
CCM	Catalyst-coated Membranes		**O₂**	Oxygen
CCS	Carbon Capture and Storage		**OER**	Oxygen Evolution Reaction
Co	Carbon monoxide		**PEM**	Proton Exchange Membrane
CO₂	Carbon dioxide		**PNS**	Purple non-sulphur
CO₂	Carbon dioxide		**PSA**	Pressure Sswing Aadsorption
DC	Cirect Current		**PSA**	Pressure Swing Adsorption
Fe	Iron		**Pt**	Platinum
FFC	Fluid Catalytic Cracking		**PV**	Photovoltaic
GDL	Gas Diffusion Layer		**Rh**	Rhodium
GDL	Gas Diffusion Layer		**SiO₂**	Silicon dioxide
GT	Generation Turbine		**SOEC**	Solide Ooxide Eelectrolyser Cell
H₂O	Water		**SOFC**	Solid Oxide Fuel Cells
HER	Hydrogen Evolution Reaction		**SRU**	Sulphur Recovery Unit
Ir	Iridium		**TiO₂**	Titanium dioxide
LCCF	Lanthanum Strontium Cobaltite Ferrite		**TML**	Technical Maturity Level
MEA	Membrane Electrode Assembly		**VB**	Valence Band
Mo	Molybdenum		**WS₂**	Tungsten disulfide
MoS₂	Molybdenum disulfide		**WSe₂**	Tungsten diselenide
N₂	Nitrogen		**ZrO₂**	Zirconium dioxide
NH₃	Ammonia			

INTRODUCTION

A crucial frontier in our drive for a sustainable energy transition and the reduction of greenhouse gas emissions is the nexus of renewable energy and green hydrogen generation technology. The green hydrogen purification procedure lies at the heart of this endeavour. Water and renewable energy are used to electrolyse green hydrogen, which has great potential as a clean and flexible energy source. However, careful purification becomes necessary in order to fully exploit it across a range of industries, including transportation.

The process of converting renewable energy sources into high-quality hydrogen fuel necessitates the painstaking removal of pollutants, such as moisture, minuscule quantities of oxygen, and other impurities that may jeopardise the effectiveness of fuel cells and hydrogen-based technology. In addition to being necessary to meet strict quality requirements, this purification procedure also improves hydrogen utilisation's energy efficiency, ultimately assisting in the development of a more sustainable energy ecology.

Modern hydrogen generation systems are focused on increasing efficiency and overcoming the drawbacks of conventional energy sources. These main energy sources cover a wide range of renewable possibilities, each with special qualities and benefits. Particularly in areas with abundant solar radiation, solar energy partners easily with electrolysis devices. Another important primary energy source for the creation of green hydrogen is hydroelectric power, a mainstay in the production of electricity that also offers stability and affordability.

Despite having a large generation capacity, wind energy struggles with variability, calling for sophisticated power stabilisation and hydrogen generation systems. Geothermal energy, obtained from the Earth's core, stands out for its dependable and steady output, making it a desirable option for the creation of vast amounts of hydrogen.

Additionally, the combination of wind and solar energy shows promise in developing a dependable and steady energy source for the manufacture of hydrogen. These two energy sources complement one another and have different generating processes, which reduces swings in the energy supply and increases sustainability and efficiency. Through a smart merger, common infrastructure components are optimised, cutting costs and raising overall effectiveness. This comprehensive approach emphasises the crucial part that green hydrogen will play in our transition to a low-carbon, sustainable energy future.

1

GREEN HYDROGEN PRODUCTION AND PURIFICATION

The interaction between renewable energy and green hydrogen production technologies has generated a great deal of interest in recent years due to their potential to drive a sustainable energy transition to reduce our greenhouse gas emissions.

A crucial step in the creation of high-quality hydrogen fuel from renewable sources is green hydrogen purification. With the help of water and renewable energy, green hydrogen is produced through electrolysis. As it contains impurities, the hydrogen produced must be carefully cleansed before it can be used in a variety of ways. Purification includes the elimination of moisture, minute amounts of oxygen, and other impurities that can jeopardise the efficiency of fuel cells and other hydrogen-based technologies. This procedure is necessary to meet strict quality requirements, improve hydrogen utilisation's energy efficiency, and contribute to a more sustainable energy environment. Unlocking the full potential of hydrogen as a clean, adaptable, and zero-emission energy carrier for various industries, such as transportation, is made possible by green hydrogen purification technologies.

In general terms, the current level of technology allows us to produce hydrogen directly from thermal, electrical, biochemical and photonic energy, which in turn are obtained from primary energy sources. This means that the development of hydrogen production technologies is mainly focused on improving efficiency and eliminating the limitations that these primary energies present.

Among the main primary energy sources is solar energy, which is one of the most abundant and accessible sources of renewable energy. This source is successfully coupled with electrolyser-based systems and is especially interesting in regions with abundant radiation, where large solar plants can be installed for hydrogen production.

Another primary energy source of high importance is hydro power, which has been used for decades to generate electricity from the movement of water. This source is suitable for hydrogen production due to its high stability and low costs. In addition, hydroelectric dams can serve as an efficient form of large-scale renewable energy storage, as water can be stored in reservoirs during periods of low demand and released during times of high demand, providing continuity of operation.

Wind energy is another renewable energy source that can contribute to the production of green hydrogen as it can provide a large generation capacity. However, the variability of wind means that this energy source has significant technological challenges related to the mechanisms required for power stabilisation and care of hydrogen generation systems.

Geothermal systems are based on harnessing heat from the Earth's core in regions with high volcanic activity. This form of renewable energy can be used to produce green hydrogen continuously and steadily, making it an attractive option for large-scale hydrogen production.

Combining wind and solar energy is a strategic approach that offers numerous benefits in the realm of renewable energy and hydrogen production. By leveraging the strengths of both energy sources, a more reliable and stable energy supply can be created while promoting sustainability. Wind and solar energy possess complementary generation patterns. While wind energy exhibits more consistency during specific periods, solar energy production reaches its peak at different times. By amalgamating both sources, uninterrupted power supply can be established, even if one source's generation is hindered by weather conditions. This synergy serves to alleviate the impact of fluctuations. When the output of one source diminishes, the other compensates, ensuring a steady energy flow for hydrogen production. This ceaseless energy supply derived from a fusion of wind and solar sources upholds unwavering stability in hydrogen production processes, thus enhancing overall efficiency. The amalgamation of wind and solar systems yields optimal utilisation of infrastructure. Shared components like storage systems and grid connections can be fine-tuned to support both energy sources, consequently trimming costs and amplifying efficiency.

Due to the numerous advantages, combining various renewable energy sources, such as solar and wind, makes perfect sense. By utilising both wind and solar energy, a strategic synergy is produced that gives the energy supply redundancy and balance.

This cooperation guarantees continuous power production even when one source encounters variations because of the weather or other circumstances. Solar energy may easily replace wind energy during times when the wind may not be blowing so strongly, and vice versa, ensuring a constant and dependable energy source. This harmonious interplay ultimately promotes sustainability and lessens environmental consequences by improving not only the stability of energy production but also the reliability of crucial operations like hydrogen production.

Hydrogen production processes can be classified according to the energy source, but they can also be grouped according to the main feedstock that supports the process, finding that water and renewable electricity are the main sources for renewable hydrogen generation.

1.1 Production of hydrogen from electrical energy

1.1.1 Water electrolysis

Water can be split into its components (hydrogen and oxygen), however, this reaction does not occur spontaneously at ambient conditions and requires energy to be supplied in order to break the molecule apart. In water electrolysis systems, the electrical and thermal energy of the system are simultaneously converted to chemical energy allowing the electrolysis reaction to take place. However, there is a minimum value of energy that must be supplied for the water molecule break-up to start, meaning that electrolysis will only start if a minimum power is supplied, which is normally related to the temperature, voltage and current intensity at which an electrolyser operates.

The way in which the energy will be harnessed by the electrolyser and how the chemical reaction will be carried out depend to a large extent on the internal distribution of the equipment and on the individual efficiency of its components. In their most basic structure, electrolytic systems are made up of an electrical power source, a fluid medium in which the reacting chemical species are found, and the electrodes through which the electrical charges flow, the latter being the point of connection between the power source and the fluid. The general schematic of an electrolyser is shown in Figure 1.
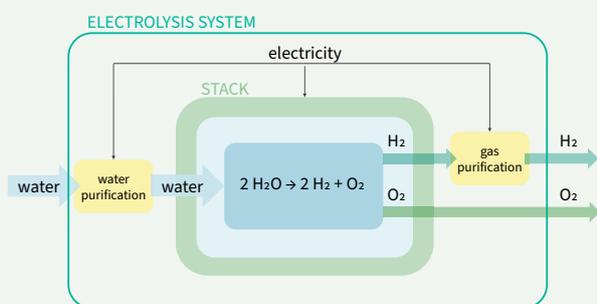
General diagram of an electrolyser

Figure 1: Own illustration

The energy supplied to the electrolyser will flow through the equipment in the same way as electricity flows through a conventional electrical circuit, and the final consumer will be the chemical reaction produced inside the electrolyte solution. Therefore, in addition to the energy required to carry out the electrolysis of the water, it is necessary to supply additional power that will be consumed by the internal resistance of all the components of the circuit. In other words, the electrolyser dissipates part of the energy supplied by the power source in the form of losses. This results from the resistance of the electrical flow through the connecting cables between the power source and the electrodes, the internal resistance of the electrodes, the resistance of the charge flow in the electrolyte solution and the other elements that may make up the electrolyser.

1.1.2 Reaction mechanisms

To understand the principle of operation of the electrolyser it is necessary to consider that some substances can split into their components when they are hydrated. For example, when dissolving a crystal of sodium chloride or table salt in water, the water molecules will interact with the atoms of the salt and separate them, generating a solution of electrically charged atoms called ions. These positively and negatively charged ions will promote the conduction of electricity through the solution, reducing energy losses in the electrolytic circuit and reducing the total power consumption required for electrolysis [3].

As a result of such improvements in power consumption, some electrolysers have implemented the use of salts such as Potassium Hydroxide (KOH) or Sodium Hydroxide (NaOH) in high concentrations, which additionally change the way water molecules interact with the electrodes. In these devices, the generation of hydrogen and oxygen occurs in different sections of the electrolyser and by different chemical mechanisms depending on the type of salts dissolved in the solution.

Thus, the production of hydrogen in an alkaline or basic medium, in which there is a high concentration of OH^- ions, occurs at the cathode and in three different reactions known as Hydrogen Evolution Reaction (HER) and described as follows [4]:

Reaction 1 - Hydrogen adsorption: A water molecule reacts by gaining an electron from the cathode, as a result, an electrically uncharged hydrogen atom is trapped by the solid surface of the electrode in a process called adsorption, while the remaining negatively charged OH^- ion is released into solution.

$$H_2O + e^- \rightarrow H_{ads} + OH^- \quad \text{(Volmer)}$$
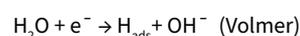
Reaction 2 - Reaction between hydrogen and water: A hydrogen atom adsorbed on the electrode surface reacts with a water molecule and an electron from the electric flux from the cathode, directly forming hydrogen gas and an OH^- ion which are released into the solution.

$$H_{ads} + H_2O + e^- \rightarrow H_{2(g)} + OH^- \quad \text{(Heyrovsky)}$$
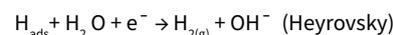
Reaction 3 - Reaction of two adsorbed hydrogens: In this stage, two hydrogens that are adsorbed on the cathode surface react with each other to produce hydrogen gas, which is released directly into the solution.

$$H_{ads} + H_{ads} \rightarrow H_{2(g)} \quad \text{(Tafel)}$$
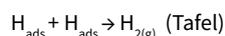
After water dissociation, OH^- ions migrate to the anode where oxygen synthesis occurs in five reactions involving the adsorption of four different chemical species in a process that is known as Oxygen Evolution Reaction (OER) and are described below [4]:

Reaction 1 - Adsorption of OH^- ions: OH^- ions present in solution are adsorbed on the anode, in this process an electron is released giving continuity to the electric flow.

$$OH^- \rightarrow OH_{ads} + e^-$$
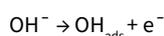
Reaction 2 - Interaction between adsorbed OH^- and in solution: The OH^- groups adsorbed on the electrode interact with the OH- ions present in the solution to form oxygen and hydrogen, which are released directly into the solution; in addition, oxygen remains adsorbed on the electrode and takes part in further reactions.

$$OH_{ads} + OH^- \rightarrow O_{ads} + \frac{1}{2} O_{2(g)} + H_2 + e^-$$

Reaction 3 - Interaction between adsorbed oxygen and OH^- ions: the oxygen that remains bound to the anode surface reacts with an OH^- ion present in the solution to form a new chemical species that remains adsorbed on the electrode and the release of an electron occurs, as shown below.

$$O_{ads} + OH^- \rightarrow OOH_{ads} + e^-$$
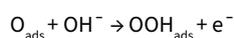
Reaction 4 - Interaction between the OOH species and OH^- ions: The OOH that remains bound to the anode surface and that was generated in the step described above, reacts with an OH^- ion present in the solution to form a new chemical species that remains adsorbed on the anode surface.

$$OOH_{ads} + OH^- \rightarrow OO^-_{ads} + H_2O$$

Reaction 5 - Final oxygen synthesis: Finally, the OO^- species adsorbed on the electrode is released from the surface and generates oxygen that flows directly into the solution, in this process it releases an electron that contributes to the electrical flux.

$$OO^-_{ads} \rightarrow O_{2(g)} + e^-$$

On the other hand, if electrolysis is carried out in an acidic medium, the reactions at each of the electrodes will change, as will the direction of ion flow in the solution. However, electrolysis will still involve two half-reactions that take place in several stages and in direct 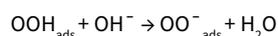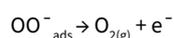interaction with the electrode, as is the case with electrolysis in a basic medium. The way in which the chemical species interact with the solid surface

of the electrode greatly influences the energy consumption of the electrolyser, which is why part of the technological development of this equipment has been directed towards the implementation of materials that facilitate the adsorption of the reactants and the release of the products of the reactions. However, many of the materials developed to facilitate these processes are not stable or do not have high durability in highly acidic solutions, limiting the application of this type of technology on an industrial scale [5].

A number of different reaction mechanisms have been proposed for electrolysis in an acidic medium based on kinetic studies in heterogeneous catalyst systems. However, none of these have been fully validated experimentally [6]. A more detailed description of the proposed reaction mechanisms will be reviewed later, when the operation of Proton Exchange Membran (PEM) electrolysers will be explained.

1.2 Electrolyser technology

At present, commercial electrolysers operate mainly in two temperature ranges, allowing them to be categorised into two groups. At temperatures below 100 °C are electrolysers handling liquid water (Alkaline Water Electrolysis (AWE) electrolysers and PEM electrolysers), and at temperatures above 500 °C, equipment handling water vapour operates, including Solid Oxide Electrolyser Cell (SOEC). Technological development was not simultaneous for both groups of equipment, as the low-temperature electrolysers made more progress in the early stages.

1.2.1 Alkaline Water Electrolyser (AWE) and Anion Exchange Membrane Water Electroyser (AEMWE)

Alkaline electrolysis stands out among the other hydrogen production technologies as the most mature and commercially available [8], as such equipment has operated industrially with KOH solutions since the end of the 19th century and has developed to such an extent that in the 1930s it was possible to find electrolysers with scales of 10,000 Nm³/h (~ 50 MW) and larger [9]. Part of the popularity of this type of electrolyser is due to the ease of construction and relatively low maintenance costs compared to other types of electrolysers. It does not require precious metals such as platinum, palladium or gold to operate at acceptable efficiencies.

This type of electrolyser normally consists of three sections, the electrolysis system where the production of oxygen and hydrogen takes place; a system of tanks and exchangers that separate the alkaline solution at the outlet of the electrolyser and recirculate it; and additionally includes a rectification or electrical conditioning unit, where the electricity is converted to direct current with the required voltage for the reaction to take place.

The alkali recirculation loop starts with a storage tank, where it is possible to dissolve the salt in high purity water, normally deionised water (type I or II, American Society for Testing and Materials (ASTM) D1193) which ensures no fouling or chemical

damage to the electrodes and low accumulation of foreign material in the alkali solution. This solution is pumped to the electrolyser where the water is separated into hydrogen and oxygen, which flow into separation tanks where the remaining alkali solution is removed and recirculated to the electrolyser. Subsequently, the gases pass through separators that allow the moisture and alkali residues to be removed by cooling and condensation, and are sent to subsequent purification processes in totally independent systems. A general representation of these systems is shown below.

General diagram of components of an alkaline electrolyser
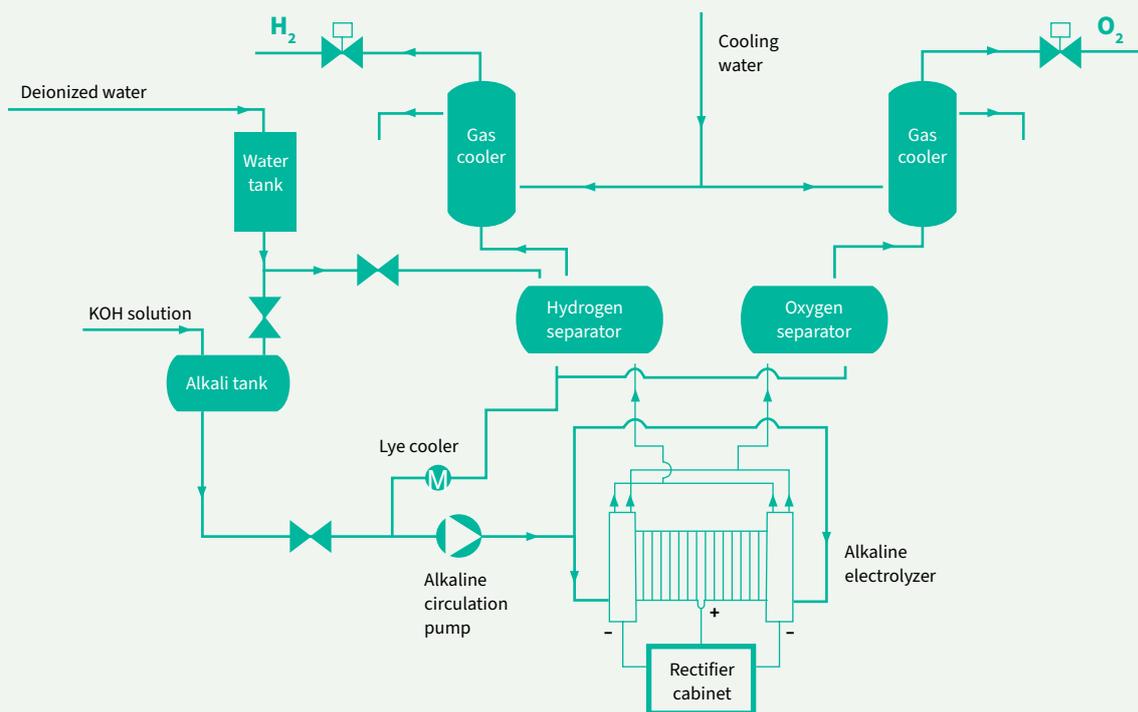
Figure 2: Based on [10]

Electrolytes

In an alkaline electrolyser, the movement of OH⁻ ions will determine the conductivity or resistance level of the solution, which is an indicator of the amount of power required for the electrolysis to take place. This is why salts such as KOH and NaOH are used as electrolytes, favouring the flow of charges and therefore reducing the energy consumption of the system.

Although both salts are used (KOH and NaOH), the amount of hydrogen produced by cells operating with KOH is usually higher as a result of its higher ionic mobility. The amount of electrolyte in solution can be modified according to the behaviour of the electrolyser and must be periodically replenished considering typical losses of 1 mg of KOH for each Nm³ of hydrogen produced [11].

In the case of the use of KOH as an electrolyte, it has been found that the conductivity is optimal when the salt concentration is between 30 and 34%, and at operating temperatures between 60 and 80 °C [12], while NaOH shows its optimum operating point at concentrations close to 24% in the same temperature range. The trend in specific conductivity presented by solutions of different concentration is shown below.

Specific conductivity of solutions with different KOH concentrations and temperatures
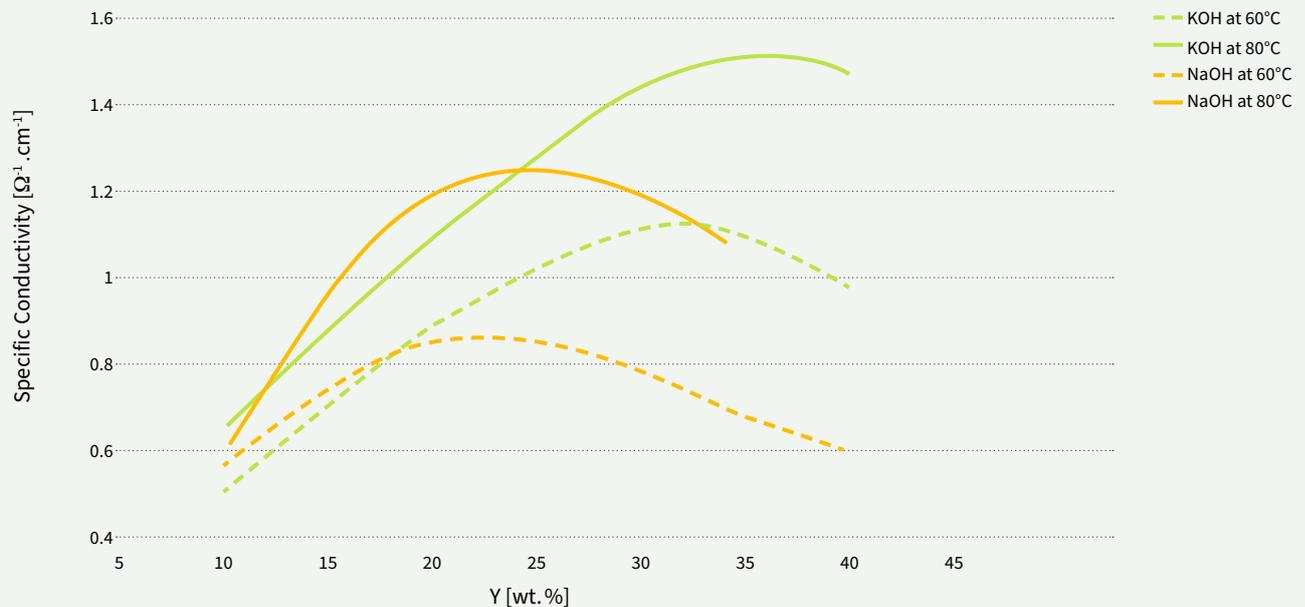
Figure 3: Based on [11]

In addition to the use of salts to increase conductivity, the use of ionic activators in the solutions has become popular, as they are a measure that allows the energy consumption of the electrolyser to be reduced at a relatively low cost. These activators work by electro-deposition of metallic compounds on the electrode surface, increasing the catalytic capacity mainly at the cathode and reducing its corrosion attack. Most ionic activators are composed of thylenediamine or trimethylenediamine-based metal chloride complex and Sodium molybdate (Na_2MoO_4) or Sodium tungstate (Na_2WO_4). Some researchers have claimed that the use of these compounds in alkaline electrolysers can reduce electricity consumption by up to 10% [13].

Another alternative to increase the efficiency of electrolysers is to feed ionic liquids to the electrolyte solution, such as 3-butyl, methyl imidazolium cations associated with anion such as tetrafluoroborate and hexafluorophosphate [13].

Electrode configuration
As mentioned above, electrolysers can be analysed as if they were traditional electrical circuits and each component offers a resistance with an influence on the power consumption of the system. This is why the distance separating the electrodes is an important design parameter, as it offers a resistance to the flow of charges, making it necessary to supply a greater amount of electricity to the system at greater distances.

In traditional cell design, the distance between electrodes can range from 1 mm to several centimetres (see Figure 4). If this distance is smaller, the concentration of the products and reagents can vary significantly inside the equipment, generating gradients that would affect the efficiency of the operation. On the other hand, the accumulation of gas bubbles would be favoured, generating a barrier on the electrode surface, preventing its contact with the alkali solution and, therefore, preventing electrolysis from occurring.

The design of zero-gap electrolytic cells allows to reduce the distance between electrodes, finding a position that optimises power consumption and reduces the problems mentioned above. In this type of configuration, electrodes are separated at a distance of less than 0.5 mm by a membrane that allows the conduction of OH⁻ ions. The central part of the Zero-gap design is called the Membrane Electrode Assembly (MEA) and includes two porous electrodes in contact with a membrane, the effect of which is to increase the surface area, increasing hydrogen production as the reaction involves the adsorption of chemical species on the electrode surface [14].

Another type of arrangement has been proposed, in which each electrode assembly consists of a separator or membrane coated with zirconium (ZrO_2) powder, an active layer, a gas diffusion layer (GDL) made of carbon or nickel, and a grid also constructed of nickel that acts as a current collector. The two-electrode assembly is separated by a 1.5 mm thick gasket through which the electrolyte solution flows at a higher pressure than that present in the hydrogen and oxygen compartments, producing flow in that direction. Although this arrangement has shown good experimental performance, it is still under development, so the maturity of this technology is still low compared to the other two architectures presented.

Different configurations of electrodes:
(a) Immersion electrodes or conventional architecture, (b) 'Zero-gap' configuration, (c) Gas Diffusion Layers (GDL)
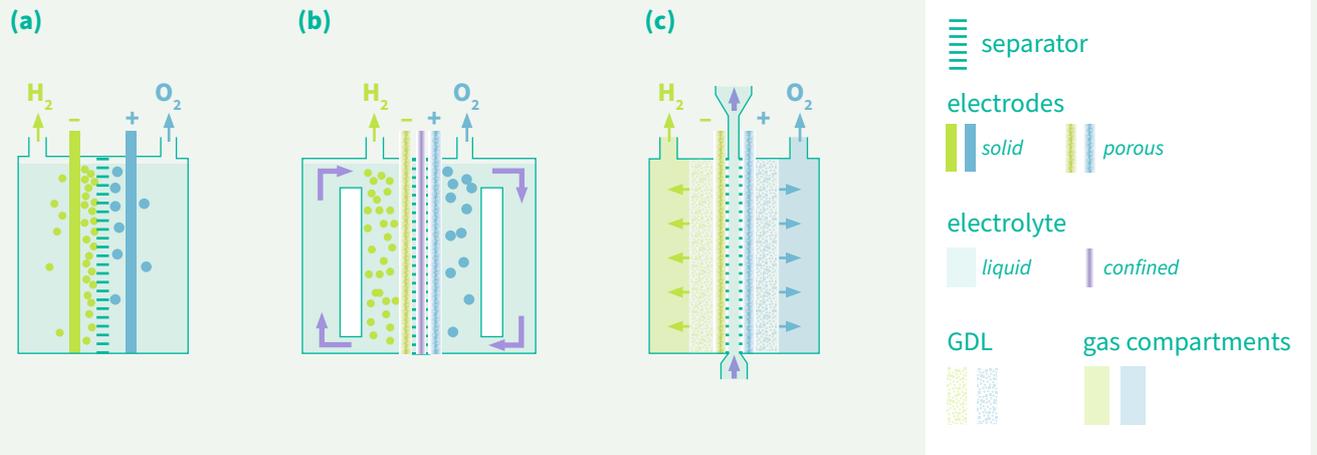
Figure 4: Based on [15]

Distribution of units cells

An additional classification of electrolysers relates to the way the Direct Current (DC) power source is connected to the array of cells and how the electricity is distributed to each cell, with two types of arrangements.

Monopolar systems are called those in which each cell has a direct connection to the power source, forming a parallel arrangement and additionally presenting the same voltage as the source. In this type of system, the same hydrogen or oxygen production reaction takes place on both sides of the same electrode, facilitating their manufacture.

In bipolar systems, only two electrodes of the cells are connected to the current source. The other electrodes of the intermediate cells are connected to each other in a series arrangement, as shown in the Figure 5 below. In this arrangement, the voltage is the sum of the individual cell voltages and different reactions take place on opposite sides of each electrode, which operate in a bipolar fashion. These systems are much more compact and have lower energy losses. However, they require more precision during construction and maintenance often requires more advanced technical knowledge compared to the monopolar arrangement.

Electrolyser configuration (a) monopolar and (b) bipolar

Figure 5: Based on [11]

A comparison of the two types of arrangements is presented in the table below.

Table 1: Comparison between monopolar and bipolar array; based on [16]

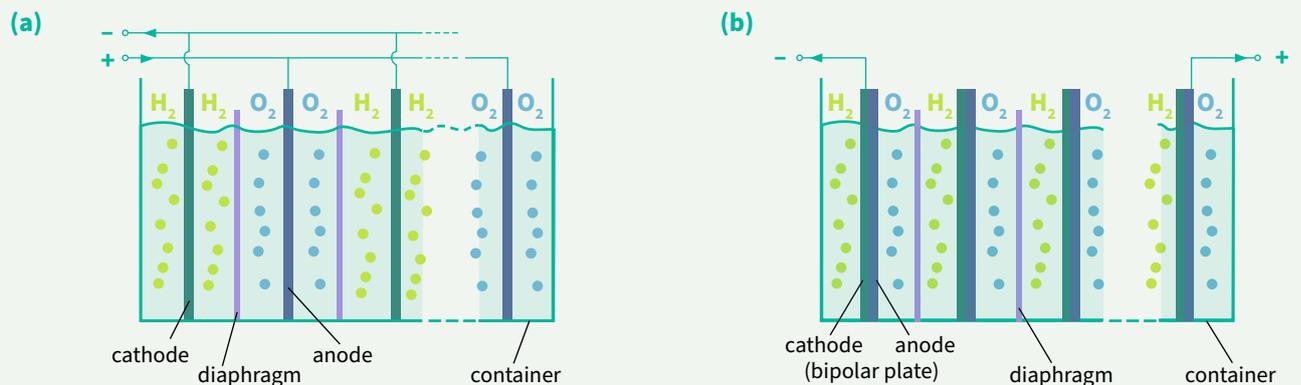| Monopolar	Bipolar
Advantages	
Simple and rugged design	Lower unit cell voltages
Relatively inexpensive parts	Higher current densities
Simple fabrication techniques	Intercell busbars greatly reduced
Few gasketed surfaces	Rectifier costs more easily optimised
Individual cells easily checked	Can readily operate at higher pressures and temperatures
Cells easily isolated for maintenance	Pressure operation elimates compressors
No parasitic currents in system	Easier to control entire system for temperature and electrolyte level
Minimum disruption to production (e.g. by single cell failure) for maintenance problems	Fewer spare parts required
Cells easily maintained on site	Individual cell frames can be very thin, thus providing a large gas output from a small piece of equipment
No pumps or filters required	Fallout from military and aerospace programmes in fuel cells as well as hydrogen oxygen production generation has greatly assisted bipolar cell development
Simple internal gas lift circulation	Mass production of plastic cell components could result in lower capital costs
	Potential to operate at very high densities
	Electrical arrangements of electrolysers can allow a ground potential where the gases and electrolyte leave the system, or electrolyte enters the system
Disadvantages	
Difficult to achieve small interelectrode gaps	Sophisticated manufacturing and design techniques required
Heavy intercell busbars	Parasitic currents lower current efficiency
Inherently higher power consumption from potential drop in cell hardware	External pumping, filtration, cooling and gas disengaging system required
Cell pressures and temperatures limited by mechanical design	Malfunction of a unit cell difficult to locate
Each cell requires operator attention for temperature, electrolyte level and gas purity	Repair to a unit cell requires entire electrolyser to be dismantled (in practice)
Sludge and corrosion products collect within cell	Higher disruption to production for maintenance problems

Electrodes

For a material to be used as an electrode in an alkaline electrolyser, it must have good resistance to corrosion in concentrated alkali solutions and at high temperatures. In addition, it must have catalytic activity allowing the absorption of the chemical species involved in each of the electrolysis reactions, and it must have low resistance to electrical transmission.

Currently, nickel is widely used in alkaline electrolysers and is recognised as an electrode with acceptable capabilities to support the Oxygen Evolution Reaction (OER) in a wide range of operating conditions and presenting one of the lowest investment costs compared to other materials of construction.

Cathode

Iron-based electrodes have been used in the manufacture of electrolysers, however, they tend to exhibit average corrosion resistance under typical operating conditions. This has led to a preference for nickel-based materials, which may have better corrosion behaviour, but have the disadvantage that under certain conditions hydrogen can be adsorbed, partially deactivating the material and increasing energy consumption.

The surface of the nickel electrodes can be treated to increase the surface area and the number of active sites for adsorption of chemical species by sandblasting, obtaining a reduction in the potential of the HER close to 50 mV for currents between 0.1 and 1.0 A/cm² [11].

Alternatively, the surface can be treated with Raney nickel coatings by sintering or electroplating with Nickel Aluminite (NiAl) or Nickel-Zinc (NiZn), where the Al and Zn are subsequently dissolved, leaving a porous structure with high surface area [17]; this coating allows to obtain reductions close to 200 mV. Additionally, nickel electrodes are activated by adding sulphur. It has been suggested that this mechanism affects hydrogen formation by increasing the strength with which it is adsorbed on the Ni-S structure, however, its mechanism is not yet fully clear [17].

In addition to activation with Raney nickel and nickel sulphide, it has been possible to increase the electrocatalytic performance of nickel cathodes by incorporating active substances such as Iron (Fe), Carbon monoxide (Co) and Molybdenum (Mo). However, the stability of these during electrolyser operation is questionable and deactivation over time has been described [17].

Finally, precious metal electrodes offer the best performance, with low corrosion rates and significantly low energy consumption, however, their high cost has led the industry to focus on developing techniques to coat nickel substrates with platinum-ruthenium or platinum-palladium alloys [11] [17]. A summary of the main cathode coatings is presented in the following table.

Table 2: Summary of the behaviour of different surfaces used in cathodes; adapted from [11] and [17]

Composition	Electrolyte	Current density (A/cm²)	Working temperature (°C)	ηH_2 (mV)
Smooth Ni	30% KOH	0.3	30	443
			50	416
			70	367
			90	335
Steeblasted Ni	50% KOH	0.1	90	270
Raney Ni	30% KOH	1	90	250
	50% KOH	0.1	90	240
Raney Ni/Co	50% KOH	0.1	90	150
Ni-S	1M NaOH	0.1	60	97
Ni-S reduced	30% KOH	1	120	150
Ni-Mo nanopowder	2M KOH	0.02	25	70
Ni-Mo alloys	30% KOH	0.5	70	60
Ni-Ru	1M NaOH	0.1		87
Ni-Ir	1M NaOH	0.1		57
N-Ti	1M NaOH	0.1	80	240
Pt	50% KOH	0.1	90	110

Anode

The oxygen production reaction usually has a higher relevance in the energy profile of the electrolyser because it is slower, involves a larger number of intermediate reactions on the electrode surface and requires the transfer of up to four electrons for each proton transferred. Under normal conditions, this reaction presents a potential of about 400 mV, representing about 20% of the total voltage of the electrolytic cell [11].

The development of materials for the construction of anodes has not been entirely satisfactory because high overpotentials are still required for the reaction to take place, and additionally, oxidation reactions occur that degrade the materials, affecting the efficiency of the electrolysis over time.

Despite this, alkaline electrolysers have the great advantage of working acceptably with non-precious metals such as nickel, cobalt and steels, without presenting efficiencies very different from those shown by precious metals such as Iridium (Ir), Platinum (Pt), and Rhodium (Rh). It is for these reasons that nickel is widely used on the market as an anode construction material.

Some oxide mixtures such as $LaNiO_3$, $NiCo_2O_4$ and Co_3O_4 exhibit high oxygen production activities, and Ni and Ni-Co surfaces treated with spinel oxides ($MgAl_2O_4$) can offer higher efficiencies than those obtained with precious metals. A summary of the main anode coatings is presented in the following table.

Table 3: Summary of the behaviour of different surfaces used in cathodes; adapted from [11]and [17]

Composition	Electrolyte	Current density (A/cm²)	Working temperature (°C)	ηH₂ (mV)
Raney Ni	50% KOH	0.1	90	240
Ni	50% KOH	0.1	90	280
Raney Ni - Co	50% KOH	0.1	90	240
Raney Co	50% KOH	0.1	90	230
Stainless steel	1M NaOH	0.25	80	406
Smooth Ni	1M NaOH	0.25	80	406
Ni + Spinel type CO₃O₄	1M KOH	0.1	25	235
Fe-37Ni alloy	30% KOH	0.2	80	230
Ni(OH)₂	30% KOH	0.2	80	180

As mentioned in previous sections, the formation of bubbles affects the efficiency of the electrolyser because they can adhere to the surface serving as a barrier for the adsorption of chemical species, in other words, bubbles can adhere to the electrodes reducing the surface area available for electrolysis.

To reduce the amount of bubbles adhering to the surface, two different routes have been proposed, the first consists of adding surfactants to the electrolyte solution, reducing the surface tension and thus the ability of the bubbles to adhere to the surface; however, this solution increases the energy requirements of the system, so it is not easy to implement at an industrial level. The second alternative is to treat the electrode surface by coating it with a porous carbon-doped NiO structure, which has been experimentally shown to have the potential to reduce the amount of bubbles adhering to the electrode surface [18]. However, their use is still restricted to experimental or small-scale units.

Diaphragm
The diaphragm of an electrolyser is the material that separates the electrodes at the shortest possible distance, allowing the passage of hydroxyl ions (OH^-) from the cathode to the anode. It prevents any other chemical species from passing through the material and thus reducing the likelihood of gas mixing with associated risks to the safety of the equipment and a loss in operating efficiency. Membranes are porous materials that can be impregnated with the alkaline solution, allowing the free flow of OH^- ions, but whose internal structure offers a sufficiently high pressure drop to prevent H_2 and O_2 gas from passing through [19].

The first diaphragms used for the production of alkaline electrolysers were made of asbestos. However, its use has been restricted as a result of the risks associated with human health, and also because it is a material that normally suffers chemical affectation under operating conditions, representing a risk of gas mixing inside the equipment. Finally, this material presents mechanical limitations making it necessary for the typical thickness to be 2 mm, increasing energy losses compared to diaphragms made with other materials.

Positive results were obtained with materials based on polysulfone and polyphenylene sulfide. However, their use showed that they had a slightly hydrophilic behaviour, affecting wetting and therefore reducing the flow of ions inside them. Subsequently, composite materials were developed that offered the right balance of properties making their use in electrolysers viable. The material most frequently used today is constructed from zirconium dioxide (ZrO_2) on a polymeric structure, whose commercial name is ZirfonTM [19].

The use of membranes made of sintered metals has also been evaluated, with the advantage of high corrosion resistance and good ionic conductivity. However, their use has been limited due to their high electrical conductivity, generating a risk of short circuits in geometries such as zero-gap and making them difficult to control.

Effect of the operating conditions of the electrolyser
As mentioned above, electrolysis is favoured by high temperatures as this form of energy is harnessed to meet the energy requirements of the reaction and complements the electrical energy supplied through the DC circuit. Generally speaking, high temperature produces higher process efficiencies, however, electrolysers normally operate at a condition that limits the temperatures to reduce any disturbance to the system. For this purpose, recirculating solution cooling systems are installed to remove the heat generated by the current passing through the electrolyser, known as the Joule effect. For alkaline electrolysers operating at low temperatures, typical maxima are in the range of 100 to 130 °C as a result of restrictions of the materials of construction (mainly the membrane) and not of any vaporisation effect of the water, as this can be easily managed by pressurising the system.

On the other hand, low pressures usually favour the efficiency of electrolysis. However, the operating pressure of these systems is determined by considering the energy requirements of the whole installation and not only those related to the thermodynamics of the reaction. To this end, it is important to consider that both the storage and consumption of hydrogen in processes such as ammonia synthesis require high

pressures achieved by means of compression systems installed after hydrogen synthesis, which usually have high energy consumption.

This is why a cost sensitivity analysis is necessary to find the optimal operating conditions, considering that the reaction of an electrolyser operating at high pressure will consume more energy and require a higher initial investment. But on the other hand, the electricity requirements for subsequent compression will be lower.

Regarding the effect of varying the electrolyte recirculation flow rate, it has been found that low flow rates generate an increase in the quality of the gas, that is, the hydrogen obtained is of higher purity than that generated at high flow rates. However, the electrolyte flow rate must be high enough to reduce the negative effect of bubble coverage on the electrode, which causes a drop in the energy efficiency of the system [21].

Finally, it is important to note that some manufacturers allow operation between 25 and 100% of the net hydrogen production capacity in order to avoid the formation of potentially flammable hydrogen-oxygen mixtures due to the diffusion of these gases through the membranes. Additionally, these equipments usually have a maximum recommended number of on/off cycles that correspond to the lifetime of the sensitive components of the electrolyser, a use above this value can generate risks by increasing the probability of equipment failure [22].

1.2.2 Proton Exchange Membrane (PEM) water electrolysis
With the start of the space race in the United States in the 1950s, the need arose to develop electrolytic cells free of liquid solutions that were not susceptible to malfunctioning in the absence of gravity in space. As a result of these efforts, a new group of polymers called ionomers was developed, which were periodic ionised elements covalently bonded to a main organic

skeleton, which allowed the use of acid electrolytes, whose main advantage lies in the fact that the protons are more mobile than the OH⁻ ions used by alkaline electrolysers.

In the 1960's, the development of PEM electrolysers took off with the synthesis of sulphonated tetrafluoroethylene-based fluoropolymer-copolymers that could be used in electrolytic cells, offering good corrosion performance. However, the main advantage was the reduction in membrane thickness (20-300 µm), making the distance between electrodes smaller compared to that of alkaline electrolysers and, therefore, reducing energy consumption and obtaining efficiencies of 80% at 1 A/cm² [20].

Unfortunately, this new technology made it necessary to use platinum-based catalysts, as these are the only electrocatalysts that exhibit good mechanical behaviour in acidic solutions. The use of these high-cost materials, coupled with the fact that the fabrication of the membranes and other parts of the electrolyser required specialised techniques, meant that the cost of manufacturing PEM electrolysers ishigh, and the industry continued to use methane reforming as the main source of hydrogen.

In the 2000's, this type of electrolyser took on new strength as global plans for energy transition began to be implemented, with major challenges focused on the development of new materials to reduce the use of noble metals, while maintaining the same levels of energy efficiency.

Functioning of PEM electrolysers
Compared to alkaline electrolysers, PEMs have a very simple overall structure, where the gas treatment downstream of the electrolysis cell is relatively small, because it does not require separation of or cordoning off of alkali solution, and the water tank can be used as an oxygen separation tank, as shown in the figure below.

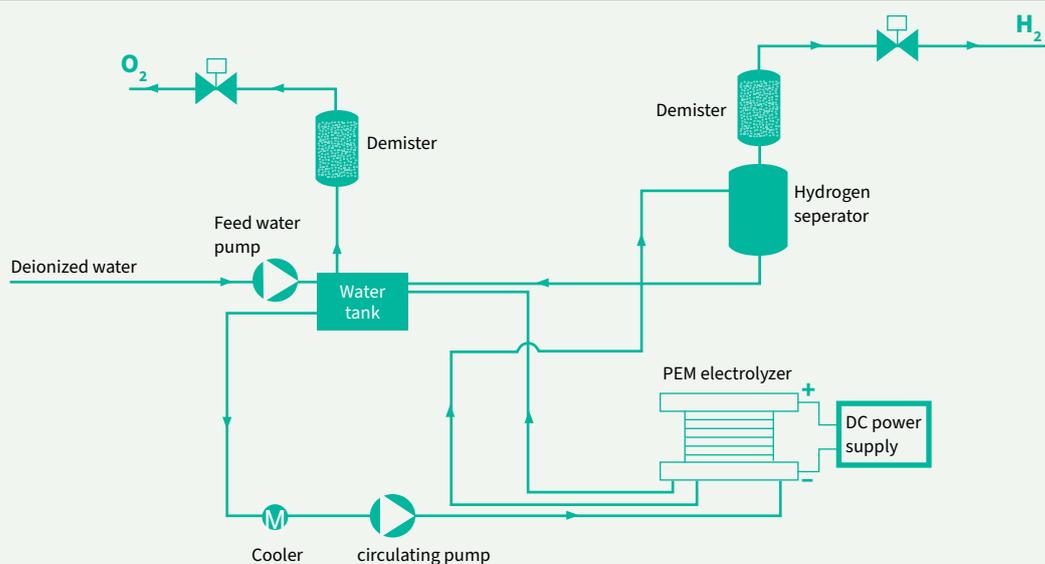**Process diagram of hydrogen production using a PEM electrolyser**

Figure 6: Based on [10]

The system starts with the feeding of de-ionised water, the quality requirement in this case being much stricter than for the alkaline electrolyser. These units operate with ultra-purified water type I (ASTM D1193) because impurities can affect the behaviour of the catalysts and increase the corrosion levels of the other parts. Once the water is electrolysed, the oxygen flows into the water tank where it is separated from any liquid it may carry, and is then filtered through molecular sieves. On the other hand, the hydrogen passes through a separator where the water is removed and filtered through molecular sieves. In this equipment there is no electrolyte, only the water is recirculated. In general terms, the electrolysis in a PEM can be described by two half-reactions shown in the schematic below. The reaction starts at the anode, where the water molecule is adsorbed on the electrode surface and decomposed, releasing oxygen, two electrons and a proton that migrates across the membrane to the cathode and reacts on its surface, for the final synthesis of hydrogen:

General reaction scheme inside a PEM electrolyser

anode: $H_2O(l) \rightarrow \frac{1}{2} O_{2(g)} + 2H^+ + 2e^-$

cathode: $2H^+ + 2e^- \rightarrow H_{2(g)}$

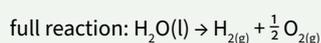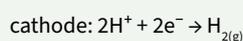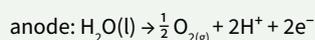full reaction: $H_2O(l) \rightarrow H_{2(g)} + \frac{1}{2} O_{2(g)}$
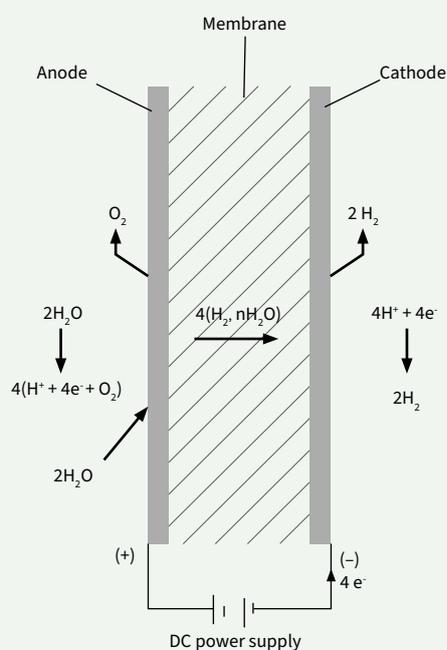
Figure 7: Based on [20]

These reactions are carried out in electrolysis cells, the central component of which is the membrane and the porous electrodes at each end of it. Normally, this arrangement is supported between two equally porous current distributors made of sintered titanium particles. Finally, the system is complemented by two plates through which electricity is supplied to the cell and allows the separation of each of the units; these plates are connected by a bipolar arrangement, as shown in previous sections, and have slots or holes that allow the evacuation of gases and the supply of water.

Membrane electrode assemblies (MEAs)
Membrane electrode assemblies are the membrane or ionomer and the catalysts that act on the cathode and anode. This arrangement is where the hydrolysis reaction takes place and is responsible for approximately 24% of the total cost of the electrolytic cell [2]. The membrane acts as a skeleton and is commonly constructed from Perfluorosulphonic acid polymer, operating satisfactorily even when its typical thickness is 0.05 to 0.25 mm. However, low thicknesses can cause gas permeability problems, reducing hydrogen purity and mechanical strength and increasing the risks associated with gas mixing.

Traditionally, PEM electrolysers operate at low temperatures as a result of the restrictions presented by the organic materials from which the membranes are constructed. However, since the reaction is favoured at high temperatures, alternative materials based on perfluorosulphonic acid-derived compounds adapted with Titanium Dioxide (TiO_2) and Silicon Dioxide (SiO_2) have been proposed that allow temperatures above 100 °C to be reached, thereby improving the energy efficiency of the system. These inorganic metal oxide fillers are hygroscopic, which allows the membranes to have better water retention and more uniform distribution, resulting in lower ohmic resistance and, in turn, better energy efficiency of the cells [23].

The membranes are coated with electrolytic catalyst, which can be either directly on the surface of the polymer, which is most often used, or on the surface of the current distributor. There are various coating methods, however, the most commonly used method of manufacture involves applying a slurry of catalyst to the surface, heating and pressing the system, which may then be chemically treated, depending on the type of catalyst to be applied.

The polymeric membranes frequently used in PEM electrolysers allow the passage of small quantities of gases, generating small oxygen contents in the hydrogen stream, which must then be treated by purification processes to obtain purities of 99.99%. This is a result of the microstructure of the polymer, in which it is possible to find interconnections that allow the passage of these elements, reducing the energy efficiency of the cell.

Catalysts
In the current state of maturity of PEM technology, platinum and iridium based catalysts are used, however, the main focus in the development of this system has been to reduce the use of these noble metals and to initiate the use of composite materials with similar behaviour.

Hydrogen evolution electrocatalysts

Platinum has been widely used to carry out the half-reaction of hydrogen synthesis at acceptable rates and optimising energy consumption. However, the high cost and scarcity of platinum has been the main reason why PEM electrolysers are not yet widely commercialised on an industrial scale. One of the approaches used to remove this barrier has been to distribute the platinum in a material that provides a large surface area for support, aiming for a platinum layer thickness of one atom; monoatomic layer deposition impregnation methodologies and electrochemical methods have been developed for this purpose. These efforts have gone hand in hand with the development of carbon-based supports, where new materials have emerged such as MXenes, metal carbides, and sulfides such as Molybdenum disulfide (MoS_2), which facilitate the deposition of platinum on their surface, offer additional catalytic active sites enhancing the activity of the material and increase the stability of the platinum over time [23].

In recent years several transition metal dichalcogenides such as MoS_2, Tungsten disulfide (WS_2) Molybdenum diselenide ($MoSe_2$) and Tungsten diselenide (WSe_2) have been developed and applied to theHER. Besides these, the use of Ni-activated transition metal carbides on nickel foams with graphene has been evaluated. In both cases the results have been acceptable, however, the level of technical maturity of these catalysts is not yet advanced [24].

Electrocatalysts for oxygen evolution reaction

It is widely accepted that the durability of anode catalysts in PEM systems suffers from high corrosion rate, which becomes an obstacle for the industrial use of this technology. However, nowadays iridium-based catalysts are a viable option offering stability and high activity in the half-reaction of oxygen production, which is why IrO_2 is the most widely used catalyst commercially, however, it is sensitive to several factors such as particle size, crystallinity and morphology, which are mainly derived from the method of synthesis of the compound.

As with platinum, a major challenge in building PEM electrolysers relates to the reduction in the use of iridium, as current consumption is approximately 2 - 2.5 mg/cm², and the requirement for industrial scale application is estimated to be between 0.05 and 1 mg/cm² [23]. To achieve these reductions, changes in the packing densities of the catalyst and the inclusion of other components such as ruthenium (RuO_2) have been evaluated, which generates a synergy with iridium, increasing the stability of the catalyst over time.

Another important focus in the development of these new catalysts has been on the development of better supports and methodologies to disperse the iridium on their surface, by studying the use of carbides and nitrides. TiO_2 has proven to be an excellent support for IrO_2 and the IrO_2-TiO_2 mixture has been used commercially in electrolysers, however, the conductivity is poor and in some cases it is necessary to increase iridium to obtain similar results to the same catalyst with a different support. In order to increase the conductivity of TiO_2, materials including niobium Nb, vanadium V and wolfram W have been created, obtaining optimal iridium loadings of 0.4 mg/cm² [23].

Unfortunately, iridium-free catalysts have not shown positive results in laboratory-scale tests, as they do not offer the right balance between stability and activity. Thus, manganese-based oxides show good stability, but very low activity, while ruthenium-based oxides show good activity, but very low stabilities under the operating conditions. Additionally, phosphide and sulfide-based compounds have not shown good behaviour in either of these two aspects. Therefore, it is considered that in the short term it is not technically feasible to replace iridium-based catalysts by iridium-free materials.

Current collectors

Current collectors are porous materials placed between the Membrane electrode assembly and the bipolar plate, on both sides of the catalytic electrodes. This material is used to conduct electricity between the electrode and the bipolar plate where the DC power source is connected. It also has the function of allowing the transport of water and gas from the reaction site to the cell outlet.

For the proper functioning of the electrolytic cell, the current collector must have high corrosion resistance and electrical superconductivity due to the strongly acidic media and oxidative environments in which it operates. In addition, the pore size and structure of the current collector are important factors, as the gases produced in the water electrolysis process must be effectively expelled and the water must reach all catalytic sites on the electrode surface.

The collectors are mainly made of titanium, which is the material that offers the best chemical behaviour and the possibility to modify the porosity to meet the requirements of each section of the cell, as in the cathode the transport requirements are simple since liquid water and hydrogen gas flow in the same direction from the catalytic layer to the bipolar plate; but in the anode compartment liquid water flows from the bipolar plate to the catalytic layer while oxygen flows in the opposite direction.

Additionally, porosity has an important effect on current transmission, as a small number of contacts between particles can lead to overheating at these points, affecting the operation of the electrolyser; conversely, a high number of contacts can lead to high pressure drops, affecting the flow of materials inside the cell. The porosity can be adjusted during material production by changing the size and shape of the titanium particles.

Representative characteristics for current collectors are presented in the table below.

Table 4: Current collector parameters for PEM electrolysers; based on [2]

Current collector thickness	0.8-2 mm
Electrical resistance	5-10 mΩ cm
Gas permeability	$1 \times 10^{-13} - 1 \times 10^{-11}$ m²
Porosity	20-50%
Pore size	5-30 µm
Particle size	25-250 µm

Bipolar plate

Bipolar plates act as separators for the different cells that make up the electrolyser, conduct heat and electrical current between the individual cells, and distribute heat and water in a way that optimises operation. Therefore, the bipolar plate must have high chemical resistance, high thermal conductivity, low permeability and high mechanical strength.

Graphite was used as a construction material for bipolar plates due to its excellent electrical conductivity. However, this material has many problems such as its high corrosion rate and low mechanical strength. Currently, the most commonly used bipolar plates are made of titanium and coated stainless steel. However, some problems remain, such as hydrogen embrittlement [24]. Thus, the development of low-cost and

stable bipolar plates under operating conditions remains a major challenge for the mass use of PEM electrolysers.

1.2.3 Solid Oxide Electrolyser (SOE-SOEC-SOWE) (high temperature electrolyser)

Solid oxide electrolyser cells have generated special attention because they can have a higher conversion efficiency compared to alkaline and PEM electrolysers, have lower power consumption and allow, without major technical problems, the co-electrolysis of water and carbon dioxide (CO_2) for the generation of synthesis gas for use in other processes. This technology is operated at temperatures between 700 and 800 °C, however, different studies have focused on reducing this temperature in order to increase the lifetime of the equipment [25]. In these electrolysers, water in the form of steam reacts at the cathode to produce hydrogen, while an O_2- ion is transported through the electrolyte to the anode where oxygen is produced. Typical efficiencies of these systems can reach 95%, which will depend on the steam production pathway.

The general architecture of the process is shown in the figure below. Water fed to the system passes through heating coils to ensure conversion to steam and the high temperature required to enter the electrolyser. In a parallel stream, air is fed as an oxygen scavenging fluid, reducing the risks associated with its handling. A series of heat exchangers allow partial energy recovery, improving the overall efficiency of the process. Unfortunately, this system is still under development and marketing of small-scale systems, so it is not expected to be implemented on an industrial scale in the short term.

Process diagram of hydrogen production using a SOEC electrolyser
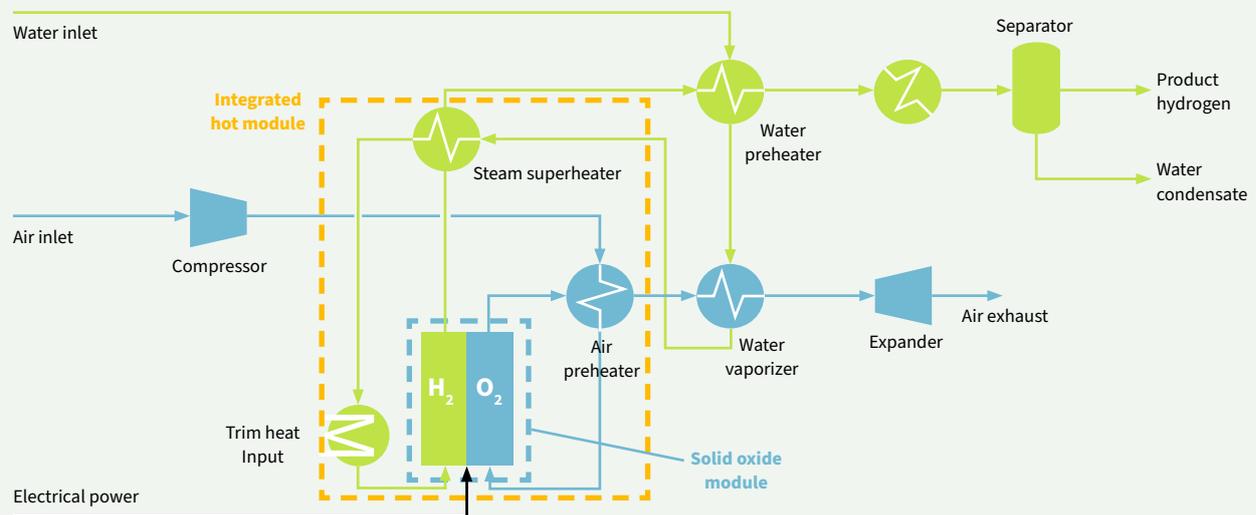
Figure 8: Based on [26]

Traditional SOEC uses a cathode made of Nickel-Yttria-Stabilized Zirconia cermet (Ni-YSZ), the anode is based on Perovskite material, typically Lanthanum Strontium Cobaltite Ferrite (LSCF) and the electrolyte typically used is Yttria-Stabilized Zirconia (YSZ).

These materials were selected based on the constraints of high temperature operation, where the materials must have similar thermal expansion and the electrodes must be highly conductive and have porosity to allow the surface reaction to take place [25].

1.2.4 Comparison parameters between electrolysers

Although there are variations in the different technological aspects of the electrolysers described above, it is possible to find representative values that allow decisions to be made when developing a green hydrogen generation project. The table below summarises the aspects that should at least be considered when making a technology selection.

Table 5: Representative values for the main technical aspects of electrolysers; adapted from [27], [8], [10], [28], [29], [16]

Description	Unit	Alkaline	PEM	SOEC
Technology status		Widespread commercialisation	Commercialisation. Small and medium scale	Lab-scale and small commercial scale
T range	°C	60-80	50-80	700-1000
P range	bar	<30	<30 (350)	1-5
Electrolyte		25-30 wt% KOH	Perfluorosulfonic acid	Y_2O_3-ZrO_2, Sc_2O_3-ZrO_2, MgO-ZrO_2, CaO-ZrO_2
Charge carrier		OH^-	H^+	O^{2-}
Anode reaction		$2OH^- \rightarrow \frac{1}{2}O_2 + H_2O + 2e^-$	$H_2O \rightarrow \frac{1}{2}O_2 + 2e^- + 2H^+$	$O^{2-} - 2e^- \rightarrow \frac{1}{2}O_2 + 2e^-$
Cathode reaction		$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	$2H^+ + 2e^- \rightarrow H_2$	$H_2O + 2e^- \rightarrow H_2 + O_2^-$
Anode catalyst		Ni_2CoO_4, La-Sr-CoO_3, Co_3O_4	Ir-Ru Oxide	$(La,Sr)MnO_3$, $(La,Sr)(Co,Fe)O_3$
Cathode catalys		Niquel foam/Ni-stainless steel. Ni-Mo/ZrO_2-TiO_2	Platinum	Ni-YSZ or Ni-GDC cement
Hydrogen purity	%	>99.8	99.999	-
Separator		Asbestos, polysulfone-bonded polyantimonic acid, ZrO_2 on polyphenylsulfone, NiO, polysulfone impregnated with Sb_2O_5 polyoxide	Polymer membrane	Ceramic
Sealant		Metallic	Synthetic rubber/ fluoroelastomer	Glass and vitro-ceramics
Current distributor		Ni	Titanium	Ferritic stainless steel (Crofer Apu)
Conventional current density	A/cm²	0.2-0.5	0-3 (up to 20)	0-2
Cell voltage	V	1.8-2.4	1.8-2.2	0.95-1.3
Cell area	m²	3-3.6	<0.13	<0.06
Eficiency	%	63-82	67-82	81-86
Capacity	Nm³/hour	1-500	1-250	1
Stack lifetime	kh	55-120	60-100	5-2
System lifetime	Year	20-30	10-20	-
H_2O specification		Type I or II	Type I	Steam
Load cycling		Medium	Good	Good
Stop/go cycling		Weak	Good	Good
Minimum partial load	%	10-40	0-10	-
T cycling		Weak	Good	Good
Degradation rate	%/1000h	0.13	0.25	2.8-1.9
Specific energy consumption	kWh/Nm³	4.2-4.8	4.4-5	2.5-3.5
CAPEX	USD/kW	500-1,400	1,100-1,800	>2,000

It is important to highlight that the values shown in the table above can serve as input information for the elaboration of the financial models of the project in early stages. However, it is important to consider the context where the project will be developed, as there are particular aspects that may favour some type of technology, such as the requirement of auxiliary support systems (water treatment, hydrogen purification, hydrogen compression systems, etc.), operational costs, tax benefits, among others.

Overall, the development of the green hydrogen production project will be based on the balance between the advantages and disadvantages.

1.3 Integration of electrolysers with renewable energy generation systems

The use of renewable energies for hydrogen production through the electrolysis of water presents important challenges related to the stability of electricity, as some energy sources, such as photovoltaic, wind and tidal, present oscillations over time, some of them completely periodic and predictable, such as the increase and decrease of radiation as a result of day and night cycles or the periodicity of the seasons. While other oscillations present a completely random behaviour such as those generated by changes in wind direction or other climatic factors such as cloud formation.

On/off cycles, such as those that occur between day and night when solar energy is used, can reduce the lifetime of electrolysers. If these shutdowns are performed in a sudden and uncontrolled manner, reverse current can be generated which has a high potential to damage electrodes and other components, reducing the energy efficiency of the system or causing total equipment failure.

On the other hand, if the fluctuations are smaller, sudden changes in the temperature of the electrolyser can occur, which in turn leads to changes in the gas flow and loss of gas purity. When fluctuations cause the production rate to be very low, backflow mixing of gases through the membranes (oxygen in the hydrogen and hydrogen in the oxygen) can occur, creating a high-risk condition due to the potential for explosion associated with this type of mixing. This is why some electrolyser suppliers have limited the minimum operating speed to 40% of the maximum capacity of the equipment.

For the case of alkaline electrolysers, reverse current has a negative effect as the catalysts oxidised at the anode and reduced at the cathode during electrolysis revert to their original chemical states during shutdown, in a cycling that is not 100% reversible. To overcome these problems, it has been proposed to add a small amount of manganese to the cobalt phosphate-based cathode catalysts as a sacrificial oxidation element at the cathode. Additionally, it has been proposed to add $Co(OH)_2$ nanosheets to the anode electrolytes to obtain a self-repairing

effect on the nickel electrodes. However, in general terms, this problem associated with intermittent operation still affects this type of technology.

On the other hand, compared to alkaline electrolysers, PEMs have a slower degradation rate when using fluctuating renewable energies such as solar and wind, and have the ability to handle much lower power loads. Although power intermittency may be seen as a disadvantage, current interruption or acidification treatment can partially restore the reversible degradation of the electrodes, which strengthens the use of PEM electrolysers in renewable energy systems given the intermittent characteristic of photovoltaic and wind generation, allowing the electrolysers to recover much of their performance during the outage time. It is for this reason that restoration periods should be taken into account during the economic evaluation of a project coupled to this type of generation technology.

Recent studies have shown that uninterrupted operation or frequent variations in the power supply can accelerate the reduction of the platinum and iridium loading of PEM electrolysers, leading to assembly thinning [30], which may require an increase in the amount of precious metals to compensate for the deterioration and avoid significant efficiency loss over time.

On the other hand, tests on SOEC electrolysers have shown that this type of technology is robust to small fluctuations in power supply. However, large variations in operating conditions will require the development of specialised materials to absorb the thermal stress generated.

1.3.1 Photovoltaic power
Photovoltaic (PV) energy has different types of fluctuations. At the beginning of the day, the power output is minimal and increases until it reaches peak radiation at around midday. However, during the hours of energy production, variations can occur as a result of the formation of clouds in the sky. Thus, the variation of solar radiation on sunny days can be less than 50 W/m² while on cloudy days it can be as much as 150 W/m² [31].

Although it is considered that small variations can be significantly reduced by increasing the number of interconnected PV plants and the distance between them, other strategies have been proposed and can be classified into three categories:

Grid independence
To address the fluctuations generated during the day in systems that are completely isolated from the grid, a DC/DC current regulator can be included in the system to match the voltage-current requirements of the electrolysers at any power with minimal conversion losses, however, it will increase the initial investment cost. Another option is to select the PV panels so that their i-V output matches the i-V polarisation curve of the electrolysers [32].

In order to reduce the initial investment, it has been proposed to eliminate the use of DC/DC regulators and to distribute the system with different electrolytic cells that can be connected independently and adjusted to the power supply offered by the photovoltaic cells. Experimentally, a power transfer close to 99% has been obtained in a scheme like the one shown below, demonstrating the viability of this type of system [33].

Grid assisted

This scheme consists of connecting the photovoltaic power supply system to an external power grid, so that the cells can operate at their design capacity and at times of low production, the system can take the remaining amount required from the grid, allowing the electrolyser to operate continuously and without fluctuations. The disadvantage of this arrangement is that it requires external power for operation, which in some cases means that the hydrogen produced is not classified as green, and a regulator must be installed to control the supply, which increases the initial investment in the project.

Peak shaving systems

This scheme is considered when the system must operate independently and in isolation. In this case, the PV system can be coupled with another power source that reconverts hydrogen into power such as hydrogen burning engines or fuel cells.

Integrated combined heat-power schemes have been proposed in which at peak production times, surplus hydrogen is sent to storage to be fed into a high-temperature solid oxide fuel cell (SOFC). Subsequently, when the amount of electricity decreases, the fuel cell consumes hydrogen for the production of electricity and the thermal energy emitted is used for cooling in absorption chillers or as direct heating. The general scheme of this process is presented below.

A variant of this system is the integration of the SOFC with an electricity generation turbine (GT) to partially harness the thermal energy from the fuel cell. A similar scheme was proposed with the use of a PEM fuel cell, in which part of the hydrogen from the electrolyser is compressed and stored in a tank, where it is taken for further use. It is possible to find variants in which the oxygen also goes through a compression and storage process to improve the efficiency of the PEM fuel cell. A general scheme is presented below.

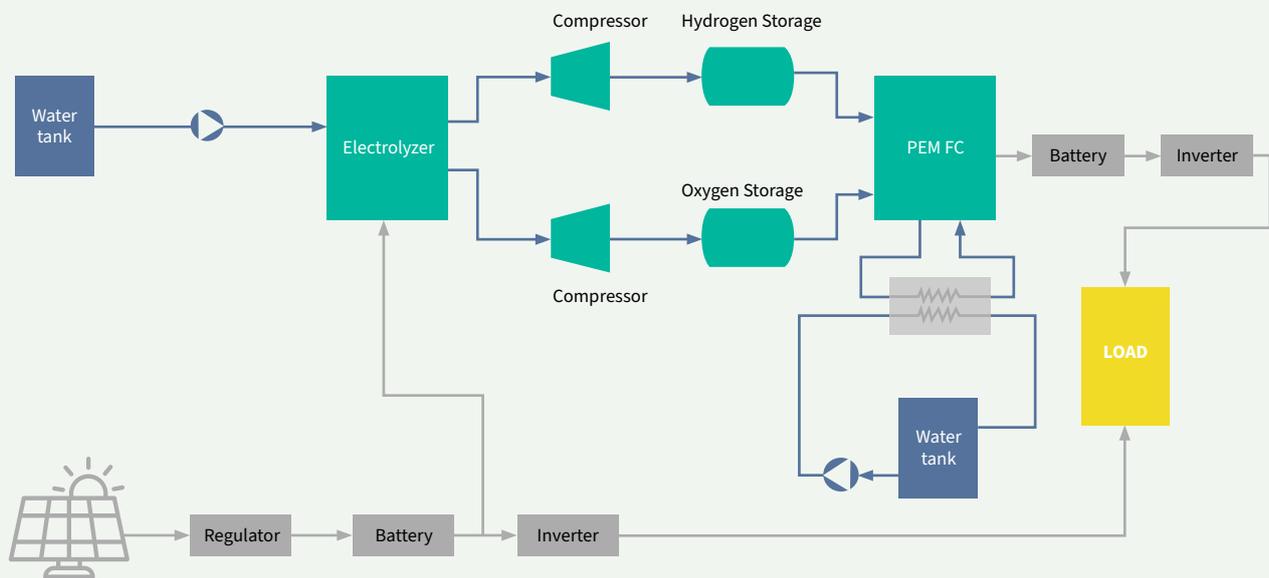**Integrated system with electricity generation using a fuel cell PEM**

Figure 9: Based on [36]

A different approach to the one outlined above is the storage of the residual energy generated at peak radiation times, in thermal systems that allow the heat to be recovered and reconverted to electricity at off-peak radiation times. These systems differ mainly in the type of substance used for thermal storage and the operating conditions of the system, as they usually use a Rankine power cycle, which is the most competitive for non-photovoltaic systems.

A proposed system is based on the integration of the hydrogen production unit with a transcritical CO_2 power cycle, since this substance allows a better use of the energy entering the system due to its thermodynamic properties. These systems are composed of three sub-systems, firstly, there is the solar energy collector in which the radiation is absorbed by water that enters a boiler in which it transfers the heat to the CO_2 and then returns to the collector. The heated CO_2 enters a turbine and expands, producing electricity and losing pressure, and is then pumped to supercritical pressure. Variations on the latter process have been proposed, in which variants are found in the turbine used for the process and the process is energetically integrated to increase its efficiency, which is why it is possible to find processes in which the feed water to the electrolyser is preheated with residual energy from the CO_2 thermal cycle. Variants replace the water with molten salts that allow higher temperatures to be reached and can be stored more easily for overnight use.

1.3.2 Wind power

Wind energy generation does not show a proportional relationship between wind speed and the amount of energy generated; rather, wind speed, wind direction, as well as the amount of generation, can vary significantly over time. This behaviour must be compensated for to avoid the same limitations described for PV systems. In this case, the amplitude of fluctuations can also be reduced when a large number of wind turbines are interconnected over a large area, however, this is not always sufficient.

For these systems, the strategy of oversising electricity generation is also applicable, so that during peak periods, energy can be stored in batteries, in the form of hydrogen or as thermal energy, and then consumed during off-peak periods, providing continuity of electricity supply to the electrolyser and avoiding fluctuations that could damage plant components. A general applicable scheme is shown in the picture below, where the energy produced by the wind turbines is split to support the consumption of the facilities, while the remaining amount is fed to the electrolyser for the production of hydrogen. This hydrogen is split in two, one part feeds the ammonia production process, while the surplus is compressed and stored for further consumption in the process and to support electricity generation with the use of a fuel cell.

General scheme of cogeneration based on wind energy
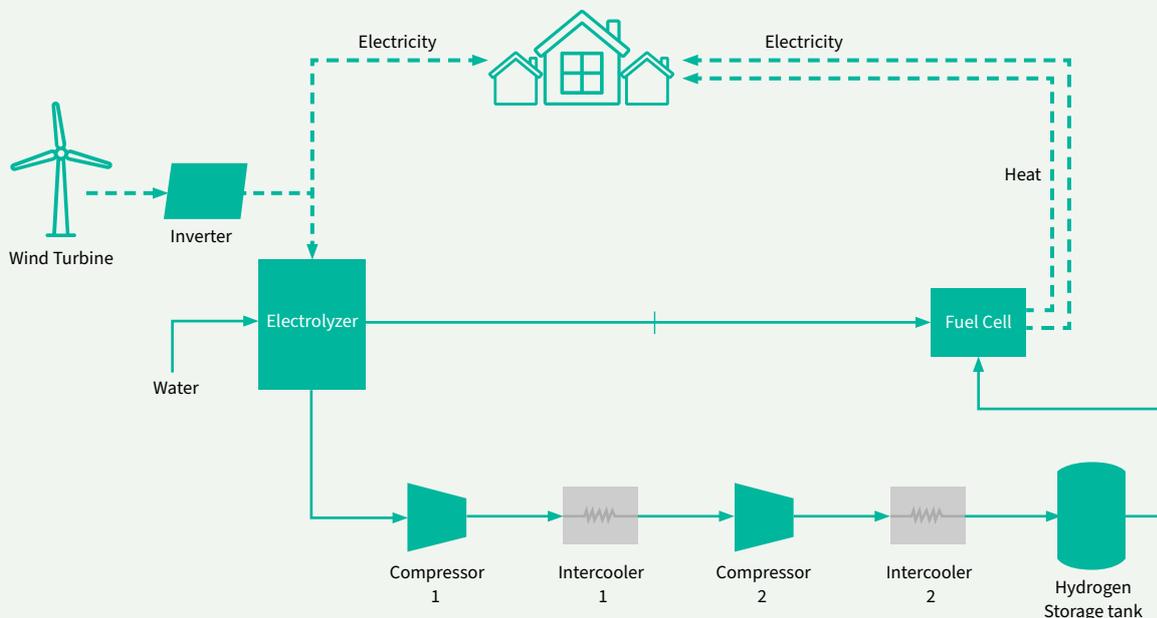
Figure 10: Based on [38]

1.3.3 Hydropower

The use of hydropower has advantages compared to other conventional renewable energies, among them are its low cost, the speed with which it can reach 100% capacity once it starts up, additionally, it is usually more stable than photovoltaic or wind energy, for this reason the generation of hydropower can be a suitable complement, helping to stabilise the fluctuations of other systems.

Hydro power generation systems consist of a water reservoir, where the potential energy is guaranteed to be converted into electrical energy by means of turbines. The electricity generated is fed into a common grid, from which a fraction is taken to be converted from AC to DC and fed to the electrolyser. The hydrogen produced goes directly to the ammonia plant or can be partially stored.

General scheme of ammonia production from hydro energy
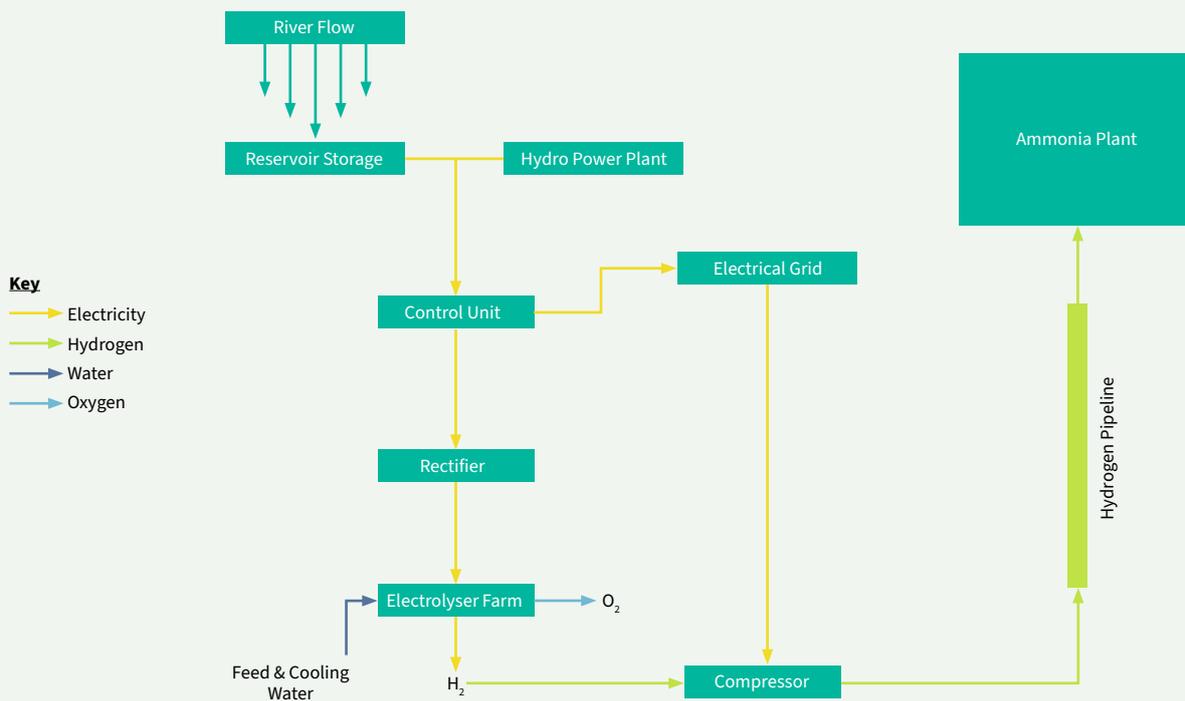
Figure 11: Based on [36]

1.3.4 Geothermal energy

Geothermal energy can be integrated with different hydrogen production systems, which can be grouped into four groups:

- Direct production of hydrogen from geothermal steam by recovering hydrogen from the gas mixture.
- Electrolysis of water using electricity produced in geothermal power plants.
- Electrolysis of high temperature water using heat and electricity produced in geothermal power plants.
- Thermochemical processes that use heat produced in geothermal power plants.

Of these routes, the thermochemical generation processes present a greater efficiency. The four general arrangements are presented in the following image.

Ways of hydrogen production through geothermal energy
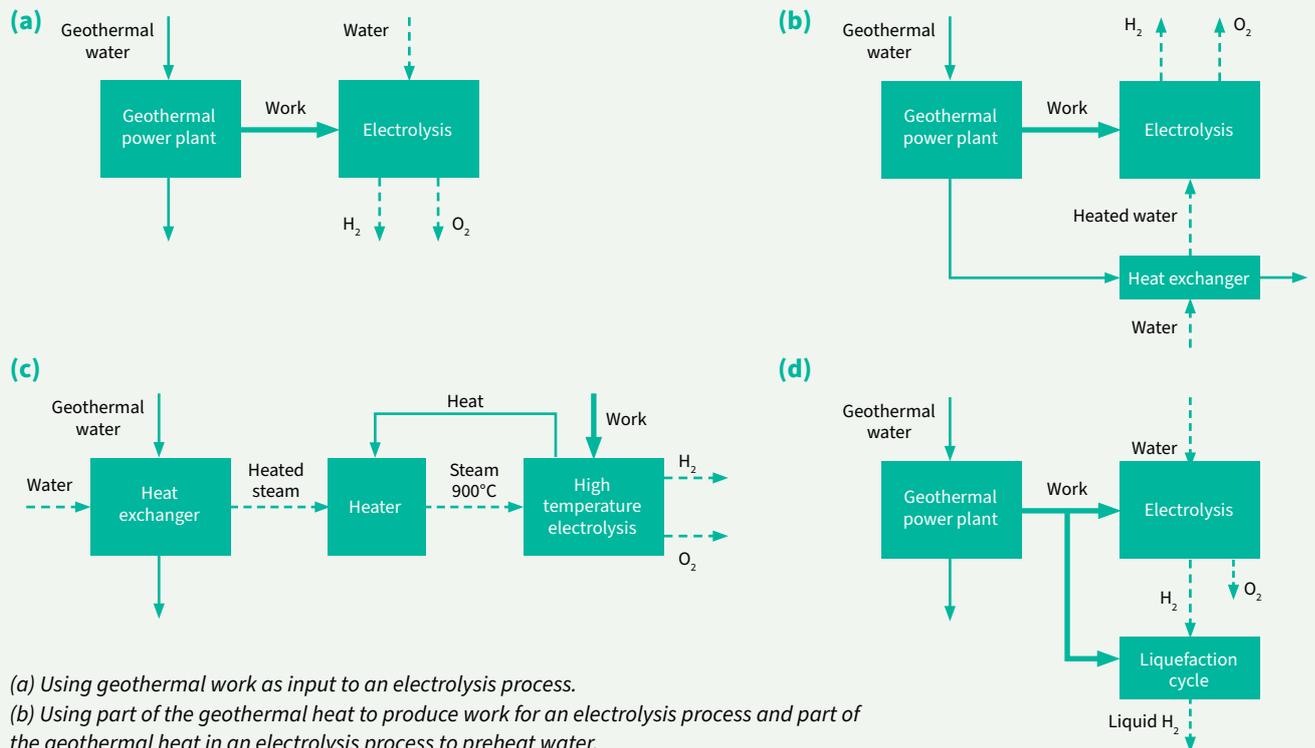
(a) Using geothermal work as input to an electrolysis process.
(b) Using part of the geothermal heat to produce work for an electrolysis process and part of the geothermal heat in an electrolysis process to preheat water.
(c) Using geothermal heat to preheat water in a high-temperature process.
(d) Using part of the geothermal work for electrolysis and the remaining part for liquefaction.

Figure 12: Based on [39]

Unlike PV and wind systems, geothermal systems do not have the problem of intermittency, so it is possible to directly connect the power source to the electrolysers without generating any type of affectation.

1.4 Production of hydrogen from biomass

Biomass is a renewable natural resource that is easily accessible by various industries and communities. Agricultural, forestry, fishing, livestock and municipal residues, such as straw, rice husks, cellulose, sawdust and animal manure can be used for the synthesis of hydrogen, making biomass emerge as a sustainable raw material for biorefineries.

Currently, the greenest way to produce hydrogen from biomass is through gasification. However, this process presents challenges given the variability in the composition of organic material, in which moisture, the energy content of the material, which are largely a consequence of external factors such as climatic conditions, the type of soil, the type of crop and its nutrition; introducing variability to the production process and making it necessary for the design of the production facilities to allow them to operate with these variations.

In general terms, the average hydrogen content in biomass is considered to be low, around 6% [40], which is equivalent to 0.672 m² of gaseous H_2 produced by 1 kg of biomass, has a relatively low content when compared to non-renewable sources such as natural gas, whose content is 25%.

Despite the wide range of biomass sources, the use of this material presents a significant challenge because its energy level is relatively low compared to other sources, making the additional use of conventional fuels or alternative energy sources necessary in some cases to meet the energy requirements of the production process.

In addition, the need to transport large quantities of biomass for processing can be seen as a constraint if one considers that the carbon footprint of the hydrogen produced can be increased by the use of fossil fuels consumed by transport vehicles. On the other hand, it must be ensured that there is effective synergy between the green hydrogen production chain and the food value chain, as the cultivation of crops for biomass production favours deforestation of regions and competes directly with the use of land for food production. This makes it clear that the integration of biomass utilisation processes with external processes makes projects based on renewable organic material

viable. Thus, this technology could eventually be used to consume biomass such as by-products or waste from industries.

The use of waste biomass is an environmentally friendly approach as it contributes positively to waste management and sustainable energy production, effectively reducing greenhouse gas emissions and mitigating climate change. Biomass is therefore emerging as an important renewable energy source with the potential to replace fossil energy and capable of driving the development of the circular bioeconomy.

There are different configurations for the gasification process depending mainly on the type of biomass, the required quality of output gases and the range of capacities, with the fluidised bed gasifier being considered the most economical and most commonly used technology option at low scales [42].

The gasification process is relatively simple. After transport, the biomass goes through a drying process in which the gases coming from the gasifier itself can be used. This stage can even be carried out inside the equipment itself and its main objective is to improve the thermal behaviour of the gasifier. Subsequently, pyrolysis is carried out in which tar, coal and synthesis gas are produced, which are then passed to the gasifier together with steam. The exhaust gases are filtered and pass to the reformer together with air and the shift reactor where the maximum conversion to CO_2 and H_2 is guaranteed.

In the conditioning stage, the gases pass through a desaturator and then the CO_2 is separated from the hydrogen by absorption with amines or with the use of a Pressure Swing Adsorption (PSA) system. In the first case an amine solution is used to trap the CO_2, when the fluid is saturated, it is sent to another equipment where it is heated in order to release the CO_2 and recirculate the amine to the adsorption tower in a cyclic process. On the other hand, in the PSA process the gas is adsorbed at high pressure on packed beds of activated carbon or zeolites [43].

The hydrogen conditioning process ends with the conversion of CO, which could not be removed in the previous processes, to methane (CH_4) in a reactor called methanator, which aims to avoid contamination of the ammonia synthesis reactor.

There is a variant of the traditional gasification process called supercritical water gasification. In this process, water is fed at high temperature and pressure, reaching a state in which the density of the water is two or three orders of magnitude higher than that of steam, and its ionic activity increases up to three orders of magnitude from its value at ambient conditions at temperatures between 200 and 300 °C. Under these conditions, water can act as a catalyst for various reactions, allowing a greater quantity of chemical compounds to be obtained than those generated by traditional gasification.

Both variants of gasification (conventional and with supercritical water) are favoured by the use of catalysts, as they allow operating at lower temperatures and improve the selectivity of the reactions to increase hydrogen production. Catalysts of an alkaline nature are the most commonly used for biomass gasification, among which KOH, NaOH, K_2CO_3, Na_2CO_3, $KHCO_3$ and $Ca(OH)_2$ stand out. These materials increase the volatility of the gas phase and enhance steam reforming reactions. Some metal oxides are also used as catalysts as they significantly increase selectivity, are recyclable materials and can be considered as abundant in nature.

Another alternative method for thermal hydrogen production from biomass is fast pyrolysis, in which biomass is decomposed by high temperature (500 °C) in the absence of oxygen to produce vapours, aerosols and some carbon. After cooling of these products, a liquid with a heating value about half the representative value of conventional fuel oil is obtained. A comparison between these production routes is presented in the table below.

Table 6: Different ways of hydrogen production by thermal treatment of biomass; based on [41]

	Steam gasification	Supercritical water gasification	Fast pyrolysis
Average hydrogen production (wt%, g H_2/100 g biomass)	Without catalyst: 4 g With catalyst: 7 g	Without catalyst: 3 g With catalyst: 5 g	Without catalyst: 2 g With catalyst: 3 g
Reactor	Uperr/lower ventiliation gasifier; fluidised bed	Batch reactor, continuous reactor	Fluidised bed; fixed bed, rotary furnaces, ablation reactor, drainage bed
Advantage	Suitable for large-scale industrial production with high gasification rate and low ash production	High conversion and hydrogen concentration without tar and coke formation and secondary pollution	Oxygen free and relatively high hydrogen concentration
Disadvantage	Separation and purification of gas products are difficult	Difficult to recycle alkaline catalysts and strict operating conditions	High equipment requirement and energy consumption with low hydrogen yield
Challenge	Decrease the tar content; optimise the catalyst composition to reduce its deactivation; reduce energtic and material costs	Technological development, reduce energetic costs	Raw bio-oil feeding; scale up of the process; optimise the catalyst composition to reduce its deactivation

Hydrogen production from microbiological action of biomass

The production of hydrogen from microbiological action can be classified into three main processes.

Dark fermentation: In this process, substrates are converted by anaerobic bacteria growing in the dark. These micro-organisms are able to utilise energy-rich hydrogen molecules, if available, and use the electrons from hydrogen oxidation to produce energy. In parallel, it is possible to obtain a mixture of commercially valuable compounds as a final result of the process.

An overview of the steps involved in dark fermentation is shown in the figure below. The first step of this type of fermentation is glycolysis, in which glucose is converted to pyruvate, the key intermediate with the formation of the reduced form of nicotinamide adenine dinucleotide (NADH). Under anaerobic conditions, pyruvate can be converted to acetyl-CoA in a reaction catalysed by pyruvate ferredoxin oxidoreductase (PFOR).

This process has the advantage of utilising different wastes; however, the overall efficiencies of the process are low and require a large infrastructure to handle the volumes of material to be treated. The main characteristics of dark fermentation with different wastes are shown in the tables below.

Photofermentation: In this process, anoxygenic photosynthetic bacteria, and in particular purple non-sulphur bacteria (PNS), are able to reduce H+ ions to gaseous H_2, using both the reducing power derived from the oxidation of organic compounds and low molecular weight fatty acids, as well as energy derived from light. In general, this process is considered very promising due to the high substrate conversion yields that can be achieved, the possibility of using a broad spectrum of sunlight, the absence of O_2 evolution reactions and the possibility of coupling this type of H_2 production with waste disposal [45].

In these processes, light supply is a very complex problem involving both light sources and the design of efficient photobioreactors. In addition, the quality of the substrate needs to be strictly controlled and it is of great importance to ensure adequate carbon/nitrogen ratios. On the other hand, large-scale production requires industrial, commercial and agricultural waste suitable for photofermentation, which is produced

throughout the year and has a stable composition, which can be a constraint in many regions; these systems should be located close to the waste production sites to facilitate logistic activities and should have a large surface area in order to provide sufficient area for the photobioreactors.

Hydrogen production through methane: Renewable CH4 is generally produced through anaerobic digestion of organic material which allows the generation of biogas with a methane content varying between 35 and 70%, with CO_2, nitrogen and water making up the remaining percentage. After being purified, the methane is subjected to the reforming process in which the molecule is dissociated into CO_2 and H_2, and subsequently fed to the ammonia plant to be treated and consumed in the synthesis reaction.

Unfortunately, this process cannot be implemented on a large scale as a result of technical difficulties in pre-treatment of the biomass, problems associated with feeding different types of biomass, inefficiencies typical of fermentation and problems in removing waste and excess volatile fatty acids [47].

1.5 Comparison of hydrogen production technologies

There are a large number of hydrogen production routes from renewable energies. The selection of the appropriate route must be made taking into account different factors such as the type of energy available and the required final purity of the hydrogen, in a balance that considers the particular context of the region where the project will be implemented, the logistical activities required for the supply of the raw material, the possibility of integration with external processes, the facility for intermediate storage of the hydrogen and the availability of specialised technical services for maintainability and operation.

Although this wide range of possibilities exists, the level of maturity of some technologies has led to a predominance of alkaline and PEM electrolysers as renewable electricity utilisation systems in the industry, and pyrolysis and gasification as applicable processes for the use of biomass.

A summary of the hydrogen production processes, with a brief description of their characteristics and an indication of the technological maturity level (TML) is shown in the table below.

Table 7: Summary of hydrogen production processes; based on [48]

Process Category	Energy I/P	Feedstock Hydrocarbons (H) Non-Hydrocarbons (N)	Technology	Eff. (%)	*Clean (C/N/CCS)	**TML (1-10)
Electrolysis	Electric	Water (N)	AR	62-82	C	9-10
		Brine (N)	PEM	67-84	C	7-9
			SOC	75-90	C	3-5
			Chlor-alkali	NA	C	2-42-2
Electro-pholysis	Electric	Water (N)	Photoelectrochemical	0.5-12	C	1-2
Photolysis	Photonic	Water (N)/ Algae (H)	Photosynthesis	1.6-5	C/N	1-3
Biophotolysis	Bioenergy	Microalgae	Photo-fermentation	<1	N	1-3
	Photonic	Cyanobacteria	Algal Hydrogen	1-3	N	1-3
		Photsynthetic-Bacteria		2-7	N	1-3
		Fat (H)		12-14	N	1-3
		Nutrients (H)			C/N	1-3
		Waste (H)/ Biomass (H)				
Bioelectrolysis	Bioenergy	Biomass (H)	Microbial electrolysis	70-80	N	1-3
	Electric	Hydrogenases	Nitrogen fixation	10		
Biolysis	Bioenergy	Microorganism	Dark fermentation	60-80	N	3-5
		Fermentative bactérias	Hydrolysis	NA	N	2-4
		Biomass (H) + Water (N)	Aqueous phase reforming	35-55	N	5-7
		CO (N) + Water (N)	Biological Shift Reaction	NA	N	2-4
Bio-thermolysis	Bioenergy-Heat	Biomass (h) (microwave) acid pretreated	Co-fermentation hydrothermal	NA	N	2-4
				35-45	N	1-3
Thermolysis	Heat	Water (N)	Waterthermolysis	20-55	C	1-3
		Biomass (H) (absence of O_2)	Pyrolysis	35-50	N	8-10
		Biomass (H)	Gasification	35-50	N	10
		Coal (H)	Coal gasification	74-85	N/CCS	10
		Fuels (H)	Steam Reforming (SR)	60-85	N/CCS	10
		Fuels (H)	Membrane Reactors	64-90	N/CCS	7-9
		Biomass (H)	Partial oxidation	60-75	N	7-9
		Methane (H) + CO_2	Autohermal	60-75	N	6-8
			CO_2 Dry Reforming	NA	C/N	
Thermo-electrolysis	Heat-Electric	Fuels (H)	Plasma Reforming	9-85	N	1-3
	Chemical reaction	Water (N)	Redox	3-5 wt	C	4-6
		Metals (N)		NA	C	
		Metal hydrides (N)		NA	C/N	
		Gas-based hydrides		NA	C	
		Metal Hydroxides (N)				
Radiolysis	Radiation	Hydrogen peroxide (H_2O_2)	Radiolysis	NA	C	1-3
		ɣ-radiolysis				

Cleanliness: Clean without emissions (C); Not clean with emissions (N); Nearly clean through the use of carbon capture and storage (CCS). Technology maturity level (TML - 0: low, 10: high).

Due to the strong impact that the implementation of sustainable pathways for hydrogen production will have in the future, it is important to invest in the advancement of some of the currently promising technologies. A list of the most promising systems currently under development is shown in the table below.

Table 8: Emerging hydrogen production technologies; based on [48]

Technology	Brief description	Current eff (%)	R&D area
Anion Exchange Membrane (AEM)	Semipermeable membrane designed to conduct anions while being impermeable to gases such as oxygen or hydrogen	67-74	Catalyst Membrane Efficiency
Membraneless electrolyser	Two independent laminar flow streams can be separated up to a certain length, which ensures the formation of a virtual layer separating anode and cathode	40-80	Increase pressure scale
Membrane reactor	A membrane is a mass selectivity structure. Membrane reactor allows hydrogen transfer under a variety of driving forces like pressure, temperature, electric pontetial, etc.	64-90	Membrane, CCS, catalyst, process intensification
Photosynthesis	Artificial photosysthesis towards solar fuels generation via CO_2 reduction	1.6-5/10	CO_2 utilisation to fuel carbonhydrate (food) efficiency
Photocatalytic generation	Semiconductor-based photocatalytic hydrogen generation by high-energy photons to drive the reaction	3-11	Efficiency, catalyst, integration with PV
Dark fermentation followed by photo-fermentation	Fermentation process followed by second stage activated by exposure to light	57	Waste-to-bio-hydrogen, catalyst, efficiency
Plasma arc decomposition	Natural gas is passed through plasma arc to generate hydrogen and carbon soot (high-temperature pyrolysis)	9-85	Graphite production, catalyst
Unitised regenerative	Reversible electrolyser and FC in one unit i. e. can generate hydrogen and power (small scale is available)	43-51 Round trip	Efficiency, scale, switching time
Battolyser	Batteries which can produce hydrogen after fully charged	76-90 overall	Efficiency, hydrogen production control

NITROGEN SEPARATION AND PURIFICATION

Three commercially available technologies can be employed to produce purified nitrogen gas from air for its later use as raw material in the ammonia synthesis: cryogenic distillation (CRD or ASU), PSA, and membrane permeation.

When using high purity nitrogen as feedstock for the ammonia manufacture, the continuous purge of the synthesis loop can be eliminated as the inert concentration (mainly Ar) is usually less than 0.2 vol.% and such low quantity will be removed with the condensed ammonia and therefore will not accumulate in the system loop increasing its pressure [49].

It should be clarified that, in an ammonia plant, the method of hydrogen combustion can also be used, this requires no separate nitrogen production unit, and it is usually used in conventional steam methane reforming, where the air is introduced in the hydrogen production section, thus the oxygen is combusted with part of the hydrogen producing water. This process can be employed in a solid oxide electrolyser to generate the heat for the hydrogen production from water formation. However, this process cannot be used in combination with other electrolysers [50]. The three processes for nitrogen separation from air are described in this section.

2.1 Cryogenic distillation

Cryogenic distillation (also known as Air Separation Unit, ASU or Low-temperature rectification) is currently the prevalent technology in large-scale industry [51]. This method consists of distillation columns operating at very low temperatures to separate air components according to their different boiling temperatures.

In this process, the air requires a pre-treatment, air passes through a series of filtration devices to remove dust particles and moisture, then through compressors and is cooled to remove additional water vapor. The objective of this purification is to remove contaminants which could freeze by the next step, the molecular sieve adsorption.

In the molecular sieve process, two beds of activated alumina and activated carbon are used to remove the contaminants by reversible adsorption, with the incoming air flow alternating between beds to allow regeneration of the depleted bed [52].

The clean compressed air is then further cooled through countercurrent heat exchange with outflowing streams of waste gas and cold nitrogen product and by passing it through an expansion turbine, this causes condensation of the air at cryogenic temperature, this liquified air is then separated into its constituents, typically in a two-distillation column arrangement (operating at descending pressures from 6 bar to 1.5 bar) at a temperature slightly below the boiling point of the oxygen, relying on the difference in the nitrogen and oxygen boiling points, $-196\,°C$ and $-183\,°C$ respectively [53]. Figure 12 shows a general diagram of the cryogenic distillation process.

Nitrogen product emerges from the top of the low-pressure column and is available at 1.5-4.5 bar. Additional refrigeration is required to accommodate heat losses in the system from process efficiencies and imperfect thermal insulation. This is provided by either expanding a portion of the incoming compressed air through an expansion turbine, or through the vaporisation of a small quantity of delivered liquid nitrogen [52]. From this air separation process, besides the high purity of N_2 gas, high purity O_2 is produced as by-product [54].

Capacities of on-site cryogenic nitrogen plants range from 250 to over 50,000 Nm^3/h with 1 ppm residual O_2, even levels of less than 1 ppb O_2 can be achieved for specific applications as semiconductor manufacturing [52].

Despite the operation at very low temperature, cryogenic distillation is heat integrated to achieve energy consumption around 0.11 MWh/ton N_2 (1 GJ/ton NH_3 [55]), less than PSA or membranes. However, this heat integration limits process flexibility as it requires hours for startup and has an operating lower bound of around 60% of installed capacity which limits intermittent operation [50].

Cryogenic distillation benefits even more from economies of scale than ammonia synthesis loops. A tenfold capacity increase for nitrogen purification only results in a threefold increase of the capital expenditure [56], which is why it is the industrial standard for large scale air separation above 150,000 ton N_2/year. In fact, the Linde Ammonia Concept already uses cryogenic distillation to obtain nitrogen feedstock [53].

Cryogenic distillation process
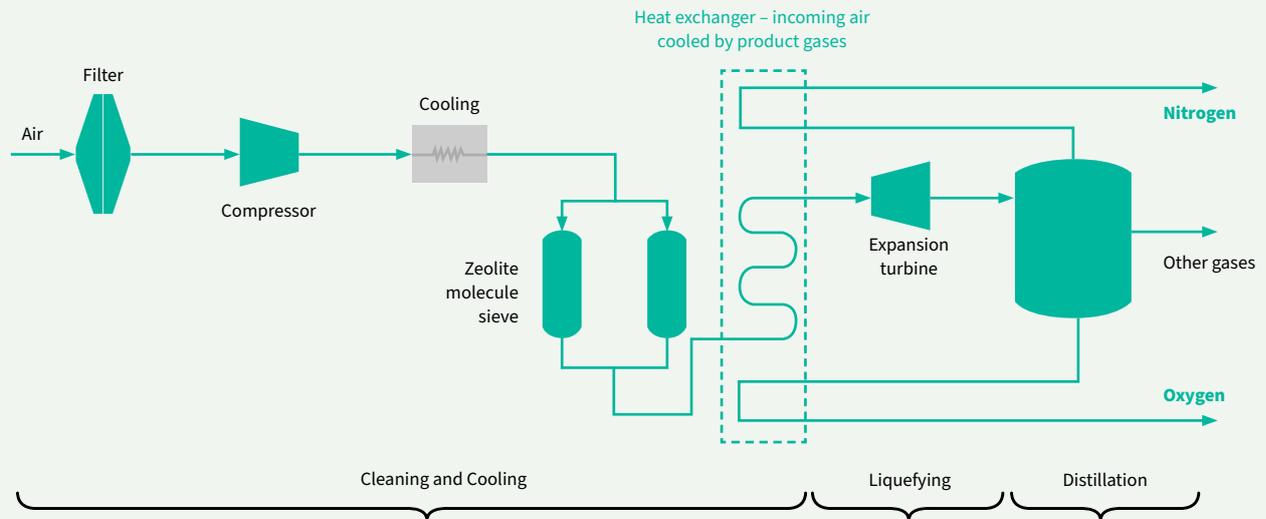
Figure 13: Based on [127]

2.2 Pressure Swing Adsorption (PSA)

Pressure Swing Adsorption is a cyclic separation process which consists of separating nitrogen from air by adsorbing the oxygen on a solid under pressure. In this process, the compressed air is passed through a bed of O_2-selective carbon molecular sieve operating at near-ambient temperature. There are at least two beds with pressure cycling between 6-8 bar for adsorption and 1 bar for desorbing the oxygen [53]. Figure 14 shows this process.

PSA units are compact and inherently modular, so they are well-suited for small production scales below 7,500 ton N_2/day. They also have good dynamic flexibility, with startup times less than an hour and a lower operating bound around 30%. The main drawbacks of PSA relative to cryogenic distillation are more expensive scale-up for larger production targets, lower nitrogen purity around 99.8%, and higher energy consumption of 0.22-0.31 MWh/ton N_2 [51].

According to suppliers, the minimum required purity of the nitrogen to not poison the ammonia synthesis catalyst is 99.999%-99.9995%, this means that the oxygen content in the nitrogen is not recommended to be higher than 5-10 ppm (it could be up to 20 ppm but only in case the hydrogen has no oxygen content), therefore a PSA process is normally followed by a deoxo unit to increase the purity of the nitrogen [51]. A deoxo unit normally remove residual oxygen content by catalytic combustion with hydrogen, after which the water is removed in a regenerative dryer [50].

Pressure Swing Adsorption process

Figure 14: Based on [128]

2.3 Membrane permeation

Membranes separate the nitrogen from the air by the principle of selective permeation across the membrane wall (see Figure 14) [57]. The separation is driven by a pressure difference between the feed and the permeate, which operate at 6 to 25 bar and atmospheric pressure respectively.

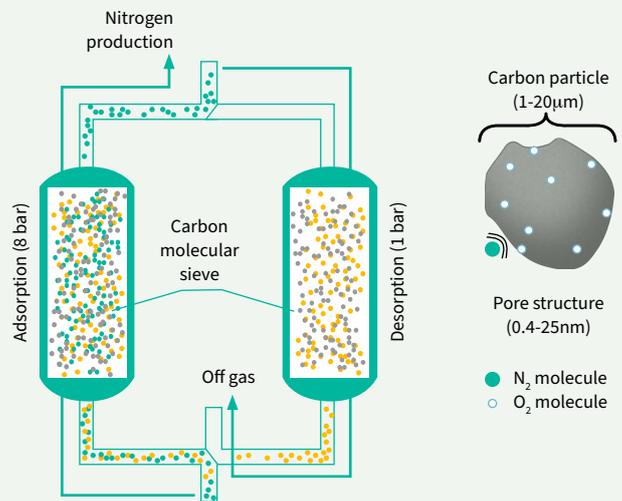This process is carried out at ambient temperature and O_2-permeable polysulfone hollow fiber or carbon molecular sieve membranes are normally used.

Membrane permeation process

Oxygen rich
fast
Nitrogen
slow
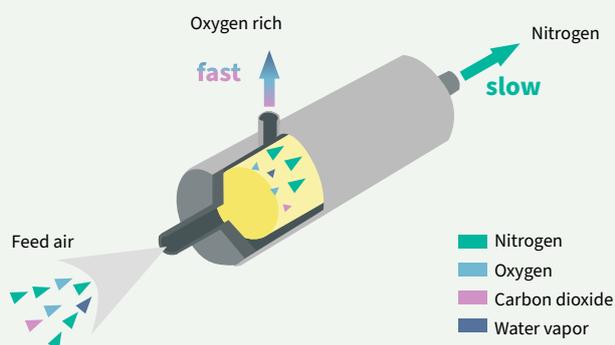Feed air

Nitrogen
Oxygen
Carbon dioxide
Water vapor

Figure 15: Based on [129]

Membranes for nitrogen production are a less developed technology than cryogenic distillation or pressure swing adsorption. This process offers many benefits including modular configuration and low capital cost, better dynamic flexibility than cryogenic distillation and simpler operation than PSA. However, to achieve nitrogen purity above 99.5%, very high pressure is required which can result in energy consumption as high as 0.65 MWh/ton N_2. Additionally, the investment cost of this process depends almost linearly on the quantity of membrane required and thus the production scale; this lack of economies of scale means that membranes may only be well-suited to nitrogen production below 750 ton N_2/day [53].

Similar to the case of PSA, due to the low purity of the nitrogen obtained, membranes require a deoxo unit.

2.4 Comparison of nitrogen separation alternatives

The preferred alternative for nitrogen separation depends on the required nitrogen purity and the scale of application. For both pressure swing adsorption and membrane permeation, a deoxo system is required to remove residual oxygen content [50].

Regarding the scale, due to economic reasons, for small-scale systems (<1MW scale), membrane permeation is the most favourable alternative, while pressure swing adsorption is preferred at intermediate scales (1-100 MW) and at large scales (>100 MW), cryogenic distillation has to be selected [51].

Generally, the life-cycle cost normalised per mole of nitrogen, increases with purity and decreases with scale. Cryogenic systems require the expansion heat exchangers and low temperature distillation to be performed in an insulated cold box, increasing the plant complexity relative to the other methods. The energy demand of the compressors and effectiveness of the heat-exchangers benefit greatly by scaling up the system. On the other hand, the capacity of a PSA unit decreases significantly with increasing purity, while the installation cost and power demand remain approximately the same. This is because the PSA packed beds need to be regenerated much more frequently to maintain the high purity [58].

However, the nitrogen production should allow flexible operation either by fluctuating nitrogen production, or by a storage tank controlling the release of purified nitrogen gas. In case of the first, pressure swing adsorption and membrane permeation offer the highest flexibility. A significant drawback of membrane permeation is the low attainable nitrogen purity at low energy consumption (up to 95 wt.% nitrogen purity), which makes this alternative unfeasible when other options are available [51]. Thus, several investigations are being carried out to obtain membranes with higher O_2 permeability and higher O_2/N_2 selectivity [59].

Table 9 presents a comparative summary of the relevant aspects of the technologies described in this section and Table 10 a brief comparative with main advantages/disadvantages.

Table 9: Comparison of nitrogen purification technologies; based on [50]

	ASU (Cryogenic)	PSA	Membrane
Temperature, °C	-195 to -170	20-35	40-60
Pressure, bar	1-10	6-10	6-25
Purity (wt. %)	99.999	99.8	99.5[1]
Energy consumption, kWh/kg N_2 (GJ/ton NH_3)	0.1 (0.3)	0.2-0.3 (0.7-1)	0.2-0.6 (0.7-2)
Capacity range (Nm³/h)	250-50,000 High	25-3,000 Medium	3-3,000 Low
Load range, %	60-100	30-100	30-100
Investment cost (k€/ tpd NH_3)	<8	4-25	25-45
TRL[2]	9	9	8-9

Table 10: Advantages and disadvantages of Nitrogen purification technologies; based on [51]

Alternative	Advantages	Disadvantages
Cryogenic distillation	High purity nitrogen production (up to 99.999 wt.%) Argon in oxygen product (up to 98 wt.% purity oxygen) (Pure oxygen product)	Requires continuous operation (Load range 60-100%) Slow dynamic response (order of hours) Cryogenic conditions Refrigeration compounds
PSA	Flexible operation (Load range 30-100%) Ambient temperature Little maintenance Automated operation Short start-up times Compact unit design High degree of fire safety Relatively easy to install and operate	Nitrogen purity up to 99.8 wt.% (however, oxygen can be as low as 0.01 wt.%) Argon in nitrogen product Additional deoxo unit required (No pure oxygen product)
Membrane	Flexible operation (Load range 30-100%) Ambient temperature Non-complex process operation Simple construction	Nitrogen purity up to 95 wt.% (oxygen removal down to 0.5 mol%) Argon in nitrogen product Additional deoxo unit required (No pure oxygen product)

2.2 Oxygen volumes and achievable purity

In the green hydrogen/ammonia projected future, where large quantities of hydrogen will be produced from renewable resources via the electrolysis process, by-product oxygen will also be produced on a large scale. The new electrical ammonia process would produce 1.4 kg of O_2 per kg of NH_3 arising from the electrolysis and air separation steps [54].

In this context, the use of the by-product oxygen could be evaluated as oxygen is an important industrial gas with applications in many processes [60], the main one being combustion [61]. The utilisation of by-product oxygen could also contribute to reducing the electricity consumed in oxygen separation technologies, such as cryogenic air separation and PSA. Table 11 shows some of the industrial applications of oxygen and their normal required purity, broadly two levels of oxygen purity are generally available on the market: high purity oxygen

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[1] In most cases membranes are used for nitrogen enrichment of air, rather than the production of highly purified nitrogen.
[2] Technology Readiness Levels (TRL) are a type of measurement system used to assess the maturity level of a particular technology. There are nine technology readiness levels, where TRL 1 is the lowest and TRL 9 is the highest [312]. See Annex A.

(concentration >99.5%) and low purity oxygen (concentration >90%) [62].

Besides, the use of oxygen would improve the energy efficiency of some industrial processes, for example, in an oxidation reaction, oxygen is much more efficient than the air as the use of pure oxygen improves efficiency through higher combustion temperature and CO_2 capture is easier by its greater partial pressure in the combusted gas mixture [49]. The use of oxygen-enriched combustion air in a number of energy-intensive industrial applications has the potential to reduce the amount of heat lost to the atmosphere by about two-thirds [60].

Table 11: Some industrial applications of oxygen

Industry	Application	Normal purity
Aerospace & aircraft	As a source of breathing oxygen for pilots and crewmembers at high altitudes [63].	99.7% [64]
Automotive fabrication	As a plasma cutting gas, an assist gas for laser cutting, and is sometimes added in small quantities to shielding gases [62].	
Chemicals	In its purest form, oxygen is used in many important chemicals such as ethylene oxide and titanium dioxide and to increase the production capacity of oxidation processes [62].	
Energy	Using oxygen in the place of air can increase performance and capital efficiency in many industries and can facilitate carbon capture processes, often used in boilers, process heaters, industrial fermenters and gasification processes to improve productivity [62].	
Glass	To enhance combustion in glass furnaces and reduce NOx emissions [62].	95% [65]
Healthcare	Medical oxygen is essential in hospital and clinical care for resuscitation and surgery, to aid in the treatment and prevention of hypoxemia and hypoxia and for various therapies [61].	95% [65]
Metal production	To replace or enrich air, increasing combustion efficiency in both ferrous and non-ferrous metal production [62].	
Pharmaceuticals & biotechnology	Critical for cell growth applications, oxygen is used in fermenters and bioreactors [62].	
Pulp & paper	Oxygen helps meeting stringent environmental regulations through use in delignification, oxidative extraction and wastewater treatment [62].	
Refining	Oxygen is widely used in refineries to increase the capacity of Fluid Catalytic Cracking (FCC) plants and Sulphur Recovery Units (SRU), and to improve wastewater treatment operations [62].	
Water & wastewater treatment	Oxygen can supplement or even replace air in the aeration basin to maximize treatment capacity, reduce odour and foam, and increase flexibility. Pure oxygen is also used in ozone production for water disinfection [65].	90-95% [65]
Welding & metal fabrication	The steel industry is the largest user of oxygen. Oxygen significantly increases gold processing and ore flow, reducing the cost of cyanide and waste products. Industrial oxygen generators are also used in the production of other metals such as copper and lead. A continuous supply of large amounts of oxygen is essential for the safety of miners [65].	<95% [65]
Fish farms	Fish need specific levels of oxygen in the water for optimal growth, so oxygen need to be dosed correctly to ensure faster growth, less disease and stress to maintain high quality [65].	90-93% [65]

However, the balance between by-product oxygen and oxygen demand is fundamental to determine the quantity of by-product oxygen that can be utilised and the quantity that will be harmlessly vented. According to [60], electrolysis itself is not attractive for producing oxygen and cannot compete with other technology but the by-product oxygen might be useful for making the hydrogen production more attractive, in this case, the authors conclude that in Japan the total oxygen demand in only three processes is larger than the potential supply of by-product oxygen from water electrolysis hydrogen, identifying an important business opportunity. This paper also concludes that selling oxygen to hospitals in Japan makes electrolysis comparable in price with steam reforming [66].

According to [67], 30% energy return can be obtained by using by-product oxygen to replace the air in the aeration of wastewater in the activated sludge process, or in the aquaculture industry.

Yet additional study is required to analyse the possibility of selling oxygen as a by-product and a study of the market that could potentially absorb oxygen needs to be undertaken.

AMMONIA PRODUCTION

Despite the fact that ammonia has been produced on an industrial scale for more than 100 years, its production process is complex since it is energy intensive. This high energy requirement is mainly due to the difficulty of breaking the diatomic nitrogen triple bond [54].

Nitrogen gas is considered an inert material, has two nitrogen atoms connected by a very strong and stable triple bond, and for breaking this bond significant energy input is required, around 941 kJ/mol [68], which is considerably higher than that of hydrogen 435.78 kJ/mol. This is why most plants and animals cannot assimilate nitrogen directly from the air and why the ammonia production reaction does not occur spontaneously.

Ammonia has been known for more than 200 years [69]. In nature, ammonia occurs almost exclusively in the form of ammonium salts [70] and natural formation of ammonia is mainly by decomposition of organic matter [71]. The earliest source of synthetic nitrogen compound was the Frank-Caro calcium cyanamide process in 1898 where ammonia was generated by the reaction of calcium carbide with nitrogen, a very inefficient process that required 190 GJ/ton NH_3 [72]. Several alternative processes were tried without much success, until in 1908 the process that dominates the market to this day [73], the Haber-Bosch process, was developed. The first commercial Haber-Bosch synthesis loop was built by BASF in Germany and started operations in 1913 with a production capacity of 30 ton NH_3/d [69].

However, the Haber-Bosch method requires significant capital investment, energy consumption and is currently powered mainly by hydrogen from fossil fuels. Therefore, although it is a mature technology, it must undergo a process of adaptation for the future production of green ammonia, and there is currently a lot of research in this direction to develop a renewable and affordable process under mild conditions [74].

Besides the former process, there are other pathways to produce ammonia, known as non-conventional or novel, and that are envisaged to enable downscaling and operation in remote areas [50], such as thermocyclic, electrochemical, photochemical and plasma-based processes, homogeneous synthesis, biological processes, and purification from animal waste or wastewater [55]. However, considering their current state of development and expectations in the near future [54], this paper only focuses on the first two alternatives mentioned, and of course, the Haber-Bosch process.

3.1 Haber-Bosch process

The Haber-Bosch process, the well-known ammonia synthesis loop, is currently used in more than 96% of ammonia synthesis worldwide [54]. Currently, all of the nitrogen used in this process is obtained from the air and the hydrogen is mostly produced from fossil fuels, by using natural gas (50%), oil (31%) or coal (19%) as feedstock [49]; nonetheless the hydrogen can be obtained from various green sources as described in section 2.1, as this process is not changed by the source of the hydrogen and nitrogen [75].

The general diagram of the ammonia production process is shown in Figure 16 where three main steps can be identified: i. compression, ii. ammonia condensation and iii. reaction.

In general, the synthesis loop consists of two compressors feeding the ammonia reactor. The first compressor handles the recycle stream of unreacted gas and the other increases the pressure of the make-up gas (a mixture of hydrogen and nitrogen). In most cases, both streams are mixed and pass through a heat exchange system to condense the ammonia produced before entering the converter [77].

In the converter, the ammonia is produced by using an iron-based catalyst (magnetite Fe_3O_4 or wustite FeO) at elevated temperatures around 400 - 500 °C and high pressures above 150 bar [49]. The reaction in the ammonia converter is as follows [51].

$$N_2 + 3H_2 \leftrightarrow 2NH_3 + 46.1 \text{ kJ/mol}$$
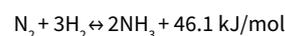
The former reaction is exothermic and favoured by high pressure and low temperature at equilibrium conditions. Although the theoretical ammonia equilibrium concentration can be close to 100% at low temperatures and high pressures, the rate of ammonia formation is extremely slow which makes it unfeasible to operate under these conditions. This is why the Haber-Bosch process is conducted at high temperature and pressure even though the unfavourable equilibrium conditions imply a lower production rate [78]. This low equilibrium single-pass conversion (in the range of 15%-25%) generated the need of recycling the unconverted part of the synthesis gas to the converter [79].
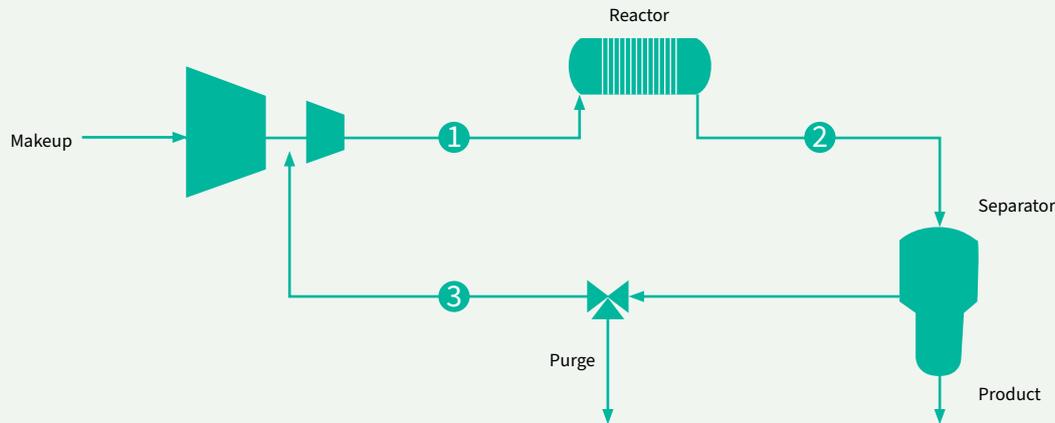
Ammonia synthesis loop

Figure 16: Based on [76]

Additionally, continuous purging may be required to relieve pressure due to accumulation of inert in the loop (methane and argon), but this depends on the purity of the raw materials (hydrogen and nitrogen).

In fact that the development of the Haber-Bosch process occurred more than 100 years ago, there has been no major change in this configuration. Even today, the synthesis section of most ammonia plants has the same basic configuration as the first plants [80] [81]. However, the process has been optimised over the years, including new catalysts, optimised reaction processes, new ways to separate ammonia, etc. and as result, its energy efficiency from natural gas currently reaches 60-70% (based on a lower calorific value and including hydrogen production) [55].

Figure 17 shows the main configurations that the ammonia loop can take, differ in the location of ammonia separation and the point at which the make-up gas is introduced [82]:

A) The make-up is fed directly to the converter, this configuration is used when the make-up gas is free of catalyst poisons, such as carbon or oxygen compounds.

The ammonia separation is carried out before the mixing of the recycle with the syngas, and because the ammonia is not diluted with the fresh gas stream, separation is favoured with a higher ammonia content, making it the most efficient energy arrangement and resulting in the lowest ammonia content at the entrance to the converter, favouring conversion as well.

B) The ammonia separation is carried out partially or entirely between the make-up gas supply point and the converter. This configuration is used when the fresh gas has contaminants in it, the unconverted gas is mixed with the recycle gas, then the ammonia is condensed and some of the contaminants are removed from the loop with the condensed ammonia.

The disadvantages of this configuration are that the efficiency of condensation is lowered by decreasing the ammonia concentration. A higher ammonia concentration exists at the inlet to the converter and all the ammonia produced must be compressed with the recycle gas.

C) In this arrangement, the compression of the recycle directly follows the condensation and separation of the ammonia, decreasing the energy waste of configuration B. This applies especially at synthesis pressures above about 250 bar when a greater portion of the ammonia formed can be liquefied by cooling with water or air.

D) This arrangement shows an additional ammonia separation stage that is used to purify the syngas and to have the benefits of configuration A in plants where the syngas contains contaminants. The following section describes the key elements in the Haber-Bosch process and their most important characteristics.

Schematic flow diagrams of ammonia synthesis loops configurations

a) Ammonia converter,
b) Ammonia condensation at low temperature,
c) Ammonia condensation at ambient temperature,
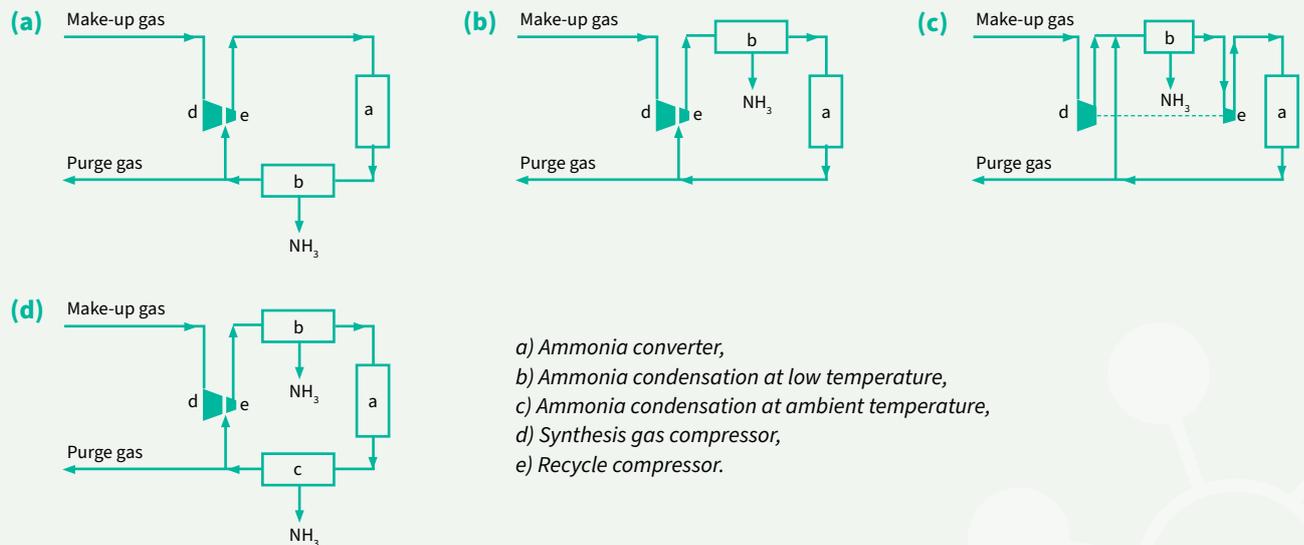d) Synthesis gas compressor,
e) Recycle compressor.

Figure 17: Based on [82]

3.1.1 Key components

The Haber-Bosch process has many variables and components; however, the following is a general description of the key components, their main characteristics and affectation by operating conditions.

Compressor

This equipment is mandatory to bring the synthesis and recycle gas to the pressure required to carry out the ammonia formation reaction. In general, two types of compressors are used in existing ammonia plants: reciprocating compressors and centrifugal compressors.

Reciprocating compressors, also known as piston compressors, are positive-displacement compressors that use pistons driven by a crankshaft to deliver gases at high pressure. They were the dominant technology to compress the synthesis gas to the level of synthesis loop up to the mid-1960s [83].

On the other hand, centrifugal compressors elevate gas pressure by adding velocity to the gas as it flows through an impeller. Since 1963, the application of this kind of compressors became standard practice in most ammonia plants irrespective of the synthesis gas generation technology [83], mainly because of the low investment (single machines even for very large capacities) and maintenance cost, less frequent shutdowns for preventive maintenance, low failure rate and because they require only a fraction of the space needed for reciprocating compressors.

In most ammonia plants, the centrifugal compressors are directly driven by steam turbines, in order to avoid losses associated with generation and transmission of electric power. For this reason, the overall efficiency of a plant with steam-driven centrifugal compressor is superior, although the centrifugal compressors are inherently less efficient than reciprocating units.

In the transition to renewable energies, it is proposed that the future is the use of large electrical motors to drive the compressor rather than steam turbines, which will make the process more efficient [49].

Typically, ammonia plants have several compressors or a variable-speed compressor, which allows to adjust the compression stage according to the conditions and flow rate, enabling variable load operation.

Converter

As previously mentioned, the ammonia production reaction is exothermic, so it releases energy and increases the temperature of the gases in the reactor, which in turn, has a negative effect on the kinetics, therefore, the temperature control of the reactor and the internal configuration of this equipment will largely define the conversion that the reaction can achieve. Typically, ammonia production reactors are divided into two or more stages, each containing a catalyst packed bed and a preceding heat exchange section. Thus, the reactor can be considered as the sum of small reactors and heat exchangers that take advantage of the low temperature of the incoming, cold streams to reduce the temperature of the outgoing, hot streams.

Most of commercial converters can be classified into three categories depending on the cooling method: tube-cooled converters (or internal direct cooling reactors), multibed reactors with direct cooling (or quench converters) and indirectly cooled multibed converters.

The tube-cooled converters are internally cooled through tubes in the catalyst bed, the cooling medium on the shell side, normally being the reactor feed gases to reach the reaction temperature [77]. This kind of converter has the disadvantage that temperature control is sluggish and temperature oscillations dampen out very slowly, if at all, which is why are suited only for small scales.

Quench convertors use multiple catalyst beds operating adiabatically (the reactor is an isolated system that does not exchange heat with the surroundings) and cooling is carried out by injecting a fraction of the cooler, unconverted synthesis gas entering the reactor between the catalyst beds [84]. A disadvantage is that not all of the recycle gas passes over the entire catalyst volume so that considerable ammonia formation occurs at higher ammonia concentration and therefore at lower reaction rate, therefore a higher catalyst volume is needed compared to an indirectly cooled multibed converter. However, no extra space is required for interbed heat exchangers, so that the total volume of the high-pressure vessel will remain about the same as that for the indirectly cooled variant. As advantages this converter have mechanical simplicity and very good temperature control [82].

Finally, in an indirectly cooled multibed converter the reaction heat is removed by indirect cooling with synthesis gas or via boiler feed water heating or raising steam [84], this approach is especially suitable when using the reaction heat for producing high-pressure steam. The indirect cooling principle is applied today in most large new ammonia plants, and also in revamps an increasing number of quench converters are modified to the indirect cooling mode [82].

Converter performance is determined by the reaction rate, which depends on the operating variables. In general, converter performance improves by increasing pressure, increasing flow rate, improving refrigeration; and decreases by increasing impurities, inert and ammonia content in the inlet of the reactor. Additionally, converter performance also depends on the H_2/N_2 ratio (the ideal one varies with the catalyst), and with temperature as there is a specific temperature at which the rate of reaction reaches a maximum for any given ammonia concentration [82].
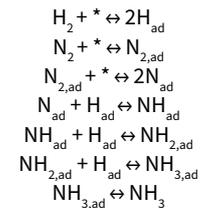
Catalyst
Basically, the function of the catalyst in the synthesis loop is to lower the activation energy, allowing the process to take place under milder conditions. The catalyst decreases the required activation energy by fixation of the nitrogen and hydrogen molecules on the catalyst surface, facilitating the reaction. This intensely reduces the required operating conditions, for example, by using iron as catalyst the reaction may proceed in the temperature range 250-400 °C, and without a catalyst the required temperature is well above 527-927 °C [83].

For a given operating pressure and desired production, the catalyst determines the operating temperature range, recycle gas flow, and refrigeration equipment. As a result, it directly fixes vessel and exchanger design in the synthesis loop. It also indirectly influences the make-up gas impurities requirement, and so the operating pressure, capital cost, and energy consumption for synthesis gas production and purification. Although the proportionate cost of catalyst compared to the total cost of a modern ammonia plant is negligible, the economics of the total process are determined considerably by the performance of the ammonia catalyst [83].

The catalytic synthesis of ammonia relies on the reaction of nitrogen and hydrogen on the catalyst surface, this surface reaction is achieved when the reactants form a chemical bond with the catalyst surface [78]. The proposed reaction mechanisms for the catalysed ammonia formation is as follows:

$$H_2 + * \leftrightarrow 2H_{ad}$$
$$N_2 + * \leftrightarrow N_{2,ad}$$
$$N_{2,ad} + * \leftrightarrow 2N_{ad}$$
$$N_{ad} + H_{ad} \leftrightarrow NH_{ad}$$
$$NH_{ad} + H_{ad} \leftrightarrow NH_{2,ad}$$
$$NH_{2,ad} + H_{ad} \leftrightarrow NH_{3,ad}$$
$$NH_{3,ad} \leftrightarrow NH_3$$

As it is a surface reaction, anything that decreases the active surface of the catalyst will impair the formation of ammonia, so for example the raw materials must be clean of impurities that poison the active sites of the catalyst.

Industrial catalysts for ammonia synthesis must satisfy the following requirements [82]:

- High catalyst activity at the lowest possible reaction temperatures to take advantage of the favourable thermodynamic equilibrium condition at low temperature.
- The highest possible insensitivity to oxygen-and chlorine-containing catalyst poisons to simplify the gas purification process. The effect of poisons may become more severe as temperatures declines.
- Long life, which is determined essentially by resistance to thermal degradation and to irreversible poisoning.
- Mechanical strength. Pressure and abrasion resistance to avoid an excessive increase in the converter pressure drop.
- A reliable primary raw material source to not depend on a scarce product.

Ammonia separation
Separating the ammonia content of the stream being recycled to the reactor is very important as a high ammonia content affects the conversion of this equipment. As with any condensation process, it is favoured by high pressures and low temperatures.

In high pressure synthesis loops (>450 bar) cooling by water or air is sufficient to obtain the required low residual ammonia concentration in the gas. In more modern plants, which operate at moderate pressures, this cooling has to be supplemented by refrigeration, for which a mechanical ammonia refrigeration cycle, with one or more temperature levels is generally used. Refrigeration below -25 °C is used, with which inclusion of the necessary temperature difference in the chiller requires ammonia evaporation at about atmospheric pressure [83].

3.1.2 Important operating variables

The variables with the greatest effect on ammonia production in the Haber-Bosch loop are summarised below [83]:

- Pressure: increasing pressure promotes conversion due to higher reaction rate and more favourable ammonia equilibrium. However, it forces higher initial investment costs due to the higher thickness of the equipment required. In addition, the operating costs of the compressor increase significantly due to the increased discharge pressure of the system. High pressure operation of the synthesis loop is recommended for large scale plants, where the initial investment cost of the equipment is so high that it is necessary to reduce the amount of material recirculated inside the loop.

- Inlet temperature to the reactor: a higher temperature accelerates the reaction but simultaneously reduces the ammonia equilibrium concentration, so these reverse effects compete.

- Space velocity: quotient of the entering volumetric flow rate of the reactants divided by the catalyst bed volume; by increasing space velocity, the outlet ammonia concentration diminishes but total ammonia production increases.

- Inert level: increasing the inert level lowers the reaction rate, therefore affects the total conversion.

- Hydrogen/nitrogen ratio: the ideal ratio depends on the catalyst as it defines operating temperature; at lower temperatures the maximum lies at lower H/N ratios. However, the position of the maximum also depends on the space velocity values.

- Recycle rate: at constant pressure and production rate, the consequence of higher recycle flow is a lower ammonia concentration which causes a higher reaction rate with the result that less catalyst is required. However, larger heat exchanger surface areas are needed, and the cross sections of piping and equipment have to be enlarged on account of the higher gas flow.

- Separator temperature: A lower temperature generates a lower ammonia concentration, which mean either a lower catalyst volume or a higher conversion.

  Catalyst particle size: smaller catalyst particles cause higher conversion but increase the pressure drop and the risk of destructive fluidisation of the catalyst.

3.1.3 General impacts

The Haber-Bosch process can be used to produce green ammonia as the current emissions of the sector come mainly from the CO_2 intensive methane-fed process, not from the ammonia synthesis loop. This is not new as large-scale hydro-powered electrolysis-based ammonia plants used to operate in Norway from the 1920's until the 1970's using the Haber Bosch process [86].

Bicer, Dincer, Zamfirescu, Vezina, & Raso [80] conducted a life cycle assessment of four non-conventional ammonia production methods, all obtaining hydrogen through electrolysis and ammonia through the Haber-Bosch process but varying the energy source (hydropower, nuclear, biomass and municipal waste). The results indicated that the predicted GHG emissions of the hydro, nuclear, biomass and municipal waste ammonia production methods are 0.38 kg CO_2-eq, 0.84 kg CO_2-eq, 0.85 kg CO_2-eq and 0.34 kg CO_2-eq per kg of ammonia, respectively.

Figure 18 shows the carbon footprint of current ammonia production process based on methane reforming and with a electrically driven Haber-Bosch process (calculations were made assuming the use of an electrolyser and renewable energy). In both cases emissions come mainly from the hydrogen production stage prior to the ammonia synthesis loop. It can be noticed that emissions from the latter are neglectable, mainly because the hydrogen is produced under pressure and this diminishes the required compression energy, the purity of the hydrogen and nitrogen makes the purge unnecessary, and the compressors are powered from electric motors rather than steam turbines [49].

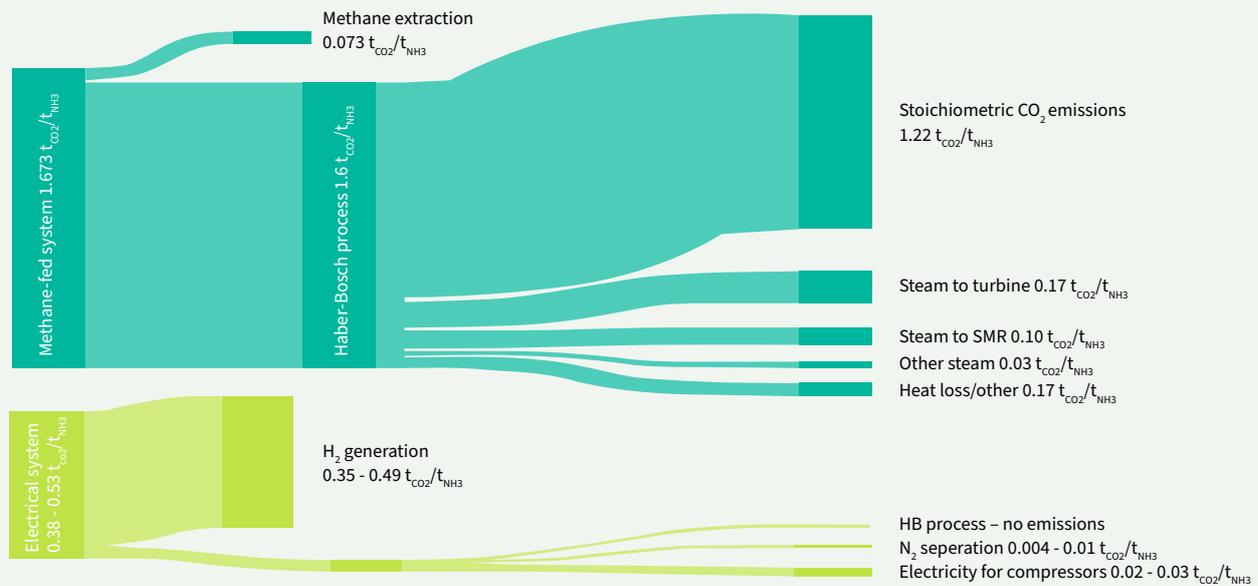**Emissions from the methane-fed and the electrically driven Haber-Bosch**

Figure 18: Based on [49]

3.1.4 Future and challenges

Haber-Bosch is expected to remain the dominant technology for ammonia synthesis in the coming decades [55] [78] and improvement on the existing process is likely to be the near-term alternative for sustainable ammonia synthesis [51] [87].

The transition to green ammonia is possible but is a matter of cost [86] and important changes are required to current configuration to enable the production of green ammonia from the Haber-Bosch process, such as decoupling methane reforming and using renewable energy to run electric compressors [49].

However, the main challenge is to align the continuous Haber-Bosch process with intermittent renewable energy [55] because the ammonia synthesis reactor requires stable operating conditions, as pressure and temperature cycling induce failure modes such as fatigue, and temperature cycling generates catalyst damage. Additionally, the cold start-up time of large-scale plant is 1-2 days. Thus, shutdown can be considered when electricity supply is absent for a few weeks (i.e., beyond the storage time of a battery) but not for short periods [75].

According to [88], because of the reactor, the turndown of operational synthesis loops is conventionally limited to 40% (minimum operation of 60%) and a dynamic ramp rate of around 20% per hour, and the variation from the nominal load likely implies a decrease of efficiency. Other components, such as compressors and chillers, are typically optimised within an operating window wide enough to provide for some flexibility. Ramp up and down can be achieved to some extent by varying the H_2/N_2 ratio in the synthesis loop as nitrogen can act as an inert gas when small amounts of hydrogen are present.

However, there always has to be some ammonia content to enable condensation, which is a reason why alternative ammonia separation methods are interesting [75].

According to [89], current design in the converter has to change for a flexible Haber-Bosch reactor that can technically and cost-effectively operate with an intermittent renewable energy source. This shall involve two key changes: parallel reactors to facilitate different ammonia production rates and thermal storage to keep a non-operating plant warm and to quickly heat it back up to operational temperatures without additional heat input.

Some suppliers have stated that they are able to supply plants that can operate at up to 10% of their nominal capacity, or 0% of capacity with electricity and hydrogen storage although the expected efficiency at this low production capacity is unknown [88].

Other references indicate that it is important to consider in the design of the plant hydrogen buffer tanks and battery storage or grid balancing to align the continuous Haber-Bosch process with intermittent renewable energy [49] and that to facilitate this, the ability to produce small-scale ammonia synthesis plants at a reasonable cost is essential [90].

Small-scale ammonia production is accelerating because of its flexibility, it can use small quantities of resources and reduce the investment risks, it is also expected that localised smaller ammonia production in the direct vicinity of the consumer will be an economically favourable option, despite the higher specific investment cost per tonne of ammonia that certainly exists for a smaller plant [91].

To scale down the Haber-Bosch process, the main challenge is reducing operating pressure, which will lower energy consumption and therefore, will reduce operating costs. It will also reduce the demand for the specifications of the equipment to be installed, thus reducing investment and the milder conditions in the synthesis loop are expected to make intermittent operation less energy intensive [75].

To achieve this pressure reduction there are two main focuses of improvements. The first one is to produce catalysts with higher activity at milder conditions (pressure and temperature), with higher conversion per pass, that can adapt to the intermittent nature of renewable energy by facilitating quick start-up and agile operation, and that have good impurity tolerance [77] [92]. On the other hand, it is important to develop alternative ammonia product separation processes, not depending on the ammonia partial pressure to be able to operate with efficient separation at milder conditions [93].

In this context, the following sections describe the two main variants of the Haber-Bosch process that are expected to allow for intermittent operation, scale-down and higher energy efficiencies [50].

3.2 Haber-Bosch process at low pressure

Currently, great efforts are being made to carry out the Haber-Bosch process at low pressures. Apart from energy savings, this is essential to scale-down for coupling with intermittent renewable energy sources, operate in remote areas and reduce risks of capital investment.

Upon scale-down, heat losses increase, and the energy consumption increases, small plants do not have the benefits of scale, and the equipment for the severe operating condition brings high cost [94]. As example, according to [75], a large-scale plant ($\geq$ 1,000 ton NH_3/d) demands around 2-7GJ/ton NH_3 for pressurising, heating, pumping, and utilities. At 3-20 tonnes NH_3/d, the consumption rises to about 13-14 GJ/tonne

NH_3, down to 5 tonnes NH_3/d losses in high-pressure synthesis processes are mostly due to scale effects and at very small scales (< 0.1 ton NH_3/d). Heat is even required to keep the ammonia synthesis reactor at the desired temperature due to heat losses, and hydrogen and nitrogen production become less efficient as well. This is why on a small scale it is essential to have milder operating conditions.

To operate plants at low pressures and temperatures it is key to have a catalyst that is sufficiently active under these conditions. The employment of wustite iron as catalyst is able to substantially reduce the operating pressure. Furthermore, a ru-based catalyst is able to perform the ammonia synthesis under an atmospheric pressure at operating temperature of 300-400 °C with significantly higher conversion rate than the iron-based catalyst.

Additionally, iron-based catalysts are not significantly affected by methane or carbon poisoning but for oxygen-containing compounds, which suits current ammonia synthesis loops receiving hydrogen from methane reforming. The opposite occurs with a ruthenium-based catalyst, which would be continuously poisoned by methane presence in a conventional plant. However, if the hydrogen is produced from water rather than from fossil fuels, oxygen compounds will be present in the ammonia synthesis loop and not carbon compounds. In that scenario, ruthenium-based catalyst will be more resistant to the poisoning [51].

However, the very low operating pressure and consequently, the very low ammonia partial pressure makes the separation step difficult, generating a higher amount of ammonia at the inlet of the synthesis reactor, and consequently a lower conversion. This forces a higher amount of unreacted gas to be recirculated, and additionally makes the equipment larger compared to the higher-pressure operation. Therefore, this process requires higher cost for the overall energy and capital compared to the conventional Haber-Bosch process which is why the use of Ru-based catalyst in ammonia synthesis is lower than 5% of global ammonia production [54]. Table 12 shows a comparative among iron-based and ruthenium-based catalysts.

Table 12: Comparison of SMR-based ammonia synthesis processes with commercial iron-based and ruthenium-based catalyst; based on [50]

	Iron			Ruthenium
	Fe_3O_4	Fe_3O_4 with CO	$Fe_{1-x}O$	Ru-Ba-K/AC
Year	1913	1979	1986	1992
Temperature, °C	360-520	350-500	300-500	325-450
Pressure, bar	120-450	100-300	100-250	70-100
Energy consumption, GJ/ t NH_3	28	28	27-28	26-27
H_2:N_2 ratio	2-3	2-3	2-3	1.5-2
Catalyst lifetime, y	>14	-	6-10	≤10
Relative activity	1.0	1.2	1.5	
Thermal stability	High	Medium/Low	Medium	2-10
Relative catalyst cost	1.0	1.5	1.1	Low

Currently, research focuses mainly on ruthenium-based catalysts as they are more active at high ammonia conversion levels and lower temperature, allowing a lower operating pressure [51], despite its higher price. According to [94] , ruthenium catalyst costs do not dominate any scale; however it is advantageous with respect to a iron-based catalyst only on small scales, especially below 100 tons/day [94].

However, the Ru material is scarce, the total global production rate is 35.5 tons/year, which means that it would be risky to depend mainly on Ru-based catalysts for ammonia synthesis plants [87]. There are as well different catalysts on the market for use at low pressures, among which iron-based catalysts with potassium as a promoter stand out, there are also catalysts based on nickel, but of lesser use in the industry [78].

Another consideration that must be made is that, by operating at lower temperatures, ammonia conversion is increased. However, as the ammonia synthesis reaction is exothermic, running the convertor at lower temperatures requires better heat removal from the converter. Therefore, implementation of new catalyst that show improved activity at milder conditions shall consider this cooling requirement [77].

3.3 Absorbent/Adsorbent- enhanced Haber-Bosch

As seen in section 2.5.2, enhancing the activity of ammonia synthesis catalysts allows to lower the reaction temperature and pressure. However, ammonia condensation efficiency is limited by its vapour pressure, complete removal of ammonia via condensation from the gas stream is difficult and operation at low pressures (<50 bar) is not feasible [95]; which is why to lower operating pressure in the ammonia loop to 10-30 bar, alternative separation technologies are required [50].

In this context, absorption and adsorption have been proposed instead of coolers. Basically, these options consist of trapping the ammonia in a fluid or solid respectively and ammonia is subsequently separated from the sorbent by heating. In this way, the absorbent/adsorbent allows to separate ammonia at substantially low pressure (0.002-0.1 bar) even at moderately high temperatures (200-300 °C), meaning that the ammonia synthesis reaction and ammonia separation could be carried out at nearly the same temperature, thereby minimising the cost for heat exchange within the ammonia synthesis section (see Figure 18). Well-designed ammonia production at these milder operating conditions can reduce capital costs relative to Haber-Bosch synthesis because high pressure and low temperature separation are the major cost drivers of that process [53].

Two Haber-Bosch processes with different ammonia separation methods: condensation (left) and absorbent/adsorbent (right)
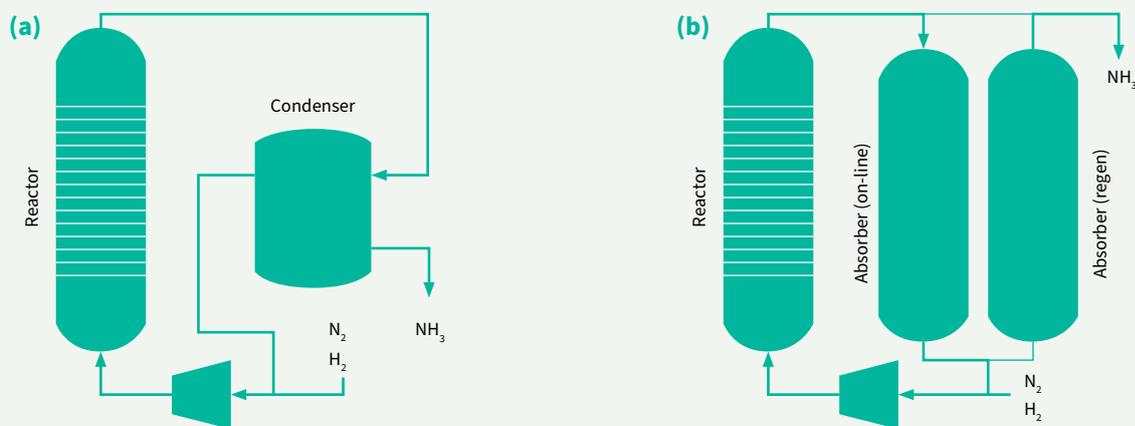

Figure 19: Based on [96]

An absorbent/adsorbent-based process must contain at least two beds. At any given time, one bed will be in operation, and the other bed will be releasing the ammonia through heating. This process is also known as regeneration or desorption [96] and energy demand is mainly dominated by the energy required to increase the temperature during the regeneration phase [54].

Furthermore, ammonia synthesis and ammonia separation can be operated in the same vessel (in-situ absorption, see Figure

19), thereby reducing the investment cost for the ammonia synthesis section. This technology does not need recycle due to its higher conversion and more complete ammonia separation; but it is at a very early stage of development. According to [95], with a Ru-based catalyst at mild operating conditions (below 200 °C and at 15 bar) and an absorption step, a single-pass ammonia synthesis process would be cost competitive compared with the conventional Haber-Bosch synthesis loop at small scale (<40 ton NH_3/d).

Additionally, an absorption/adsorption process allows for a higher efficiency in ammonia separation, which decreases the ammonia inlet concentration in the reactor and in this condition, the catalysts are usually more active. Therefore, the resulting energy consumption of a small-scale absorbent/adsorbent enhanced Haber-Bosch process is lower than that of a small-scale, high-pressure Haber-Bosch [50].

According to [98], based on modelling the system, the absorbent-enhanced ammonia synthesis requires less investment than the traditional process at production scales up to 75,000 ton NH_3/y (around 205 ton NH_3/d) and is increasingly advantageous at small production scales, but uses three times more energy due to endothermic desorption of ammonia, which explains the motivation on investigating less energy intensive absorbent cycling conditions.

The Haber-Bosch process with absorption/adsorption is considered a low-hanging fruit for the upcoming decades, as a large decrease in pressure can be achieved with little technological innovation allowing that the ammonia synthesis loop operates at the same pressure as the hydrogen and nitrogen production stages [50] and through replacing the condenser with absorption/adsorption of ammonia, the potential for highly active novel ammonia catalyst greatly increases [77].

However, it must be clarified that this technology is at lab/pilot plant scale [51], absorber/adsorbent development is still in an early stage and optimisation of its operating conditions as well [49]. In this context, a wide range of solid and fluid materials has been proposed for ammonia separation, such as activated carbon, covalent organic frameworks, deep eutectic solvents, ionic liquids, metal-organic frameworks, metal halides, oxides, porous organic polymers and zeolites. However, metal halides and zeolites are considered the most promising ones, as these materials are applied in industry for various processes and the material cost is typically low. Furthermore, the mechanisms for ammonia separation on these sorbents are well understood and reasonable ammonia capacities have been reported [50].

Tables 13 and 14 compare the relevant characteristics of some ammonia separation methods and their advantages/disadvantages respectively.

Table 13: Comparison of ammonia separation technologies; based on [51]

	Advantages	Disadvantages
Condensation	Well-known technology	Large temperature swing in process (-20 °C to 250-400 °C) High heat exchange and refrigeration cost High pressure Not capable of intermittent operation No sharp separation
Absorption (metal halides)	Small temperature swing in process (150-250 °C to 250-400 °C) Low pressure Capable of intermittent operation Sharp separation	Lab/pilot plant scale Absorption material required Temperature swing for regeneration (to 300-400 °C)
Adsorption (zeolites)	Separation at low conversions (1 mol% ammonia) Low pressure Capable of intermittent operation Sharp separation	Lab/pilot plant scale Adsorption material required

Table 14: Comparison of ammonia separation technologies; based on [50] and [95]

	Condensation	Metal Halides	Zeolites
Separation temperature, °C	-20 to 30	150-250	20-100
Desorption temperature, °C	-	300-400	200-250
Pressure, bar	100-1,000	10-30	10-30
Energy consumption, GJ/ton NH$_3$	3-5 [3]	6-11	8-13
Ammonia at outlet, mol%	2-5	0.1-0.3	0.1-0.3
Ammonia storage capacity, wt.% [4]	100	5-30	5-15
Ammonia density, kg/m^3 [5]	680	100-600	30-90
Chemical stability	-	Low/Medium	High
Technology readiness level (TRL)	9	4-5	4-5

3.4 Electrochemical synthesis

Electrochemical ammonia synthesis is a process inspired in the enzyme nitrogenase, that fixes nitrogen by proton-coupled electron transfer under mild conditions. The method is emerging as a future compelling alternative to the Haber-Bosch process due to its mild operating conditions. It can also be powered by renewable energies [99] and enables the delivery of modular production solutions on small and medium scales [100]. Additionally, it is considered that its simple configuration (see Figure 19) can reduce system configuration and control complexity, as the hydrogen production from water and the nitrogen fixation are integrated in a single unit [101].

Basic schematic diagram of electrochemical ammonia synthesis

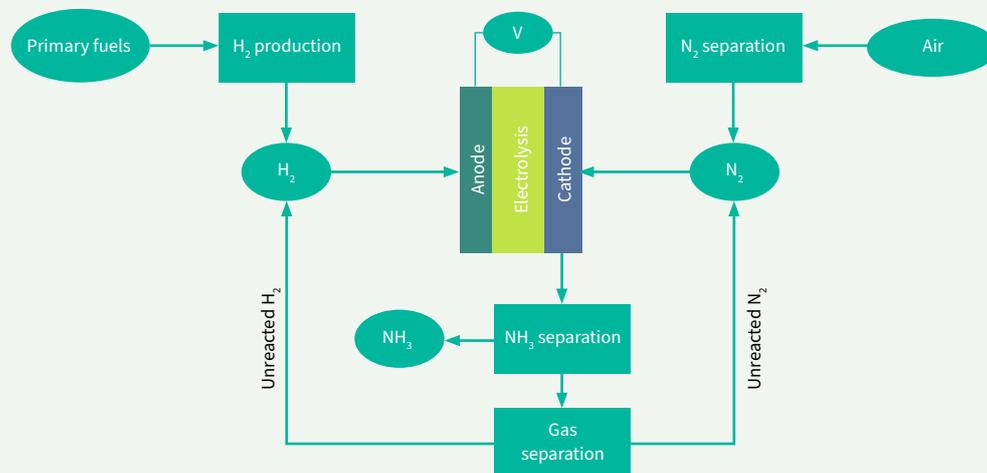Figure 20: Based on [54]

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[3] Energy consumption increases to 20-25 GJ/ton NH$_3$ at 20 bar.
[4] Weight fraction of ammonia as part of the weight of the fully loaded absorbent (tank material excluded).
[5] Ammonia density per volume storage vessel

The electrochemical ammonia synthesis is a process in which nitrogen molecules are activated by electricity to promote the non-spontaneous nitrogen reduction reaction (NRR), and then react with the provided electrons and hydrogen to produce ammonia [73]. The system consists of proton transfers from the anode to the cathode. Following the reaction with N_2, the produced ammonia is separated. In a further step the unreacted H_2 and N_2 are recycled back to each corresponding electrode [1]. The reactions involved are as follows:

$$\text{Anode: } 3H_2 \leftrightarrow 6H^+ + 6e^-$$
$$\text{Cathode: } N_2 + 6H^+ + 6e^- \leftrightarrow 2NH_3$$
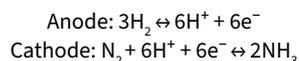
This technology also allows to eliminate the hydrogen production stage by using water oxidation directly as a counter reaction in an electrochemical cell [50], in this case the reaction at the anode is as follows:

$$3H_2O \leftrightarrow 6H^+ + 6e^- + \tfrac{3}{2}O_2$$
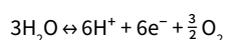
The mechanism for the electrochemical ammonia synthesis reaction is currently discussed, three alternatives reaction mechanisms in the catalyst have been proposed (see Figure 20) and there is no experimental support to clarify which mechanism is dominant [50].

It is proposed that the mechanism depends on the catalyst used and the operating conditions. In the dissociative pathway, dinitrogen is dissociated on the surface before the hydrogenation. This mechanism is predicted to occur at elevated temperatures due to the high activation barrier for breaking the triple dinitrogen bond. Thus, associative pathways with the breaking of the nitrogen bond after partial hydrogenation to N_2HX species are more likely to occur at low temperatures. There is some evidence pointing out that an associative pathway may be relevant on Au surfaces in alkaline electrolytes. The last proposed mechanism may occur in the case of metal nitride catalysts, in which N from the catalyst lattice is hydrogenated to ammonia, leaving an N vacancy on the surface, which can be regenerated with a nitrogen atom [50].

One of the major challenges in this system is the low selectivity towards ammonia formation, because of the competing HER which only requires two electrons, as follows:

$$2H^+ \text{ (aq.)} + 2e^- \leftrightarrow H_2 \text{ (g)}$$
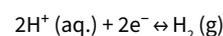
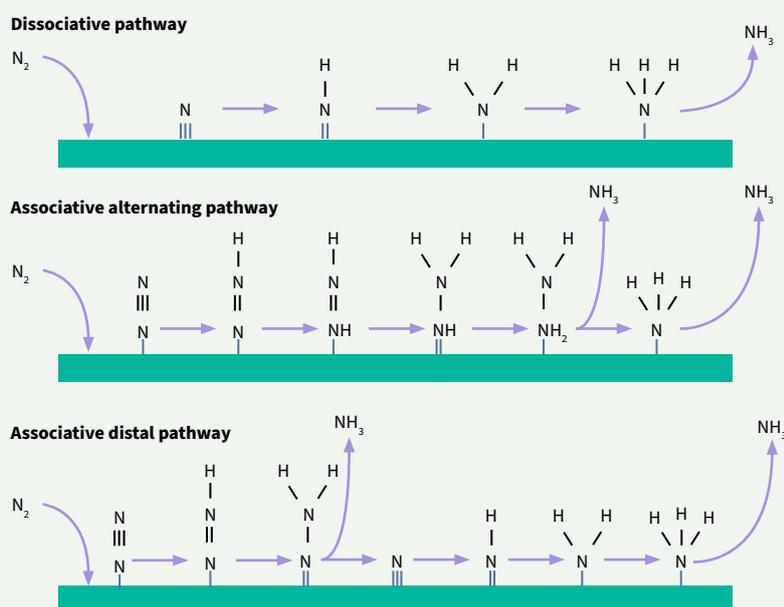**Proposed reaction mechanism for the electrochemical ammonia synthesis**

Figure 21: Based on [50]

3.4.1 Key components

As mentioned before, one of the advantages of the electrochemical ammonia synthesis is its simple configuration compared to the Haber-Bosch process. The following is a brief overview of the most important components of this configuration.

Electrolytic cells

The electrolytic cells used in the electrochemical ammonia synthesis mainly include back-to-back cell, Polymer Electrolyte Membrane (PEM)-type cell, H-type cell, and single chamber cell [102] [103].

Back-to-back cell: In this cell, an ion exchange membrane separates the two gas-diffusion electrodes. During ammonia synthesis, nitrogen is passed though the cathode to allow for its reduction, water is supplied at the anode and protons are transferred though the membrane [103].

The arrangement typically consists of bipolar plates, Gas Diffusion Layers (GDL) and catalyst-coated membranes (CCMs). Bipolar plates separate the reactant gases and distribute them on each side over the whole active area of the Membrane Electrode Assembly [104]. The GDL are a fibrous porous medium that ensure a uniform distribution of reactive gases on the surface of the electrodes, and the transport of electrons from the external electrical circuit [105].

This cell results in improved nitrogen transport. However, this is not ideal for nitrogen reduction measurements as many factors can influence NRR activity, including anode and cathode catalyst loadings and ratios, the type of membranes used, active area, the fabrication process of CCMs, etc. [106].

PEM-type cell: This cell is fed with a liquid electrolyte at the anode and nitrogen at the cathode. The electrolyte water electrolyses during ammonia synthesis, the proton is generated in the anode side and transferred to the cathode side via the proton exchange membrane, participating in cathode reaction to generate NH_3. The use of liquid can ensure the wetting of the membrane to reduce the conductivity loss [107].

The current collector gathers electrons and serves as a mechanical support for the electrode [108]. The working electrode (WE) is the electrode on which the reaction of interest is occurring. The working electrode is often used in conjunction with an auxiliary electrode, and a reference electrode in a three-electrode system.

A reference electrode (RE) is an electrode that has an established electrode potential. The overall chemical reaction taking place in a cell is made up of two independent half-reactions, which describe chemical changes at the two electrodes. To focus on the reaction at the working electrode, the reference electrode is standardised with constant (buffered or saturated) concentrations of each participant of the redox reaction.

A counter electrode (CE), also known as auxiliary electrode, completes a conventional three-electrode system's electrochemical circuit by allowing current to flow through [109].

PEM-type and back-to-back are gas-solid reaction systems, which effectively limit the supply of protons and inhibit hydrogen evolution [102] [103].

H-type cell: In this case, both anode and cathode are filled with a liquid electrolyte and separated by a proton exchange membrane.

In this case, the nitrogen gas is bubbled into the electrolyte at the cathode and reduced into ammonia. The membrane help preventing the transport of products to the anodic chamber. Hydrogen evolution occurs during ammonia synthesis, which affects the selectivity of ammonia formation [102].

The H-type cell is the most frequently adopted reactor in the literatures [110]. It is simple, can accurately measure the applied potentials and is easy to control, which minimises instrumental errors in measurements [106].

In this case, similar for the PEM-type, the advantage is that the membrane inhibits the mixing of anodic and cathodic products, but this membrane and the liquid electrolyte leads to larger resistances in the reactor [106].

Single-chamber cell: The cathode and the anode are kept in the same liquid electrolyte without any separator. Nitrogen gas is bubbled into the electrolyte to be reduced into ammonia at the cathode with protons being produced at the anode.

As both anode and cathode reactions occur in the same chamber, there is a high probability of oxidation of produced ammonia at the anode due to the absence of a membrane [103] and reduction of the oxygen at the cathode [106].

Hydrogen evolution occurs during the nitrogen reduction, which reduces the selectivity of ammonia formation (Faraday efficiency). Therefore, catalysts focused on hydrogen evolution inhibition and catalytic device improvements have become top research priorities [102].

As advantage, this cell has higher energy efficiency, but the mixture of products at the cathode and anode is unavoidable, resulting in great losses of ammonia during characterisation [106].

In general, electrolytic cells based on solid electrolyte membrane are more versatile as these allow easy separation of hydrogen feed from ammonia product.

Electrolyte

Electrolytes are required to transport the proton from anode to cathode. The type of electrolyte used defines the operating temperature, which allows to carry out the process at low or high temperatures. Four types of electrolytes are currently available:

- Liquid electrolytes: It is the only variant in which the ammonia synthesis can be carried out at low temperature (near room temperature) and room pressure. With a liquid electrolyte, about 58% of the current supplied to the

system is converted into ammonia. However, the research related to this issue is still limited to lab experiments, in small dimensions of cells and limited operation times [54]. Ammonia synthesis using aqueous electrolytes is generally considered to be a simple and less costly method because water can be used directly as the hydrogen source. In order to avoid the oxidation of synthesised ammonia at the anode, a proton exchange membrane (PEM) is usually used to separate the anode and cathode. However, the ammonia synthesis rate and the selectivity of ammonia formation (also known as Faraday efficiency) of aqueous electrolytes are low and affected by the pH of the electrolyte [73].

• Molten salt: Generally operated at a temperature range of 300-500 °C with an efficiency of about 72% [54], this kind of electrolyte has a strong ion transfer ability and a wide electrochemical window to facilitate the adjustment of electrode potential, so its Faraday efficiency and ammonia yield are high [111]. However, the molten salt is highly corrosive, so the durability of the electrode is low [73] and energy efficiencies are below 35% [53].

• Solid state electrolytes: Generally, they work in very wide operating temperatures, from room temperature to about 800 °C, depending on the type of electrolyte membrane used. The challenges of this type of electrolyte include their structural stability, degradation over time when in contact with ammonia due to their acidic nature and the high sintering temperature (up to 1700 °C) which is required to achieve a high density. Solid electrolytes can effectively inhibit the side reaction of hydrogen evolution, thus helping to improve Faraday efficiency [73] but negatively affects thermodynamics equilibrium limiting conversion. The high temperature process using this electrolyte has successfully converted 78% of H_2 to NH_3 [54] but usually the efficiency of this system is below 50% [50]. The solid electrolytes have the disadvantage that high operating temperatures can cause issues due to material degradation, so research is focused on the development of more stable electrolytes with a higher conductivity at milder operating conditions [50].

• Composite electrolytes: consisting of a traditional solid electrolyte mixed with a low melting salt [101] with the objective of improving its conductivity and other properties [54], they can withstand harsh operating conditions, and have an operating temperature of 300-700 °C.

Table 15 summarises the characteristics of the different types of electrolytes available.

Table 15: Comparison of different electrolytes in electrochemical synthesis of ammonia; based on [73] and [101]

Electrolytes	Advantages	Disadvantages
Liquid electrolytes [73]	Low temperatures Simple and cost-effective	Slow reaction rate Low ammonia formation selectivity (Faraday efficiency)
Molten salt [73]	High ionic conductivity High current efficiency	Corrosion problems, poor durability
Solid state electrolytes [73]	Effective inhibition of HER High ammonia formation selectivity (Faraday efficiency) Fast reaction kinetics	High requirements for related equipment High operating temperature
Composite electrolytes [101]	Improved conductivity Withstand harsh operating conditions	Low ammonia synthesis rates

Liquid electrolytes have the advantage that parameters including pH, types of cations/anions and concentration of electrolytes can be easily controlled, which facilitates in-depth research of the effect of these variables and as a drawback, their low selectivity and limited efficiency. Nonaqueous electrolytes have high nitrogen solubility, which facilitates its transport and a low water content as well as less HER, but their performance is limited by poor ionic conductivities and high overpotentials [106]. Reference [101] shows various options for electrolytes currently under consideration.

Catalyst

A catalyst is required to facilitate nitrogen fixation on the cathode. The elements used in the catalysts for electrochemical ammonia production are classified in three groups [112]:

- Noble metals (Au, Ru, Rh, Pd, Pt, Ag, Ir, etc.): They have shown satisfactory performance with good Faraday efficiency, and outstanding selectivity but scarcity and high prices severely limit their use.
- Non-noble metals (Y, Sc, Zr, Cr, Nb, Mo, Fe, Co, Mn, Ni, Cu, etc.): They are abundant and low-cost but currently, almost all of them are unstable in long-term tests and do not meet the requirements of practical applications [107].
- Non-metal elements (B, C, N, O, F, P, S, Se, Te, etc): They have gained new attention as promising alternatives because of their advantages as low-cost, environmental friendliness and stability. Currently, there is a lot of research on the application of these materials.

Reference [107] reports a list of catalysts currently in evaluation and a comparative among them.

3.4.2 Important operating variables

Parameters affecting the rate of ammonia formation are quite complex and extensive; however, a brief explanation of the main ones will be given below [113].

- Operating temperature: Initially, the rate of ammonia formation increases as the operating temperature is increased which could be attributed to the rise of protonic conductivity in the utilised electrolyte. However, a rate degrading tendency is obtained when the operating temperature is further increased from a value, which may result from decrease of proton conductivity due to water loss or the ammonia decomposition [113]. Indeed, one of the important challenges of the current technology is that generated ammonia can be thermally decomposed into H_2 and N_2 at high operating temperatures [87].

- Operating pressure: The effect of pressure is essentially reversed compared to the Haber-Bosch process. The reaction from the Haber-Bosch process is replaced by the reaction in the electrolytic cell.

$$N_2 + 3H_2 \leftrightarrow 2NH_3$$

$$N_2 + 6H^+ + 6e^- \leftrightarrow 2NH_3$$
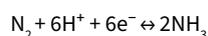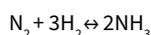
The reaction is favoured by high pressure as there are less moles on the right side than on the left side of the equation. However, the electrochemical ammonia synthesis is favoured by low pressure as one volume of reactant produces two volumes of product [114].

- Cell potential: There is a minimum voltage difference, below which it is not possible to produce ammonia electrochemically [114], the reaction rate grew upon increasing the potential up to a value above which, the rate is essentially potential independent [113].
- Current: The effect of applied current is similar to that of the potential. The reaction rate increases with the imposed current up to a certain value and remained almost the same by further increasing the current.

This is because at higher currents the coverage of H^+ on the catalyst surface, or the three-phase boundary, is much higher and thus protons combine with each other rather than with Nads, forming H_2 rather than NH_3 [114].

- Electrolyte: The electrolyte properties, and in particular the protonic conductivity, are crucial because they determine the maximum rate of proton supply [114]. According to [110], the yield rate of H_2 formation is dependent on the proton and electron concentrations, whereas the rate of NH_3 is not, which suggests that limiting the proton and electron supply can retard the HER. This is why researchers are aiming at designing an electrolyte that can limit the proton or electron supply and increase the N_2 solubility.

Additionally, in a solid electrolyte, the conductivity is inversely proportional to the thickness of the electrolyte. By reducing the electrolyte thickness, the operating temperature could be lowered, which has as advantages the lower manufacturing costs, more flexible choice of materials and longer lifetime; however, reducing thickness may reduce mechanical stability [113].

3.4.3 General impacts

The electrochemical ammonia synthesis is environmentally friendly and has low energy consumption, requires no fossil fuel and the electricity required for the reaction is supplied by renewable energy sources integrated with an energy storage system [54].

For high temperature electrolytic routes for ammonia production, the use of waste heat from thermal or nuclear power plants or heat from solar/renewable energy sources would make the overall process more environmentally friendly [101].

However, currently, the electrochemical synthesis of ammonia shows no advantages over the Haber-Bosch process in terms of energy consumption as electrochemical synthesis with minimum Faraday efficiency of 72.5% is required to achieve an energy consumption of 28 GJ/tonne NH_3 without considering heat losses and with only 2.4% energy for the separation and purification of the product [106], similar to the

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current consumption of the Haber-Bosch process. However, electrochemical synthesis presents a low selectivity and low throughput at present, which increases its energy consumption far beyond the methane-fed Haber-Bosch process [49].

3.4.4 Future and challenges

Currently, the electrochemical ammonia synthesis under mild conditions is far from the scale of industrial nitrogen fixation. A lot of attempts and significant progress have been made, but the electrochemical synthesis of ammonia is still in an early stage with great challenges remaining to be addressed [115]. Unfortunately, the study of electrochemical Nitrogen Reduction Reaction lacks systematic investigations, and is still unable to meet commercialisation [107] and will probably remain so for at least a decade [53].

In general, research on the electrochemical synthesis of ammonia is related to the development of catalysts, innovations on the configurations of electrolytic cells, strategies to improve the selectivity, and verification of ammonia synthesis results. In the latter the control experiments should be as rigorous as possible to rule out false-positive results caused by the ubiquitous contaminants as ammonia is easily present in the environment [112].

An electrochemical cell that can operate at high temperatures is advantageous compared to a low-temperature cell, since much higher reaction rates can be obtained on the same electrode area [116]. However, the electrochemical process with solid-state electrolyte and molten salt needs further progress to lower their operating temperature which could minimise the ammonia dissociation. As for the electrochemical with aqueous electrolyte, the main research will be focusing on the way to increase ammonia yield and Faradaic efficiency by increasing the catalyst activity and ammonia selectivity [3] [110].

Another drawback of the electrochemical synthesis is the competition between the ammonia formation (NRR) and HER. To handle this, a lot of efforts in different aspects have been proposed, such as the construction of the precise modelling to understand the ammonia formation and to investigate its relationship with HER in atomic level, to suppress the HER hindering the proton adsorption on the catalyst active site by capsulation of the electrocatalyst and innovations on the configurations of electrolytic cells. Also, the migration of proton to the electrode can be prevented by providing high concentration of K^+ ion into the electrolyte solution. Meanwhile, increasing catalyst activity by optimising the catalyst design and manufacture, can provide more active sites in the catalyst and improve both the activity and selectivity. Furthermore, the exploration of other membrane materials is needed to effectively reduce the ammonia crossover and increase the ammonia yield [54].

The low solubility of N_2 severally affects the electrochemical NRR performance, so extended efforts should be put into breaking the diffusion limit of N_2. In this regard, electrolytic cells that employ GDEs are promising because the GDEs can shorten the diffusion distance of N_2 and facilitate the contact between the N_2 gas and electrolytes, thus achieving high ammonia partial current densities [112].

Moreover, in the study of electrochemical NH_3 synthesis, the economic cost is often ignored. Although all research aim at improving efficiency, there are few reports on energy cost close to the current H-B process [107]. According to [117], current electrolytes are expensive which also hinders the commercialisation of electrocatalytic NRR.

3.4.5 Mechanisms of electrochemical NO_3 - RR

To reduce the environmental impacts, removal of nitrogenous pollutants has been widely investigated in the environmental field. Compared with N_2, nitrogenous pollutants are much more reactive and can be reduced more easily. On this account, researchers conducted investigations on electrochemical synthesis of ammonia employing nitrate, nitrite, or NO as the feedstock, which is emerging as a new category of electrochemical ammonia synthesis [112]. The reactions that take place are as follows:

$$2NO_3 + 12H^+ + 10e^- \rightarrow N_2 + 6H_2$$
$$NO_3 + 9H^+ + 8e^- \rightarrow NH_3 + 3H_2O$$
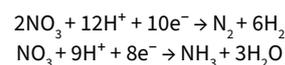
However, this process is still in the initial stage, the studies are relatively few, there is a lack of in-depth research and there is a lot of work to be done although some reported catalysts exhibited excellent performance [107]. According to [112], the main aspects to be investigated are:

- Similar to NRR, the detailed mechanisms of electrochemical nitrogenous pollutants reduction are unclear and need to be clarified to guide the design of high-performance catalysts. Reference [107] shows the proposed mechanism.
- More advanced and stable catalysts that allow to lower energy consumption must also be developed.
- In most of the reported investigations so far, electrolytes with high NO_3 concentration are employed, while the components in the real sewage are complex and the actual NO_3 concentration is low. It is needed to evaluate the performance of catalysts using real wastes containing nitrogenous pollutants, which can help to better understand the feasibility of this technology and promote its application.

3.5 Thermocyclic production

The thermocyclic process proposes the production of ammonia via a two-step cyclic process. The main characteristic of this method is that is does not require a catalyst, which has pros and cons, as on one hand catalysts lower the required reaction temperature by lowering the activation energy required to break the strong nitrogen-nitrogen bond, but they also have a relatively low reaction yield due to its thermodynamically unfavourable reaction equilibrium [54].

The first step is nitrogen reduction with a metal oxide, which is an endothermic reaction that requires thermal energy, yielding the metal nitrides, and has been carried out in electrical furnaces with reasonable rates [118]. The following stage is an exothermic reaction, where the metal nitride is oxidised with steam at a lower temperature. Both of the steps allow the reactions to occur at ambient pressure and using water directly [119]. However, that requires a much higher temperature than the Haber-Bosch process. An example of the reactions involved in each step is shown below:
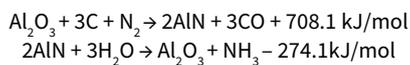
In this case, using Al_2O_3, the reduction is carried out at 1,300-1,500 °C in a N_2 atmosphere. The subsequent process is the oxidation of AlN by high temperature steam, converting back to solid Al_2O_3 and producing ammonia, the Al_2O_3 from the oxidation reaction is recycled to the first step for another cycle. The exothermic oxidation of AlN is carried out at 950-1,200 °C and allows to recover a portion of thermal energy and the CO from the reduction reaction is delivered to the combustion module and reacted with O_2 to generate thermal energy, improving the overall energy efficiency [120]. According to the literature, integrated systems of thermocyclic process and power generation showed an efficiency up to 70% [54]. Figure 22 shows a general diagram of the process.

$$Al_2O_3 + 3C + N_2 \rightarrow 2AlN + 3CO + 708.1 \text{ kJ/mol}$$
$$2AlN + 3H_2O \rightarrow Al_2O_3 + NH_3 - 274.1 \text{kJ/mol}$$

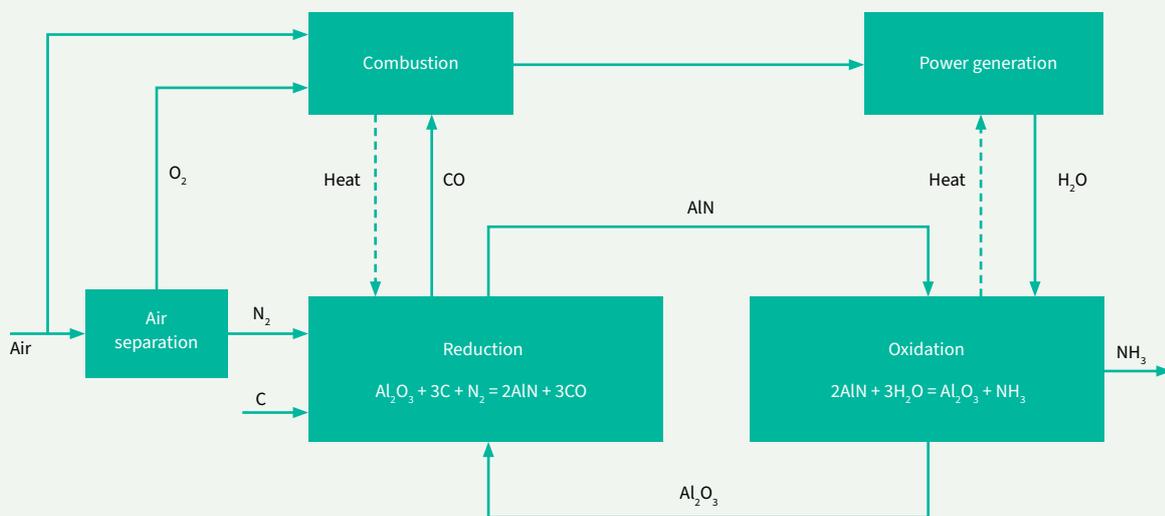**Schematic flow diagram of the thermocyclic ammonia synthesis**

Figure 22: Based on [54]

The carbon monoxide produced in the first step may be further processed by the water-gas shift reaction to syngas and used as a fuel or as an intermediate to methanol or Fischer-Tropsch products [118].

The reduction reaction can also be carried out using methane as a reducing agent as follows:

$$Al_2O_3 + 3CH_4 + N_2 \rightarrow 2AlN + 6H_2 + 3CO$$
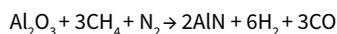
Besides Al_2O_3, other tests have been performed with MoO_2-based or MgO-based systems. The disadvantage of this method, apart from the high temperature, is that it requires the use of carbon compounds as CO and CH_4 [50].

3.5.1 General impacts

For the thermocyclic process to be green, the reducing agent used in the first stage must be of biological origin. Carbon material can be obtained by carbonization process of biomass, through pyrolysis or hydrothermal processes [120].

In addition, the energy that is supplied to carry out the endothermic reaction must be renewable. In this regard, the literature states that this thermal energy can be supplied from concentrated solar energy [54].

According to a preliminary economic analysis presented in [119], where the thermocycle process coproducing ammonia and methanol was evaluated comparing it to their separate productions processes via coal gasification to syngas. The latter requires a fuel consumption of 44.5 GJ/ton CH_3OH and 165.9 GJ/ton NH_3 and produce emissions of 2.088 ton CO_2/ton CH_3OH and 16.7 ton CO_2/ton NH_3. The predicted fuel saving by the thermocyclic process relative to the coal-gasification-based processes was 81%, and the CO_2 emission avoidance was reported as 84% [119]. Although the figures still do not seem competitive with the potential of the green Haber-Bosch process.

However, the information obtained about the operation of this system to produce ammonia is based mostly on Lab scale/pilot plant scale investigation, the thermocyclic process to produce ammonia is still in an early stage and requires further research [54].

3.5.2 Future and challenges

The thermocyclic process for the synthesis of ammonia has been studied by means of thermogravimetry and gas chromatography resulting in high efficiency rates and energy consumption [118]. However, according to [120] there is no evaluation which has been conducted related to the integrated system of ammonia synthesis by a thermochemical cyclic process together with the nitrogen separation process from the air and its post-synthesis treatment, they assess this theoretically.

In general, the thermocyclic ammonia synthesis is at an early stage and still requires further analysis of technical aspects as well as the economic feasibility for practical implementation in industrial scale [54].

3.6 Comparison of ammonia production alternatives

Haber-Bosch is expected to remain the dominant technology for ammonia synthesis in the coming decades [55] [78] and improvement on the existing process is likely to be the near-term alternative for sustainable ammonia synthesis [51], as other production technologies are currently under-developed compared to it [115]. They are also relevant only for small-scale synthesis, with capacities below 10 tonnes per day where the energy consumption of the Haber-Bosch process is typically high due to heat losses, and downscaling is costly due to the high pressures [55]. However, it is expected that the nonconventional technologies will allow for scale-down and operation in remote areas, reducing the investment risk compared to conventional, large-scale plants [50].

The most promising alternative option seems to be the electrochemical process using electricity produced by renewable energy, although it is currently far from the scale of industrial nitrogen fixation under mild conditions [115], and it is only expected to become a commercial technology after 2030 [51]. The main challenges are increasing selectivity of ammonia production over the HER, the energy efficiency of the overall process, and the system throughput of ammonia synthesis [99].

The high temperature electrochemical process has a relatively higher ammonia yield and efficiency compared with the low temperature one. The improvement of the low temperature electrochemical process is focusing on the nanostructured catalyst to enhance the mass and energy transfer that is finally determining the process efficiency [54].

Table 16 presents a comparative summary of the relevant aspects of the technologies described in this section and Table 17 a brief comparative with main advantages/disadvantages.

Table 16: Comparison of some methods of ammonia production

	H-B (with methane reforming)	H-B at low pressure (with electrolyser)	H-B with absorbent/adsorbent and electrolyser	Electrochemical (high temp.)	Electrochemical (low temp.)	Thermocyclic[6]
Reactor temperature (°C)	400-500 [49]	300-500 °C [50]	370-400 °C [51]	400-700 (solid state) 200-300 (molten salt) [54]	Ambient [54]	500-1300 [54]
Pressure (MPa)	15-35 [49]	10-20 [51]	1-3 [50]	Ambient [54]	Ambient [54]	Ambient [54]
N_2/H_2 source	N_2 (from air)/ H_2 (from methane reforming[7])	N_2 (air separation)/ H_2	N_2 (air separation)/ H_2	N_2 (air separation)/ H_2 & H_2O	N_2 (air separation)/ H_2O	N_2 (air separation)/ H_2O
Reaction	$N_2 + 3H_2 \leftrightarrow 2NH_3$	$N_2 + 3H_2 \leftrightarrow 2NH_3$	$N_2 + 3H_2 \leftrightarrow 2\ NH_3$	$N_2 + 6H^+ + 6e^- \leftrightarrow 2NH_3$	$N_2 + 2H_2O + 6H^+ + 6e^- \leftrightarrow 2NH_3 + H_2O$	$Al_2O_3 + 3C + N_2 \rightarrow 2AlN + 3CO$ $2\ AlN + 3H_2O \rightarrow Al_2O_3 + NH_3$
Catalyst	Fe-based [54]	Wustite, Ru-based	Mainly Ru-based	Pd, Ru, Fe-based, Rh (solid state) [54]	Ru, Fe, etc. [54]	-
NH_3 conversion rate (yield)	15-25% per pass [79]	-	-	78% of H_2 (solid state from H_2) [54]	58% [54]	~88% [54]
Energy requirement (GJ/ton NH_3)	26 [50]	33 [75]	46-50 [50]	135 [75]	-	64 [50]
Potential energy requirement (GJ/ton NH_3)	24 [121]	26 [75]	30-35 [50]	27-29 [75]	-	55 [50]
Energy efficiency (%)	60-70 [55] 62-65 [54]	-	-	88.5 [54]	~14 [54]	~70 [54]
By-products	CO_2 (from H_2 production)	-	-	-	-	CO
TRL	9 [51]	9 [51]	4-5 [49] 1-3 (in-situ absorption) [49]	1-3 [49]	1-3 [49]	-

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6 Depends on the metal selected; in this case Al2O₃ is used as an example.
7 The hydrogen source can be green, but for comparative purposes the current situation was used.

Table 17: Advantages/disadvantages of some methods of ammonia production; elaborated with information from [73], [51] and [111]

	Advantages	**Disadvantages**
H-B	Mature technology Large scale	High energy consumption High capital investment
H-B at low pressure	Low pressure	Difficult to separate ammonia Higher cost for the overall energy and capital compared to the conventional HB process Lab scale/pilot plant scale
H-B with absorbent/adsorbent	Low pressure Lower Capex and Opex [51] Low hanging fruit	Lab scale/pilot plant scale
Electrochemical (high temperature)	Water as a possible hydrogen source A variety of routes Low pressure	High temperature Low durability of the electrodes (consequence of the high temperature) Low Faradaic efficiency Side reactions (HER) Lab scale/pilot plant scale
Electrochemical (low temperature)	Low temperature Ambient pressure Water as hydrogen source	Lower ammonia yield and efficiency compared with the high temp. electrochemical options Lab scale/pilot plant scale
Thermocyclic	No catalyst required Atmospheric pressure Water as hydrogen source High efficiency	High temperature Not carbon-free Lab scale/pilot plant scale
Photochemistry	Can be combined with solar energy	Slow reactions kinetics Lab scale/pilot plant scale

3.7 Other technologies for ammonia production

Besides the technologies previously described in the chapter, other methods have been investigated for the ammonia synthesis. However, these have not found practical applications, have not proven to be feasible so far or are at a very early stage of development [95]. Yet, those that appear to be the most important will be briefly described below.

Plasma

A plasma is an ionised gas with electrons, photons, activated molecules, as well as positive, negative and neutral radical species in which highly energetic electrons may activate strong chemical bonds in gas molecules [111]. This is why Plasma technology was proposed as a novel solution for the activation of the stable nitrogen-nitrogen triple bond via vibrational or electronic excitation in combination with a catalyst.

Thermal and nonthermal plasmas exist, where the former operates at high temperatures (>1000 °C), whilst the latter have the electrons at elevated temperatures and the other species at near ambient conditions. Thermal plasmas are not practical, as the equilibrium ammonia content is low in these conditions and catalysts are not stable at such high temperatures [50].

Nonthermal plasma technology is still to be investigated on a small scale [87]. However, is has shown great results in the ammonia synthesis. The activation barrier for ammonia synthesis over Ru-based catalysts was found to decrease from 60-115 kJ/mol to 20-40 kJ/mol, which can be attributed to nitrogen activation in the plasma [50].

However, according to [95], in practice, too much of the energy is lost as heat, which means plasma-based NH_3 processes cannot compete with the electrolysis-based Haber-Bosch process. Plasma-based ammonia synthesis does not provide

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a cost advantage over the electrolysis-based Haber-Bosch process, not even in the best-case scenario when the plasma would be able to supply photochemical.

Nevertheless, small-scale applications with highly intermittent energy supply may provide a niche market for processes with non-thermal plasma technology with low operating temperatures and pressures combined with an absorbent or adsorbent for separation, given that the energy input for plasma-catalysis can be decreased substantially [50].

Plasma catalysis requires a multidisciplinary approach, the effects of the plasma on the catalyst and vice versa are often mutual, leading to a high level of complexity [50]. Current strategies to produce more ammonia at a lower energy input include plasma-reactor optimisation such as pulsed plasmas, a change in operating pressure, and catalyst optimisation.

Photocatalysis

Analogous to electrochemical synthesis where electric potential is provided, photocatalytic ammonia synthesis produces a potential on a semiconductor or plasmonic material using light in order to fix nitrogen, but this has only been applied at the lab scale [49].

There are three main steps in the photochemical reaction. First the photoexcitation, where light is absorbent by a semiconductor, generating electrons that migrate from the valence band (VB) to the conduction band (CB), which will allow the photo-generation of electrons while leaving holes on the VB [111].

In a second step, the electrons and holes migrate to the surface of the semiconductor, where reduction and oxidation reactions can take place. Then, in the last step water is oxidised to O_2 and H^+ by surface holes, whereas N_2 can be reduced by electrons from the conduction band and hydrogenated by water-liberated H^+ [68] (Figure 22).

The main advantage of this approach is the possibility to use water as a reducing agent in ambient conditions. However, there are some unsolved issues such as inertness of the nitrogen molecule, HER, transport of nitrogen to the active sites of the catalyst due to its low solubility in commonly used electrolytes, generated ammonia can be oxidised, poor stability of the photocatalyst and the low utilisation of the light [50].

In general, due to the lower efficiency and stability, this technology is still in the fundamental research phase, far from practical application [111]. There is currently research focusing on potential reaction mechanisms, generating catalysts which activate nitrogen in ambient conditions and materials that capture solar energy efficiently, also on photoelectrochemical systems, because even though there is limited data available, it may improve the charge separation after photoexcitation. It is estimated that an energy efficiency of 0.1% for solar-to-ammonia is required to evaluate the process as a potential option for ammonia synthesis, which has only been reported in a few cases [50].

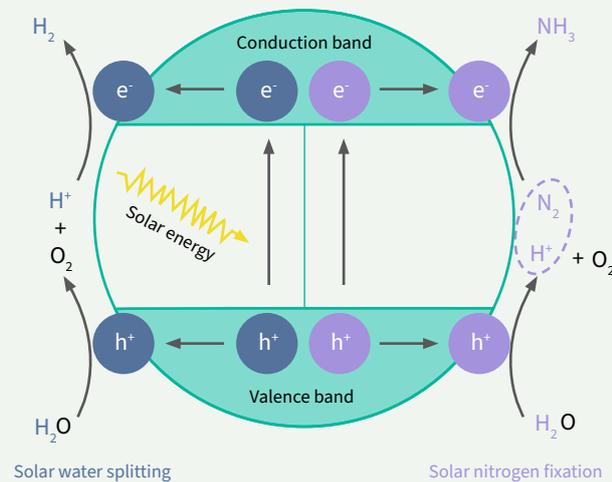**Schematic diagram showing photocatalytic N₂ reduction to NH₃ with water as the reducing agent**

Figure 23: Based on [54]

3.8 Ammonia quality

The quality specifications of the ammonia product depend to some extent on the production plant operating conditions and storage. For example, seal oil can pass from the synthesis compressor to the synthesis loop, but it usually settles out on storage because of its low solubility in liquid ammonia, so that only a slight concentration will remain in the ammonia dispatched [83].

There are two commercial qualities of anhydrous ammonia and Table 18 shows their normal specifications. The first is the commercial or technical grade, which is basically ammonia as it is produced in the synthesis loop. This grade is sufficient for fertiliser production. To inhibit stress corrosion cracking, a water content of at least 0.2% for shipped and pipelined liquid ammonia is generally recommended and is mandatory in USA [123], it also inhibit this kind of corrosion in the carbon steel used in equipment for the agricultural industry.

On the other hand, the refrigeration grade is commercialised for industrial uses, which require a higher-purity level. This quality is achieved through distillation or molecular sieve adsorption which reduces the level of water and impurities. These higher specifications prevent damage to the cooling systems, the higher the water level, the higher the energy consumption and the lower the cooling capacity of the system [124]. In addition, a high-water content can cause pipes to freeze and rupture; a high oil content can also force the cooling system to work overloaded, and high oxygen levels can produce corrosion in the pipes and cracks in the steel [125].

A research grade that contains 99.999% ammonia is available as well as high purity grade for semiconductors that have a purity as high at 99.99999% (Grade 7.0) [123]. This market has grown recently primarily led by the bright LED industry [126].

Table 18: Ammonia quality specifications; based on [123]

		Ammonia quality			
		Commercial grade		Refrigeration grade	
		USA	Germany	USA	Germany
Purity	wt.%, min	99.5	99.5	99.98	99.98*[9]
Water	wt.%, max	0.5	0.2	0.015	0.02
Inerts[10]	mL/g, max	Not spec	Not spec	0.1	0.08
Oil	ppm by wt.	5.0	5.0	3.0	Not spec

Aqueous ammonia with concentrations normally between 25-30% and iron content lower than 10 ppm is also commercialised, mainly to be used as cleaning agent. Solutions with ammonia content higher than 25% must be shipped in pressure vessels

because of their elevated vapor pressure, in case of more stringent purity requirements the containers should be made of seawater-resistant aluminum (magnesium alloyed) or austenitic steels [123] [83].

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[9]   Allowable boiling point change on vaporisation of 5-97% of the test sample, 0.9 °C.

[10]   The non-condensable gases dissolved in ammonia are H_2, N_2, CH_4 and Ar. Their amounts depend on the methods of synthesis and storage. The inerts amount to about 50 mL/kg for atmospheric storage.

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