State-of-the-art and Technologies in Hydrogen Production and Distribution

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Abstract of the master's thesis

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Abstract

Global energy demand has been constantly rising for several decades due to industrialization, technological advancement, urbanization, and population growth. This has caused big environmental damage since the main energy sources are all fossil fuel-based that release carbon dioxide into the atmosphere and greenhouse gas emissions. Lately, interest in the usage of renewable energy sources has grown significantly, especially solar and wind energies. Although the technological development in the renewable energy field has significantly progressed, it is still far from its full potential due to its variable and fluctuating output that is negatively affecting renewable system reliability. From here, the idea of using hydrogen as an energy carrier has emerged since it can help make renewable power systems more reliable and complement their usage, unlocking their full potential.

This thesis is a literature-based state-of-the-art review that studies different hydrogen production, storage, and distribution methods. Conventional hydrogen production technologies and their environmental impacts are discussed since they are mainly depending on hydrocarbons that release an enormous amount of greenhouse gases. Future biomass and water-splitting hydrogen production methods with different levels of maturity are also studied, their advantages, disadvantages, and environmental impact are evaluated. More detailed research is carried out on three main types of electrolyzers; Alkaline, Proton exchange membrane, and Solid oxide electrolyzers. In addition, storing hydrogen in gaseous, liquefied, and hydride forms is studied and different types of storage vessels are mentioned and compared based on the changing hydrogen properties in different states and forms. Furthermore, different hydrogen transportation methods are discussed with the aim to find the most suitable distribution means for different scenarios, whether for local or international distribution. Overall, this study aims to provide ideas for different integrated hydrogen systems that can complement renewable energy sources usage in different scenarios and conditions in order to reach carbon neutrality.

Keywords Green hydrogen, Renewables, Electrolyzers, Hydrogen storage and transport

Preface

I want to thank Professor Anouar Belahcen and Dr. Floran Martin for their guidance and constant support.

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Abbreviations

IEA	International Energy Agency
IRENA	International Renewable Energy Agency
CO_2	Carbon dioxide
H_2	Hydrogen
NH_3	Ammonia
GHGs	Greenhouse gases
ATR	Autothermal Reforming
POX	Partial Oxidation
SMR	Steam Methane Reforming
CCS	Carbon Capture and Storage
WGS	Water Gas Shift
AEC	Alkaline Electrolyzer
PEM	Proton Exchange Membrane Electrolyzer
SOEC	Solid Oxide Electrolyzer
LOHC	Liquid organic hydrogen carriers

1 Introduction

With a goal of providing for a continuously growing human population, the consumption of energy on a global scale has been steadily rising. It is anticipated that this rise in energy consumption will continue in the succeeding decades; it is predicted that it will reach 48% in the succeeding 20 years [1]. This expected growth in consumption of energy can be linked, in large part, to the rise in population around the world, as well as the expansion of economies and industries, especially in developing countries and the Asia Pacific area, and most notably in China and India [2, 3].

Since the 18th century saw the start of the industrial revolution, there has been nothing but an increase in the significance of fossil fuels as a source of energy. For many years, around 80% of the energy in the world has been by using fossil fuels, most commonly in the form of coal, oil, and natural gas, and this percentage has remained extremely stable over the course of several decades [4]. Unfortunately, we will no longer be able to rely on fossil fuels as our primary source of energy because their availability is finite and they have a large damaging effect both on the climate and the ecosystem. The production of greenhouse gases (GHGs) is considered as one of the most serious environmental issues associated with the usage of fossil fuels that lead to global warming and create issues related to climate change.

As an attempt to mitigate the detrimental consequences of GHGs, an international climate change treaty with the name "the Paris Agreement" was signed by 196 countries on December 2015. The goal of this agreement is to keep the global warming below 2 °C, with a preference for keeping it below 1.5 °C relative to pre-industrial levels [5]. This agreement demonstrates the global community's dedication and commitment to addressing the issue of climate change.

As a result, there is a growing interest in renewable carbon-free energy sources such as solar and wind energy since these sources offer the most practical means of avoiding the effects of climate change. In spite of the fact that the COVID-19 pandemic caused a delay in a significant number of energy projects throughout the year 2020, renewables still represented more than 80 percent of all new electrical capacity installed [6]. According to IEA, the amount of renewable energy being used climbed by 3%, and the percentage of renewables used in the production of global power increased to 29% in 2020, rising from 27% in 2019 [7].

Unfortunately, we are a far from being able to rely exclusively on renewables as a primary source of energy. This is mainly due to the high fluctuations generated by the solar and the wind power output, which can render both sources unreliable along with other factors, such as efficiency and cost compared to fossil fuels. The installation of more solar and wind power capacity, in conjunction with the ongoing development of technology for energy storage, can play a significant role in stabilizing the output of renewable power sources, thereby making it more reliable. Even though batteries' technologies are currently in a mature phase of development, they are only appropriate for short-term storage and cannot be utilized for seasonal storage. Consequently, there has been an increase of interest in Hydrogen and the promising role it can play in attaining carbon neutrality.

Hydrogen is not a source of energy; however, it can serve as an energy carrier. This means that hydrogen is capable of storing and distributing electrical energy not through combustion but rather through chemical reactions. Hydrogen has emerged as a promising alternative energy source for energy storage and distribution due to its versatility and applicability in numerous technologies, including fuel cells. Additionally, it can be employed in the building sector to heat homes, the transportation sector to power vehicles, and in a wide variety of other applications [8, 9].

Hydrogen technologies can significantly increase the development of the renewable electricity market and widen the reach of renewable solutions, especially through the large-scale adoption of hydrogen. Moreover, the generation of hydrogen could help limit the amount of curtailment that occurs in power grids that have a high percentage of variable renewable electricity. In addition, the role that hydrogen plays in seasonal storage is quite important, particularly in electrical networks that have a significant amount of renewable renewable electricity [10, 11].

Every significant roadmap being developed for achieving carbon neutrality in the future makes clear reference to the role that hydrogen technology will play. According to IRENA, there is a global economic potential for the production of 19 EJ of hydrogen from renewable sources by the year 2050. This fact makes hydrogen technologies a primary driver in the energy transition towards carbon neutrality, having the potential direct responsibility of cutting approximately 3.7 gigatonnes of annual CO_2 emissions by the year 2050 [10, 12, 13].

This thesis's objective is to look into both the present and the foreseeable future of technological developments in the areas of hydrogen generation, storage, and distribution, and it seeks answers to the following primary questions:

- What are the most promising hydrogen production, storage and distribution methods?
- What kinds of barriers are limiting the widespread adoption of hydrogen-based technologies?
- How can hydrogen contribute to the reduction of emissions of greenhouse gases?

2 Research material and methods

The Thesis has been conducted as a literary evaluation to achieve the stated goal and provide clear answers to the research questions.

Various ideas and aspects related to hydrogen technologies have been extensively studied in the thesis work, starting with production methods, to storage and means of transportation. Conventional and potential technologies have been equally studied, evaluated, and compared in different scenarios.

The whole thesis is a literary review and the information provided in this review is mainly depending on relevant journal scientific articles and reports.
Journal articles have been reviewed to find scientific definitions, working principles, operating conditions, advantages, and disadvantages of different technologies. In addition, new research findings and suggestions for areas of development have been gathered.

Reports from internationally renowned organizations that have a clear interest in the thesis topic have been checked. The information gathered from these reports is in the form of statistical data, future expectations, and recommendations that serve the same purpose as the thesis. Reports from DNV, IEA, and IRENA about hydrogen current and future status have been used.

The combination of information gathered from the aforementioned sources helped the thesis reach its objective and form a general and wholesome idea of the current status and prospects of the topic. Since the topic of the thesis is quite large, the main focus has been on covering different technologies with a sufficient amount of information to present a general overview and some immature technologies have not been covered in the thesis.

It is also worth mentioning that a simulation that involves and integrates all parts of the thesis was implemented. However, it was decided not to include it in the thesis because the results were incomplete.

3 Hydrogen as an element

Hydrogen has been a known element for more than 200 years and has the simplest atomic structure. It was first introduced to humanity in 1761, when Robert Boyle was able to generate hydrogen by reacting iron filings and dilute acids [14, 15]. Henry Cavendish identified hydrogen as a distinct substance in the year 1776. Seven years later, Antoine Lavoisier was successful in extracting hydrogen from iron and gave the element the name hydrogen [14, 15]. In the year 1839, Sir William Robert Grove constructed a cathode, an anode, a ceramic membrane, and a mixed acid conducting medium, which enabled him to produce an electric current flow. This finding ultimately led to the development of the modern fuel cell [14]. Hydrogen is arguably the most studied element [16] and it was discovered early in comparison to other elements. Hence, its properties became well known. This led to hydrogen's current widespread industrial applications [14]. In this chapter, the properties of hydrogen, as well as the safety precautions to take in relation to those properties and the industrial applications of hydrogen, are discussed.

3.1 Hydrogen Properties

Hydrogen (H_2), which has an atomic number of 1, is the element that is found in the greatest quantity in the universe. It is a colorless, scentless, and combustible gas that can be found mainly in water and organic substances on our planet. [17, 18]. The atomic weight of hydrogen is equal to 1.00794 atomic mass units [8]. The energy content of hydrogen at its higher heating value is 141.8 MJ/kg at 25 °C, and the energy content of hydrogen at its lower heating value is 120 MJ/kg at 25 °C. Both of these values are significantly higher than those of the majority of fuels (for example, gasoline's heating value is 44 MJ/kg at 25 °C) [8, 19]. Liquid hydrogen, on the other hand, has a density of just 8 megajoules per liter, while gasoline's is 32 megajoules per liter [20, 21]. This means that the amount of energy that can be stored in the same volume of liquid hydrogen is significantly lower [8]. Hydrogen has a high energy density when measured considering its weight, but a lower energy density when measured in terms of its volume in comparison to hydrocarbons; as a result, it must be stored in a larger tank [8, 20, 22]. Hydrogen is a combustible gas that has a broad a volumetric flammability range of 4% to 75%, and a low ignition energy (0.02 millijoules), both of which contribute to a significant amount of the danger that is connected with its utilization [8, 14, 23]. The table below summarizes the most important hydrogen properties:

Properties	Values	References
Date of discovery	1776	[59]
Autoignition temperature/in air	400 °C / 571 °C	[14]/[27, 26]
Critical temperature	-239 .9 °C	[14]
Critical pressure	1296.212 kPa, abs	[14]
Critical density	30.12 kg/m^3	[14]
Cp	14.34 kJ/(kg)(°C)	[14]
Cv	10.12 kJ/(kg)(°C)	[14]
Ratio of specific heats	1.42	[14]
Molecular weight	2.016 g/mol	[61]
Gas density at boiling point and 1 atm	1.331 kg/m^3	[27, 14]
Liquid density at boiling point and 1 atm	67.76 kg/m^3	[14]
Boiling point at (101.283 kPa)	-252.8 °C	[14]
Freezing/Melting point at (101.283 kPa)	-259.2 °C	[27, 14]
Lower heating value, weight basis	120 MJ/kg	[26]
Higher heating value, weight basis	141.8 MJ/kg	[26]
Lower heating value, volume basis at 1 atm	11 MJ/m^3	[26]
Higher heating value, volume basis at 1 atm	13 MJ/m^3	[26]
Maximum flame temperature	1526.85 °C	[26]
Latent heat of vaporization at boiling point	445.6 kJ/kg	[14]
Density	70.8 g/L	[9]
Explosion limit	18.3-59%	[9]
Flammability limit	4-74%	[9]
Specific gravity of the gas at 0 °C and 1 atm	0.0696	[27, 14, 60]
Specific gravity of the liquid at boiling point and 1 atm	0.0710	[14]
Vapor pressure at (-252.8 °C)	101.283 kPa	[27, 14]

Table 1: Hydrogen properties table, adapted from [8].

3.2 Safety

Like every other type of fuel, hydrogen has a certain level of risk and can be hazardous if it is not handled or regulated in the appropriate manner [8, 24]. Hydrogen is distinguished from other common fuels like gasoline, propane, and natural gas by a number of distinct features that set it apart. There are some characteristics of hydrogen that could theoretically make it less dangerous, while there are others that could make it more hazardous in some situations. Consequently, increased control measures are required to ensure that its use is carried out in a safe manner [8, 24, 25].

Hydrogen has a broad range of flammable concentrations in air, which can range from 4% to 75%. Additionally, hydrogen has a lesser ignition energy than gasoline (it takes one tenth as much energy to ignite gasoline) or natural gas, which indicates that it can be ignited with less effort. Thus, sufficient ventilation and the detection of leaks are essential components in the layout of safe hydrogen systems [8, 25, 26, 27].

When ignited, hydrogen produces a flame that travels at a speed that is seven times greater than that of natural gas or gasoline. Because of this, a hydrogen flame has a greater potential to develop into a deflagration or even an explosion. On the other hand, a hydrogen explosion in the free atmosphere is an extremely rare case [24]. In the event of an explosion, hydrogen has the lowest explosive energy energy per unit stored energy; more specifically, the same volume filled with hydrogen has 22 times less explosive energy compared to the same volume full with gasoline vapor [24]. Because of these qualities, the use of hydrogen in boilers and the transportation industry necessitates the implementation of additional safety precautions [28].

People who are in the proximity of a hydrogen flame might not even be aware that there is a fire because the flame is almost undetectable and invisible. This poses a potential risk to their safety. This may be addressed by adding some chemicals that will produce the required light intensity to the flame in order to fix the problem [25, 24]. Because hydrogen flames have a low emissivity, nearby materials and individuals have a significantly reduced risk of being burned or injured by the radiant heat transfer that results from the flames. Those who breathe in the smoke from a gasoline fire could potentially be exposed to harmful gases and ash, whereas hydrogen flames create just water vapor (until secondary things start to burn) [24].

In addition, hydrogen has the power to attack some materials, such as those used for the construction of storage containers, pipelines, valves, and other appurtenances, to the point where they begin to leak. Hydrogen embrittlement is a term that's occasionally used to allude to this destructive capacity [29, 14, 8].

Hydrogen can cause some high-strength steels to become embrittled and brittle. Steel can lose its strength over time if it is subjected to hydrogen for an extended period of time, particularly at high temperatures and pressures. This can eventually cause the steel to collapse. However, the vast majority of other materials used in building, tanks, and pipes are not susceptible to hydrogen embrittlement. Therefore, by carefully choosing the materials to use, hydrogen embrittlement should not be a factor in the dangers associated with hydrogen [24, 25].

Furthermore, the current gas distribution systems are not equipped to handle the transportation of hydrogen in its purest form since it has such a high permeability that ordinary materials are not suited for its transportation and storage because hydrogen corrosion can occur [28].

A comprehensive understanding of the properties of hydrogen, the incorporation of safety features into hydrogen systems, as well as training in safety protocols for handling and storing hydrogen, are essential components for ensuring the safe utilization of hydrogen [8, 27]. In addition, the testing of hydrogen systems, including garage leak simulations, hydrogen tank drop tests, and tank leak tests, demonstrates that hydrogen can be produced, stored, and distributed in a risk-free manner [25]. According to a statement that can be found on the website of the United States Office of Energy Efficiency & Renewable Energy, "As more and more hydrogen demonstrations get underway, hydrogen's safety record can grow and build confidence that hydrogen can be as safe as the fuels in widespread use today" [25, 8].

In conclusion, it would appear that the dangers posed by hydrogen are relatively similar to those posed by other fuels. In spite of widespread belief, hydrogen is, in many respects, a more secure fuel option than either gasoline or natural gas [24]. In actuality, hydrogen possesses an exceptionally good safety record, when used industrially, commercially, as a fuel in space projects, as well as an element of the infamous "town gas" that was popularly used within Europe and the United States throughout the late 19th and early 20th centuries. Despite the fact that accidents have happened, no evidence would presume that hydrogen is a fuel that is particularly dangerous. [24].

3.3 Industrial uses of Hydrogen

Hydrogen has been used in industrial applications for over 100 years and is well understood for many uses [14]. The most common applications are ammonia production Oil industry and methanol synthesis. It is also used in smaller quantities in industries such as glass manufacturing, semiconductor manufacturing, and as a fuel for fuel cells [14, 114, 21]. The oil industry uses hydrogen for refining crude oil and removing sulfur from transportation fuels. As demand for low-sulfur fuels grows, the demand for hydrogen is increasing [21].

4 Hydrogen Production

Methods for producing hydrogen can be broken down into two primary groups, depending on the type of raw material that is utilized: hydrogen production from fossil fuels renewable sources [9, 30]. In this chapter, the different ways that hydrogen can be produced from fossil fuels are discussed. Some of these ways include autothermal reforming (ATR) , steam methane reforming (SMR), partial oxidation (POX) and hydrocarbon pyrolysis. Moreover, the current state of producing hydrogen from renewable sources is looked into , as well as its potential future uses, with a deep focus on electrolysis. The figure that follows demonstrates various production methods that can be utilized.

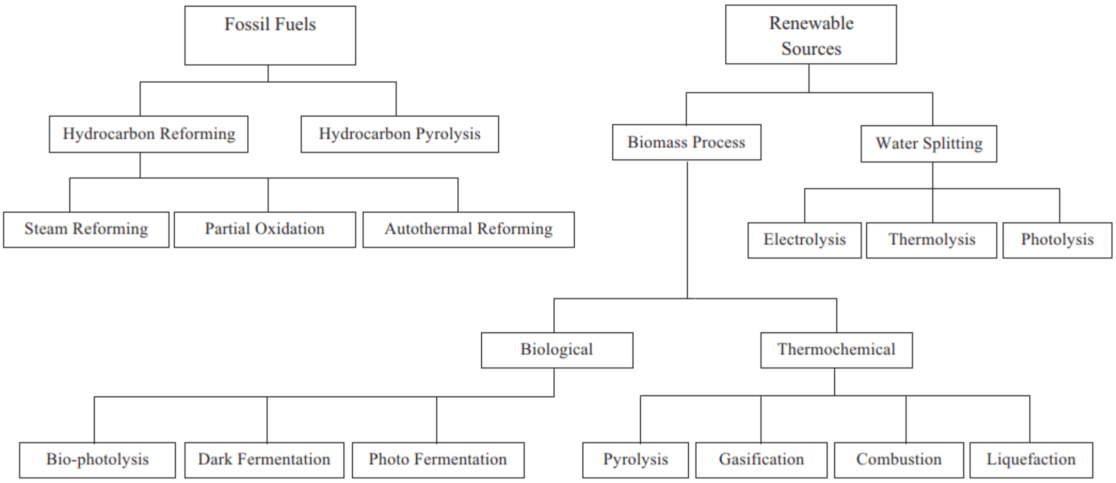


Figure 1: Hydrogen Production Method [30]

Based on IEA's Global Hydrogen Review 2021, around 80% of the world's hydrogen comes from fossil fuels. In the year 2020, roughly 60% of it was coming from natural gas, 19% from coal, and 21% of hydrogen was produced as a byproduct, primarily from the reformation of naphtha into gasoline [31]. The International Renewable Energy Agency (IRENA) indicates on its website that by the end of 2021, roughly 47% of the world's hydrogen production comes from natural gas, 27% from coal, 22% from oil (as a by-product), and only about 4% comes from electrolysis [32], which indicates that around 96% of the energy used to produce hydrogen comes from fossil fuels. Despite the fact that these numbers are not identical, they both point to the same conclusion, which is that the creation of hydrogen is now highly reliant on the use of fossil fuels as the primary source.

Despite this, IEA forecasts that hydrogen production will rise in the coming decades additionally to becoming less polluting. The rise in the demand for hydrogen and the many shifts in production methods are depicted in Figure 2. The total demand for hydrogen in 2050 would be 530 million tons, and practically the entire supply would come from electrolysis and natural gas with carbon capture and storage (CCS) [33].

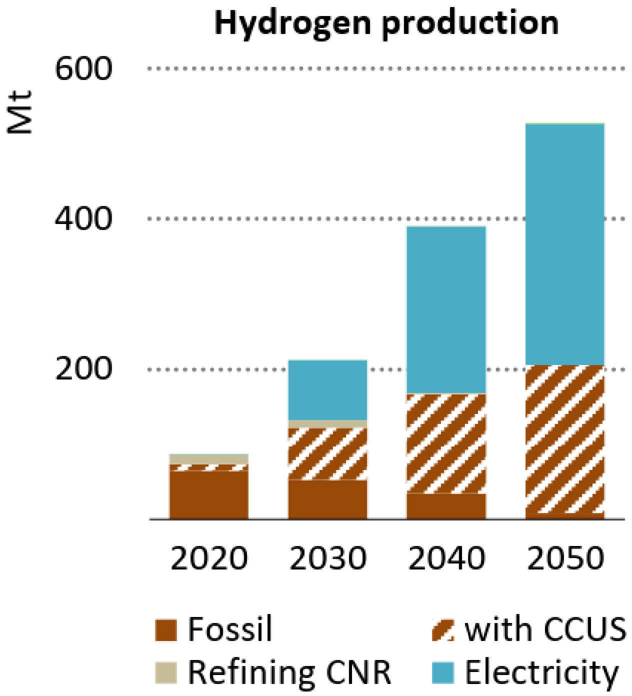


Figure 2: Predicted Hydrogen Production from 2020 to 2050 [33]

It is also necessary to keep in mind that different techniques for producing hydrogen are frequently described using color coding [8, 31], which is utilized in the industry to differentiate between the different kinds of hydrogen. Different colors are given to hydrogen, based on the method of production that was utilized. However, there is no single naming method that is universally acknowledged, and the definitions of colors may shift over time and even vary between countries [34]. Gray, blue, and green are the colors that are most frequently used as color codes to differentiate between the various forms of hydrogen.

Gray hydrogen refers to the hydrogen produced from fossil fuels which is the most common form of hydrogen production. Blue hydrogen refers to hydrogen coming from fossil fuels with the use of CCS, while green hydrogen refers to hydrogen production from completely renewable energy sources [8].

This color coding has been criticized in the literature due to the fact that the degree to which that hydrogen is clean cannot be determined using the color coding system in use today. This is due to the model's incapability to estimate the amount of GHG emissions from the production process, individual components, or the equipment lifecycle that was utilized. In addition, this color coding is used to signify the utilization of renewable energy or CCS instead of the actual level of cleanliness of the hydrogen that is created [8].

4.1 Fossil Fuels

As mentioned earlier, the production of hydrogen currently makes primary use of fossil fuels as a source because the processes used to create hydrogen from fossil fuels have already been commercialized and mature technologies have been established at higher efficiencies and lower product price ranges [35]. It is likely that the generation of hydrogen utilizing fossil fuels will continue to be a common practice in the near future [35]. Hydrocarbon reforming and pyrolysis are the most common methods for extracting hydrogen from fossil fuels since they are the most advanced and they satisfy nearly the whole world's demand for hydrogen [30].

4.1.1 Hydrocarbon Reforming

The term "hydrocarbon reforming" refers to the procedure used to transform hydrocarbons to hydrogen through the use of various reforming techniques. Hydrogen is produced as a byproduct of the reforming reaction, which involves the realignment of hydrocarbons establish a new molecular structure. In addition to hydrocarbon, several reactants are required for the hydrogen reforming process. These reactants can be steam, in which case the reaction is called steam reforming; alternatively, they can be oxygen, in which case the process is called partial oxidation and the result of combining the two reactions is referred to as autothermal reactions. Hydrogencarbon reforming is the most commonly used way in industrial settings to produce hydrogen [9, 37, 38, 39].
A desulphurization unit, a reforming and cleanup section, and auxiliary units such as pumps, compressors, expanders, heat exchangers, coolers, and combustor, among other types of components make up a traditional reforming plant [30, 40].

4.1.1.1 Steam Methane Reforming

Steam reforming is the most known and mature method to produce hydrogen with an efficiency that ranges between 74% to 85%. Due to the endothermic nature of the process, heat should be added to start the reaction. In a typical process, Syngas (H_2 and CO_2) is created by the reaction of steam and natural gas together with a nickel-based catalyst at 850–900 °C. [41, 9, 42, 43, 30].

This steam reforming process can be broken down into three primary stages: the formation of synthesis gas, the water gas shift, and gas purification or methanation [9, 44].

The operation parameters of the reforming reaction stage are selected at high temperatures (700–850 °C) [44], pressures up to 3.5 MPa, and steam-to-carbon ratios of 3.5 in order to create the necessary pure H_2 product and prevent coking formation on the catalyst surface [30, 40]. Following the reformer comes a heat recovery stage, and then the gas mixture is sent into a water gas shift reactor, which is where the carbon monoxide interacts with steam with the help of a catalyst to produce extra hydrogen. After that, the mixture goes through either a CO_2-removal and methanation process or a pressure swing adsorption process, ultimately resulting in H_2 with a greater purity that is close to 100% [30, 45].

The set of three equations (1-3) [9] that are shown below provides a concise summary of the most important reactions that take place in the reformer:

$$C_nH_m(g) + nH_2O(g) + heat \rightarrow nCO(g) + (n + \frac{m}{2}H_2(g)) \tag{1}$$

$$CH_4(g) + H_2O(g) + heat \rightarrow CO(g) + 3H_2(g) \tag{2}$$

$$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g) + heat \tag{3}$$

The creation of syngas through the steam reformation of a hydrocarbon is characterized as a general process by equation (1). In this equation, n and m indicate the share of carbon and hydrogen atoms, respectively. The reaction between methane and water, which produces carbon monoxide and hydrogen gas (syngas), is represented by the equation (2). You can obtain this reaction by putting n = 1 and m = 4 in the corresponding equation (1). Water and carbon monoxide reaction is represented by the equation (3). This reaction results in the generation of carbon dioxide and more water (Water gas shift reaction) [9].

4.1.1.2 Partial Oxidation

Partial oxidation is a reforming technique that turns oxygenated hydrocarbons into syngas. It takes place when the portion of oxygen (pure oxygen or air) that is delivered into the reformer is less than the comlete oxidation requirement, and it results in the production of hydrogen (H_2), carbon dioxide (CO_2), and carbon monoxide (CO).Close monitoring of the oxygen supply is required to achieve optimal hydrogen output, because complete oxidation can take place if the oxygen supply is too much, then the fuel or reactant totally burns, which results in a lower amount of hydrogen being produced [9, 43].

The type of hydrocarbon that is being utilized in the POX process determines whether the process should be catalytic or non-catalytic, and it also determines the temperature range that the POX process can be carried out in. While light hydrocarbons like methane and naphtha go through a catalytic process at temperatures around 950 °C, heavy hydrocarbons and coal go through a non-catalytic process at temperatures that range between 1300 and 1500 °C. These higher temperatures are necessary to reduce the amount of carbon that is formed [9, 45, 43, 44]. POX is the most convenient way to produce hydrogen from heavier feedstocks like heavy oil residues and coal [30, 46, 47].

The process of reforming in POX is quite similar to that used in SMR; the only difference is that oxygen is added. After the first reforming step, extraction of sulfur takes place to retrieve pure oxygen, which is then utilized to partially oxidize the hydrocarbon feedstock. The syngas that is obtained is then treated in the same way as as for the steam reforming output. [30, 43].

The extraction of hydrogen from coal is accomplished primarily through the employment of a process that is known as coal gasification. Although the reaction mechanisms of this approach are comparable to the POX of heavy oils, the method's costs are higher because of the extra processing of the fairly unreactive fuel as a solid and the removal of vast quantities of ash [30].

The main POX reactions are summarized below [48, 49, 9]:

$$C_nH_m(g) + \frac{n}{2}O_2(g) \rightarrow nCO(g) + \frac{m}{2}H_2O(g) \tag{4}$$

$$[CH]_{coal}(s) + O_2(g) \rightarrow CO(g) + H_2(g) \tag{5}$$

$$CH_4(g) + \frac{1}{2}O_2(g) \rightarrow CO(g) + 2H_2(g) \tag{6}$$

$$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g) \tag{7}$$

$$CO(g) + 3H_2(g) \rightarrow CH_4(g) + H_2O(g) \tag{8}$$

Equation (4) presents the main partial oxidation reaction in a reformer. Equation (5) shows the reaction for coal gasification. Equation (6) shows the surface reaction on the catalyst while using methane as a hydrocarbon. Equation (7) shows the water gas shift reaction and equation (8) represents the methanation or gas purification process.

4.1.1.3 Autothermal Reforming

The production of hydrogen and carbon monoxide (syngas) from natural gas or other hydrocarbon fuels can be accomplished using a method known as autothermal reforming (ATR). It is a hybrid process that involves steam reforming and partial oxidation. Exothermic partial oxidation generates heat, while endothermic steam reforming increases the amount of hydrogen produced [50, 30, 43, 44, 51, 49]. It takes place in an enclosed system in which the hydrocarbon fuel is partially oxidized with pure oxygen in a burner, so changing a portion of the hydrocarbon feed into carbon monoxide and hydrogen [9]. In most cases, steam with O2 or air is fed into the reformer chamber in order to facilitate the simultaneous occurrence of the oxidation and reforming reactions [43, 9].

Within the reactor is a zone known as the combustion zone, which is where processes leading to partial oxidation take place. After leaving this zone, The actual reactions that lead to reformation occur when the mixture is permitted to pass through a catalyst bed. In the reforming zone, the heat generated in the combustion zone as an outcome of POX reactions is used, so it is theoretically conceivable for the autothermal reforming process to achieve a state of heat balance in an ideal scenario [49, 52]. The proper functioning of te ATR process is ensured when both the oxygen to fuel ratio and the time span over which it is controlled are managed in such a way as to prevent the production of coke, as well as to regulate the reaction temperature and gas structure [44, 53].

Just as in SMR and POX, The choice of The catalyst significantly affects how efficiently the process works overall.. Nickel-based catalysts are the most popular choice since they are both efficient and inexpensive [49].

A typical autothermal reactor contains a burner, a combustion chamber, a catalytic zone, a refractory lining, and a reactor pressure shell. In the burner, the feed streams are combined together in a flame that is produced by turbulent diffusion. The combustion zone is the area where partial oxidation reactions create a combination of carbon monoxide and hydrogen, while the catalytic zone is the location where the gases that are exitting the combustion zone find thermodynamic equilibrium [9, 52].

Some of the advantages of ATR are:

- The initial investment required for ATR projects is 15–25% less than that required for SMR projects, and 50% less than that required for coal gasification projects [30].
- Compact design [52].
- High degree of flexibility coupled with rapid load shifts and minimal startup periods [52].
- procedure that is soot-free [52].
- In comparison to SMR, it operates at lower temperatures and has a greater tolerance for the presence of impurities [52].

The main equations that take place in ATR are shown below: [9, 44, 54]

$$CH_4(g) + \frac{3}{2}O_2(g) \rightarrow CO(g) + 2H_2O(g) \tag{9}$$

$$CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g) \tag{10}$$

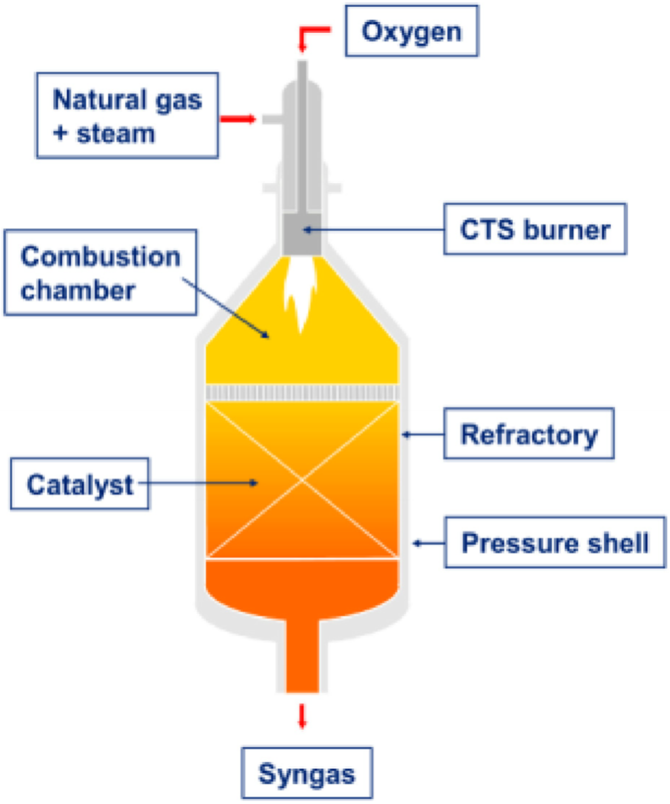


Figure 3: Autothermal Reformer Standard Design [9]

Equation (9) represents the POX exothermic reaction of methane while equation (10) shows the endothermic steam reforming reaction.

4.1.2 Hydrocarbon Pyrolysis

Hydrocarbon pyrolysis is a chemical process in which hydrocarbons are exposed to high temperatures in the absence of oxygen, this is known as a thermal decomposition of hydrocarbons. This results in the hydrocarbons disintegrating into smaller molecules, such as hydrogen and carbon monoxide, along with a variety of other byproducts [9, 30, 49]. The general pyrolysis reaction can be described with the equation as follows:

$$C_nH_m(l) \rightarrow nC(g) + \frac{m}{2}H_2(g) \tag{11}$$

After investigating a wide range of variables and conditions, researchers came to the conclusion that the previously described reaction is successful for light liquid hydrocarbons with a boiling point ranging from 50 to 200 degrees Celsius. The thermo-catalytic decomposition of light liquid hydrocarbons breaks them down into their elemental carbon and hydrogen forms [9, 30, 43].

Pyrolysis can also be used to transform heavy residual hydrocarbons, such as heavy oil or coal, into lighter molecules that are more easily processed. The pyrolysis procedure is significantly altered when working with heavy residual fractions that have a boiling point greater than 350 degrees Celsius. The generation of hydrogen must be done in two stages: first, hydro-gasification, and then, methane cracking. This is necessary because, in the event of direct decomposition, these elements would be transformed into coke, rendering it unfit for any further applications due to the significant amount of sulfur and metals content in heavy residual fractions [9, 43, 30, 49, 55, 56]. The following equations are used to describe the hydro-gasification and methane cracking reactions:

$$CH_{1.6}(l) + 1.2H_2(g) \rightarrow CH_4(g) \tag{12}$$

$$CH_4 \rightarrow C + 2H_2 \tag{13}$$

Equation (12) shows the hydro-gasification process, while equation (13) represents the process of methane cracking.

The energy requirement per mole of hydrogen produced by pyrolysis is 37.6 kilojoules per mole, which is significantly lower than that for the SMR method (63.3 kilojoules per mole). This energy requirement could be easily met by combustion of around 15–20% of the hydrogen output of the process [9, 43, 30, 57].

One of the primary benefits of hydrocarbon pyrolysis is that it can produce hydrogen and other useful chemicals from a wide range of feedstocks, such as natural gas, crude oil, and waste materials. This ability to produce hydrogen and other useful chemicals from a wide range of feedstocks makes the technology versatile and flexible. In addition, pyrolysis does not include WGS and CO_2 removal, and the energy-intensive stage of CCS is replaced with carbon management, which could be utilized in the metallurgy and chemical sectors, or it could be stored for later usage underwater or on land. Thus, the initial investment required for large-scale hydrogen production plants is far less than that required for SMR or POX processes, which results in a 25–30% reduction in the cost of producing hydrogen. If the carbon output is employed in other businesses, this cost can be reduced even further [43, 30, 57, 58]. The generation of carbon and hydrogen through the catalytic breakdown of natural gas would be more advantageous from an environmental standpoint than the production of hydrogen through SMR in conjunction with CCS [30, 43].

Moreover, Pd-Ag alloys are commonly used for H_2 separation because They decrease the formation of coke and allow operation at cooler temperatures. The main shortcomings of this method relate to the weak hydrogen separation caused by low H_2 partial pressures in the reaction mixture and decreased membrane durability due to high temperatures necessary for the decarbonization equilibrium [9, 30, 47].

Finally, despite producing less hydrogen than systems that utilise light hydrocarbon fractions, the hydrocarbon pyrolysis method enables the concurrent synthesis of valuable byproducts like sulfur or metals [49, 58].

4.2 Biomass

Hydrogen production from biomass is the process of extracting hydrogen from organic materials using various ways. Because of the rising demand for renewable energy sources, this procedure has recently become more popular.
Biomass sources can be [135, 44, 63] :

- Energy crops: non-food plants like herbaceous and woody plants.
- Agricultural residues: wheat and barley straws are a good example.
- Forestry residues: dead trees and timber.
- Industrial and municipal waste: sewage sludge and wastes from residential buildings.

Chemical linkages in these organic compounds serve to store solar energy [64]. A crucial component of the energy supply, biomass accounts for 14% of the energy produced globally [9] and, according to one estimate, will provide more than 25% of the world's energy needs by the year 2050 [49, 53].

Hydrogen can be a product of biomass from thermochemical or biological methods. Thermochemical processes are liquification, combustion, gasification, and pyrolysis but Gasification and pyrolysis are processes that involve heating biomass in the presence or absence of oxygen respectively to generate a mixture of gases, including hydrogen. Contrarily, biological processes that use microorganisms to produce hydrogen from organic materials. These processes include bio-photolysis, dark fermentation, and photo-fermentation [65, 49, 63]. Biological processes produce low outputs and efficiencies (mol H_2/mol feedstock) of hydrogen according to the raw materials employed, although being more energy efficient and less harmful to the environment [66]. On the other hand, due to their speed and larger stoichiometric production of hydrogen, thermochemical processes are faster and appear to be a feasible alternative for gasification [30, 62, 67].

Biomass is seen as a renewable source of energy; however, it is debatable as to whether or not it produces completely green hydrogen. This is due to the fact that even though CO_2 is emitted during the process of converting biomass into energy, this quantity of gas emission is equivalent to the quantity that was taken in by organisms while they were alive [68].

4.2.1 Thermochemical

Thermochemical techniques are efficient ways to extract hydrogen and hydrogen-rich gases from biomass. Pyrolysis and gasification are the fundamental components of these technologies. The reactions of steam reforming and water-gas shift can be used to boost the production of hydrogen from the CO and CH4 that pyrolysis and gasification create [49, 65, 69, 70].

4.2.1.1 Pyrolysis

Pyrolysis is the thermochemical process of heating biomass at high temperatures around 377-527 °C at a pressure of 0.1-0.5 MPa withiut the presence of air to produce liquid oils, solid charcoal, and gaseous chemicals. In some circumstances, partial combustion is permitted to supply the process's required thermal energy. It is regarded as all thermochemical conversion technologies' starting point [30, 49, 71]. Following thermal breakdown, the biomass is converted into pyrolytic products such as charcoal, bio-oil, and non-condensable gases like hydrogen, methane, carbon oxides, and other gaseous hydrocarbons [9].

There are two categories of pyrolysis: slow and fast [9]. Slow pyrolysis mostly yields charcoal, hence it is typically not taken into account for hydrogen generation. Fast pyrolysis is a procedure that requires high temperatures, in which biomass is heated swiftly without the presence of air to create vapor, which is condensed afterwards, creating a dark brown mobile bio-liquid. Hydrogen, methane, carbon monoxide, carbon dioxide, tar, oils, char, and pure carbon are among the byproducts of fast pyrolysis that can be found in gaseous, liquid, and solid phases. Fast pyrolysis is favoured for the generation of liquid fuel because it has benefits over other processes in terms of transport and storage, as well as having relatively cheap investment costs and high energy efficiency [49]. H_2 can be produced as follows for fast pyrolysis with enough high temperature and volatile phase residence [44]:

$$Biomass + heat \rightarrow CO(g) + H_2(g) + CH_4(g) + other\ products \tag{14}$$

The kind of biomass, pretreatment conditions (such as physical, chemical, and biological procedures), pyrolysis temperature, heating rate, particle size, catalytic effect, and carrier gas type are all factors that impact the end products of biomass pyrolysis [9, 72]. The yields and product compositions are impacted by these variables. A pyrolyzer must be able to process a variety of feedstocks, have minimal requirements for the feedstock's properties, and have high heat transfer efficiency and processing capacity to minimize running costs in order to be used commercially [73]. Product yields also depend on the conditions under which they are produced, with biochar creation preferred at temperatures under 450°C and bio-oil serving as the primary product at 450–800°C [49, 74]. However, pyrolysis produces primarily gases if a higher temperature than 800 °C is applied [9].

The application of catalysts is used to increase the quality of bio-oil by eliminating the oxygenated chemicals, raising the calorific value and the reaction's stability, and reducing its viscosity [9, 75]. Additionally, it can boost hydrogen production. It has been demonstrated that both metal- and non-metal-based catalysts, such as Nickel and activated carbon, can boost hydrogen yields [76]. Nickel-based catalysts have a maximum yield of 90% and methane as well as other hydrocarbon vapors are created by fast pyrolysis, they are processed using the steam reforming technique followed by WGS to produce additional hydrogen [44, 63].

4.2.1.2 Gasification

Gasification is a method for biomass to get thermally processed using air, oxygen, steam, or a combination of these gases to create syngas [9]. Depending on the size of the plant, how the produced syngas will be used after production, and the types of reactors, it operates at temperatures between 500 and 1400 °C and pressures ranging from atmospheric pressure to 3.3 MPa [30, 77], and creates a gas that contains carbon monoxide, methane, and trace amounts of hydrogen [9]. Compared to pyrolysis, which yields bio-oil and charcoal, biomass gasification reduces the carbon-to-hydrogen mass ratio and creates gaseous products [44]. Moisture level must be less than 35% for the method to be effective [62]. The primary biomass gasification reaction is [44]:

$$Biomass + H_2O(g) + heat \rightarrow H_2(g) + CO(g) + CO_2(g) + CH_4(g) + hydrocarbons(g) \tag{15}$$

Indirect gasifiers, fluidized-bed reactors, and fixed-bed reactors are the three primary varieties of biomass gasification reactors. While fluidized-bed reactors offer superior heat and mass transmission, resulting in higher carbon conversion and less tar formation, fixed-bed reactors are noted for creating less dust and particles in the product gas than other varieties and are also more cost-effective [78, 79].

The variables that have an impact on hydrogen output in both gasification and pyrolysis are the same; biomass type, particle size, temperature, steam-to-biomass ratio, and catalyst type [43, 77], but fast pyrolysis does not produce as much hydrogen as steam gasification, which has a thermal-to-hydrogen conversion efficiency of up to 52% [30].

Catalytsis with biomass gasification is mentioned in the literature as a way to maximize syngas production. A catalyst accelerates the cracking reaction and lower the activation energy, resulting in less energy being used. Different kinds of catalysts can be employed, such as alkali metal, mineral, or noble metal catalysts. Alkali metal catalysts stand out compared to other Nickel-based catalysts due to their high activity and low cost, which accounts for their widespread use in biomass catalytic gasification [80, 49].

The main problems of biomass gasification are low thermal efficiency due to moisture content and tar production, which can produce tar aerosols and choke pipes [9, 81]. Ash deposition and sintering are additional difficulties that might result in fouling and clustering [82]. These difficulties can be overcome using strategies such operational parameter management, additive use, and suitable gasifier design [9]. Dolomite, olivine, and char within the gasifier, according to Corella et al. [83], can prevent tar from forming.

Separating and purifying hydrogen from other gases in the syngas is also a key challenge. Ishida et al [84] .has an innovative approach that relies on the reactions of biomasses, alkali metal hydroxides, and water vapor at relatively low temperatures (200-350 °C) at atmospheric pressure to produce H_2 without CO or CO_2 for fuel cells. The primary reaction for this approach is:

$$C_6H_{12}O_6(l) + 12NaOH(s) + H_2O(g) \rightarrow 6Na_2CO_3(s) + 12H_2(g) \tag{16}$$

Where $C_6H_{12}O_6$ is glucose, NaOH is sodium hydroxide and Na_2CO_3 is sodium carbonate.
Sodium hydroxide (NaOH) and water vapor were used to react with glucose in a standard mass controlled gas flow system at 1 atm. Particularly, the production of H2 was improved when nickel (Ni), cobalt (Co), rhodium (Rh), or ruthenium (Ru) catalysts combined with aluminum oxide (Al2O3) were used. At 100–500 °C, the overall production of H_2 generated by catalytic reactions increased from 62% to almost 100% [84, 85]. While thermal catalytic conversion appears to be a promising method for generating relatively pure H_2, more study is required to optimize catalysts usage, enhance reactor performance, and address the primary issue with tar and char disposal [85].

4.2.2 Biological

Biochemical hydrogen generation is the process of generating hydrogen gas from biomass using microorganisms and enzymes. As a result of its promise for waste decrease and environmental sustainability, research in this area has lately increased.

Processes for producing biological hydrogen use renewable energy sources and run at room temperature and pressure. Their low energy demand makes them more efficient and sustainable than traditional techniques like steam reforming or thermochemical [86].

Direct and indirect bio-photolysis (phototropic processes), photo-fermentation, and dark fermentation are the primary biological processes that are employed to produce biological hydrogen. The dark fermentation method is favored than the phototropic process due to the unnecessity of having external energy input or oxygen, and because the rate of hydrogen synthesis is higher than in the phototrophic process [9].

Water and biomass are the two main inputs for the generation of biological hydrogen. While photolysis utilize water, fermentation operations use biomass [9]. For fermentation processes, the carbohydrate-containing substances are turned to organic acids and then into hydrogen through bio-processing technologies, while for photolysis, the feedstocks are transformed into hydrogen by means of bacteria, algae, and enzymes like hydrogenase or nitrogenase for photolysis [30, 87, 88].

Enzymes that produce hydrogen, such nitrogenase and hydrogenase, regulate biological processes involved in creating hydrogen [44]. Nitrogenase may produce hydrogen by reducing several substrates, including protons, using magnesium adenosine triphosphate (MgATP) and electrons, as seen in the following process, where ADP stands for adenosine diphosphate and Pi for inorganic phosphate [63]:

$$2e^- + 2H^+ + 4ATP(s) \rightarrow H_2(g) + 4ADP(s) + 4Pi(s) \tag{17}$$

Most photosynthetic bacteria have hydrogenases, which can be divided into two groups: uptake hydrogenases and reversible hydrogenases. Uptake hydrogenases serve as catalysts for hydrogen consumption, such as Nickel-Iron (NiFe) hydrogenases and Nickel-Iron-Selenium (NiFeSe) hydrogenases [63]:

$$H_2(g) \rightarrow 2e^- + 2H^+ \tag{18}$$

Depending on the circumstances of the reaction, reversible hydrogenases can both release or consume hydrogen [63]:

$$H_2(g) \leftrightarrow 2e^- + 2H^+ \tag{19}$$

To get rid of the undesirable components in a used material, pretreatment is necessary. Pretreatment techniques can generally be categorised into four types: physical, chemical, physicochemical and biological. Consequently, a biological pretreatment including microbes and enzymes is required before generating hydrogen from biomass can begin in this method [9].

In this chapter, the discussion of direct and indirect photolysis is then followed by that of photo and dark fermentation for the generation of hydrogen.

4.2.2.1 Direct photolysis

Direct photolysis is a process in which green microalgae use sunlight to generate energy and chemically separate water molecules into hydrogen and oxygen [63, 89].

$$H_2O(l) \rightarrow H_2(g) + \frac{1}{2}O_2(g) \tag{20}$$

The enzyme hydrogenase then transforms the created hydrogen ions into hydrogen gas [30].

Because they have chlorophyll and the photosynthetic systems Photosystem I (PSI) and Photosystem II (PSII), green microalgae can use light to perform photosynthesis [89]. Two photosynthetic systems, photosystem I (PSI) and photosystem II (PSII), are in charge of the photosynthesis in microalgae. While PSII splits water and releases oxygen, PSI creates a reductant for CO_2 reduction. In the direct pyrolysis, two photons from water can result in either hydrogen production with hydrogenase present or CO_2 reduction via PSI in the direct photolysis process. Green plants can only reduce CO_2 since they lack hydrogenase, whereas microalgae like Cyanobacteria and green algae do have hydrogenase and can make hydrogen. When PSII receives light energy, electrons are created. These electrons are subsequently transported to ferredoxin using the solar energy that PSI also absorbed in order to create hydrogen [63].

Due to the oxygen sensitivity of the hydrogenase enzyme, which is used in direct photolysis, hydrogen generation must be sustained at low oxygen levels (sub 0.1%) [30]. High intensity light is also necessary for this process. However, 90% of the photons collected by the photosynthetic machinery at high sunlight intensities are not utilised in photosynthesis and are instead wasted as heat or fluorescence, resulting in low efficiency. Chlamydomonas reinhardtii, a green alga that can reduce oxygen during oxidative respiration, can be used to maintain low oxygen levels, however this also results in low efficiency because a large fraction of substrate is respired and consumed [63]. Recent research has shown that mutants produced from microalgae have high oxygen tolerance and can create larger levels of hydrogen. This shows that a large boost in efficiency can be achieved when employing these mutants to produce hydrogen [63].

4.2.2.2 Indirect photolysis

Indirect photolysis is a two-step mechanism by which Cyanobacteria (blue-green algae) can create hydrogen [9]. When exposed to sunlight, water molecules split into protons and oxygen in the first stage. The second stage involves fixing carbon dioxide to create stored carbohydrates, which is then turned into hydrogen gas by hydrogenase [90, 89] [20]. (11). These reactions can be used to display this process [91]:

$$6H_2O(l) + 6CO_2(g) + light\ energy \rightarrow C_6H_{12}O_6(aq) + 6O_2(g) \tag{21}$$

$$C_6H_{12}O_6(aq) + 12H_2O(l) + light\ energy \rightarrow 12H_2O(l) + 6CO_2(g) \tag{22}$$

According to Ni et al. [63], indirect photolysis consists of the following four steps:

- Biomass is created through photosynthesis.
- The biomass is concentrated.

- Aerobic dark fermentation results in the production of 2 mol of acetates and 4 mol of hydrogen/mol of glucose in the algal cell.
- Acetates in the amount of 2 mol are transformed into hydrogen.

Blue-green algae, or cyanobacteria, are attractive microorganisms for producing hydrogen via indirect photolysis. This approach has the advantages of segregated hydrogen and oxygen evolution and effective by-product hydrogen conversion. Low yield, the need for a sizable surface area to collect light from a continual light source, and no waste utilization are drawbacks, nevertheless [92, 89, 44]. The potential for hydrogen production with this approach is constrained by these disadvantages.

According to Troshina et al.'s research on indirect photolysis using the cyanobacterium gloeocapsaalpicola [93], the pH range for ideal hydrogen generation is between 6.8 and 8.3. In addition, when the temperature was raised from 30 to 40 degrees Celsius, hydrogen production doubled.

It should be noted that research and development on indirect biophotolysis technology is still ongoing and although it currently has many limitations, there can be a breakthrough in the future.

4.2.2.3 Photo-fermentation

Photo-fermentation, a method that involves solar energy, nitrogenase, and organic acids or biomass, can be used by photosynthetic bacteria to create hydrogen. This method uses sunlight as an energy source to break down organic materials into hydrogen and carbon dioxide. The reaction is catalyzed in part by nitrogenase [9]. The main reaction is [89]:

$$CH_3COOH(l) + 2H_2O(g) + light\ energy \rightarrow 4H_2(g) + 2CO_2(g) \tag{23}$$

Where CH_3COOH is acetic acid.
Numerous variables, including pretreatment, the properties of the raw materials, the design of the photobioreactor, the scattering and intensity of the light, and the mass-transfer of light and heat, affect the synthesis of biohydrogen by photo-fermentatio and fermentation can occur at different temperature ranges [9].

Major limitations to the photo-fermentation method for producing hydrogen include using nitrogenase enzyme, which has a high energy requirement, low solar energy conversion efficiency, and the need for large anaerobic photobioreactors [44]. Additional drawbacks include the requirement for nitrogen-limited environments and the processing of industrial wastewater, which may be hazardous [92]. While increasing light intensity can boost hydrogen output and production rates, it can also decrease the efficiency of light conversion. Wastewater's color and the presence of harmful substances like heavy metals can both be issues that necessitate pretreatment before usage. These elements, together with the insufficient supply of organic acids make photo-fermentation uncompetitive in the present [94, 89].

4.2.2.4 Dark fermentation

Dark fermentation is a method that combines anaerobic bacteria and microalgae to create hydrogen from carbohydrate-rich substrates in an oxygen- and light-free environment at temperatures between 30 and 80 degrees Celsius [95, 63]. Depending on the reaction method and substrate utilized, the results of dark fermentation are primarily hydrogen and carbon dioxide, but they may also contain additional gases such methane or hydrogen sulfide. The maximum theoretical yield of hydrogen using glucose as the model substrate is 4 mol per mole of glucose when the final product is acetic acid and 2 mol when the final product is butyrate. However, in fact, the final products frequently include both butyrate and acetate, which lowers the actual yield of hydrogen [63]. The acetate and butyrate fermentation reactions are respectively shown [30]:

$$C_6H_{12}O_6(aq) + 2H_2O(l) \to 2CH_3COOH(l) + 4H_2(g) + 2CO_2(g) \tag{24}$$

$$C_6H_{12}O_6(aq) + 2H_2O(l) \to CH_3CH_2CH_2COOH(l) + 2H_2(g) + 2CO_2(g) \tag{25}$$

Where $\mathrm{CH_3CH_2CH_2COOH}$ is butyric acid.
The methods used for pretreatment are the key factors that influence dark fermentation. The pH value would be optimally kept between 5 and 6, hydrogen partial pressure should be maintained to prevent reduced substrate formation, and according to Ueno et al. [96], the hydraulic retention time should be of value 0.5 day. Other factors to consider include the source of the inoculums, the organic substrate, the reactor type, and the temperature [9]. Utilizing additives such as metal additives (metal monomers, metal ions, and metal oxides), biomass immobilization carriers, L-cysteine, boosting microorganisms, and enzymes will maximize the hydrogen yield of dark fermentation [63, 9, 97].

Dark fermentation provides a variety of benefits over other biological processes, including the ability to continually generate hydrogen without light and a greater rate of hydrogen generation, the simplicity of the procedure, a lower net energy input, and the capabilities to use waste with lesser value as raw materials. Additionally, it generates useful byproducts including butyric acid, lactic acid, and acetic acid. However, compared to commercial procedures, it produces relatively less hydrogen, and the resulting gas combination contains carbon dioxide that needs to be separated. Despite these drawbacks, dark fermentation is a potentially valuable commercial technology because it does not require much area since solar energy is not required and it is not impacted by weather conditions [63, 9, 98, 89].

4.3 Renewables (Water Splitting Technologies)

Despite the fact that only a very small part of the world's total hydrogen output is produced via renewable sources, the majority of its technologies are not commercially mature yet, and even the cost of production is not competitive when compared with fossil fuels, it is still a very promising field. This is especially true when considering the noticeable research focus on those technologies and the urgent need to reduce reliance on fossil fuels. In the near future, the proportion of renewable technology will increase, and in the more distant future, it is anticipated to predominate over the use of conventional technologies [36, 30]. In this section, we will go over the water splitting techniques for producing hydrogen.

Water splitting, a method that turns water into hydrogen and oxygen, is implemented to produce hydrogen [99, 100]. This can be accomplished by several techniques, such as electrolysis, thermolysis, and photo-electrolysis, each of which can be driven by different energy sources, like electrical, thermal, and photonic energy [49]. The hydrogen produced by water splitting is classified as 100 percent green if the energy input originates from renewable sources [30]. Water splitting main reaction is as follows [49]:

$$H_2O + 2e^- \rightarrow H_2(g) + \frac{1}{2}O_2(g) \tag{26}$$

In the previous reaction, water can be in liquid or gaseous form, depending on the operating temperature and pressure.

4.3.1 Electrolysis

Electrolysis is one of the most efficient methods for creating hydrogen from water; it is a process that uses an electrical direct current to breakdown water into hydrogen and oxygen. It is an endothermic procedure that is carried out in an apparatus known as an electrolyzer [101, 9, 49].

An electrolyzer is a machine that separates water into hydrogen and oxygen using electricity. The type of electrolyzer is defined by the material employed for the membrane, which separates the anode and cathode [9]. Proton exchange membrane electrolyzers (PEM), alkaline electrolyzers (AEC), and solid oxide electrolyzers (SOEC) are the three primary types of electrolyzer membranes [102, 103]. Electrolysis main reaction is [49]:

$$H_2O(l) + 2e^- \rightarrow H_2(g) + \frac{1}{2}O_2(g) \tag{27}$$

Electrolyzers are discussed in detail in section 4.4.

Water electrolysis is an environmentally friendly method of producing high quality hydrogen that can be utilized in a variety of applications such as fuel cells and ammonia synthesis. Its efficiency ranges from 60 to 81%, and it is already commercially more advanced than other clean technologies [104]. However, compared to the conventional fossil fuel-based processes, the cost of electrolytic hydrogen is still considerably higher [49], but carbon emissions impact on the enviroment and carbon tax prices should always be taken into consideration.

4.3.2 Thermolysis

Thermolysis is the process of breaking down water into hydrogen and oxygen by heating it to high temperatures, usually above 2500 degrees Celsius. This method is based on the large Gibbs free energy of water at these temperatures, which makes it possible to separate hydrogen from the equilibrium mixture [105].

In order to manufacture hydrogen in a more environmentally friendly way, many thermochemical water-splitting cycles have been developed that use catalysts based on Copper(I) Chloride (Cu-Cl) or Tin(IV) Oxide (SnO_2) to lower the temperature and increase overall efficiency [43, 106]. In these cycles, heat is transformed to chemical energy in the form of hydrogen through a sequence of chemical reactions at different temperatures that can be powered by solar or nuclear energy [64, 68]. Cu-Cl and Magnesium Chloride (Mg-Cl), which don't emit any greenhouse gases and need at least 550 degrees Celsius, are the most promising low-temperature thermochemical cycles [63, 77, 107]. With increased sun intensity, hydrogen generation becomes more efficient and faster [30]. The chemical equations (28) through (34) provide two examples of thermochemical cycles, and the single-stage water decomposition is shown in equation (27) [30].

- Single-stage [108]:

$$2H_2O(g) + heat \rightarrow 2H_2(g) + O_2(g)\ (T > 2500C) \tag{28}$$

- Multi-stage Cu-Cl [109]:

$$2CuCl_2(s) + H_2O(g) + heat \rightarrow CuO^*CuCl_2(s) + 2HCl(g)\ (T \approx 400C) \tag{29}$$

$$CuO^*CuCl_2(s) + heat \rightarrow 2CuCl(l) + \frac{1}{2}O_2(g)\ (T \approx 500C) \tag{30}$$

$$4CuCl(s) + H_2O(l) + heat \rightarrow 2CuCl_2(aq) + 2Cu(s)\ (T = 25 - 80C) \tag{31}$$

$$CuCl_2(aq) + heat \rightarrow CuCl_2(g)\ (T = 100C) \tag{32}$$

$$2Cu(s) + 2HCl(g) + heat \rightarrow 2CuCl(l) + H_2(g)\ (T = 430 - 475C) \tag{33}$$

- Two-step SnO_2/SnO [110]:

$$SnO_2(s) + heat \rightarrow SnO(g) + \frac{1}{2}O_2(g)\ (T = 1600C) \tag{34}$$

$$SnO(s) + H_2O(g) + heat \rightarrow SnO_2(s) + H_2(g)\ (T = 550C) \tag{35}$$

Because the thermolysis process is reversible, one of the main challenges is separating the created hydrogen and oxygen because the mixing of those two gases could produce an explosive mixture. Another challenge is the lack of materials that can withstand the necessary temperatures [49].

4.3.3 Photo-electrolysis

The photo-electrolysis procedure includes breaking water into hydrogen and oxygen using a visible-light-absorbing semiconductor electrode [111, 43]. The method is similar to electrolysis, except it also incorporates solar energy. Electricity is also needed for this process in order to transform photonic and electrical energies into chemical energy, such as hydrogen [112, 49].

Semiconducting materials absorb sunlight, which is then used to decompose water into hydrogen and oxygen. An electron-hole pair is produced and kept apart by an electric field when a photon with sufficient energy strikes the surface of a semiconductor. The holes hydrolyze at the anode to yield hydrogen ions and oxygen while the electrons travel via an external circuit to the cathode, where they mix with hydrogen ions to make hydrogen gas. [30].

The performance of this system depends on the type of photon absorbing material, surface properties, crystalline structure, corrosion resistance, and reactivity [112, 49].

Without any additional bias potential, the extraction of the electron from the hole requires a lot of bandgap energy, which significantly lowers overall efficiency [30]. This is true even though the free energy needed for the breakdown of water into H_2 and O_2 is just 1.23 eV. According to Akikusa et al. [113], the mixture of Silicone Carbide (SiC) and Titanium Dioxide (TiO_2) results in a self-driven system with appropriate band locations and a low photoconversion efficiency of 0.06%.

4.4 Electrolyzers

An essential tool for the shift to a hydrogen economy fueled by renewables is the electrolyzer, which can transform clean electricity into hydrogen. Hydrogen can be created using these machines for a variety of uses. While there are now only small-scale electrolyzers available, bigger demonstration projects are also being studied [43]. In a conventional electrolyzer, water molecules are divided into hydrogen and oxygen by an electrical direct current applied to a cathode and anode in an electrolyte [30, 101].

The electrodes must be adequate in terms of structure, strong electric permeability, high catalytic characteristics, and corrosion resistance. The electrolyte mustn't interact with the electrodes because any variation in the electrolyte during the operation must be avoided. To prevent the hydrogen and oxygen produced at the electrodes from recombining, a diaphragm or separator must be used during the electrolysis process. The diaphragm's electrical resistance protects the electrodes from short-circuiting. The diaphragm must, nonetheless, have a strong ionic conductivity. Finally, diaphragms must possess high levels of chemical and physical stability. The components that make up the electrolytic cell are the electrodes, the diaphragm, and the electrolyte [101].

Since electrolyzers don't have mechanical components, they often don't need ongoing maintenance. They are suited for decentralized applications in residential, commercial, and industrial locations since they are quiet and provide a significant level of modularity. Although electrolyzers have been utilized for a long time, there are still many areas that might be improved, including the price associated with production and installation [132].

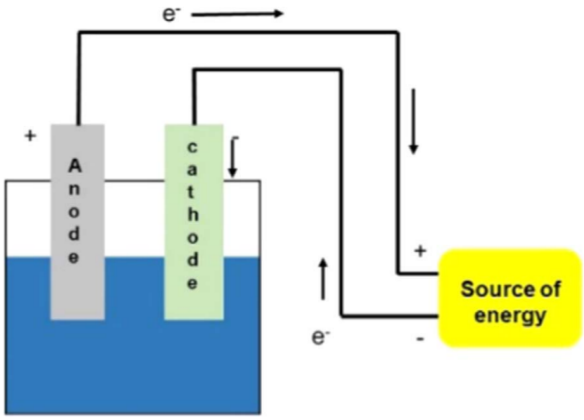


Figure 4: Electrolyzer [131]

The types of electrolyzers discussed in this section are Alkaline (AEC), proton exchange membrane (PEM) and solid oxide electrolyzers (SOEC).

4.4.1 Alkaline Electrolyzers

Commercial production of hydrogen uses the well-established process of alkaline electrolysis [132]. Alkaline electrolyzers (AEC) contribute with an overall energy usage of 53.4 kWh/kg of hydrogen and can produce 380,000 kg of hydrogen annually with a conversion efficiency ranging between 63 to 70% [133, 30, 104]. AEC is deemed safe and efficient, and it has relatively inexpensive investment costs since it does not employ precious expensive materials like in PEM for example. A common AEC runs between 60 and 80 °C with a current density of roughly 400 mA/cm^2 with cell voltages between 1.85 and 2.2 V [9, 134]. Large AECs with capacities near 165 megawatts electrical had already been constructed in nations with an abundance of hydropower, such as Canada, Egypt, and Norway. Unfortunately, the majority of them were taken out of service in the 1970s in pursuit of producing hydrogen from conventional fossil-based processes [104].

AEC comprises two electrodes, a cathode and an anode, kept apart by a diaphragm, all submerged in a liquid electrolyte to promote the reaction [134]. The application of an electrical direct current leads the electrodes to create oxygen and hydrogen at the anode and the cathode, respectively [132]. The diaphragm permits the passage of ions while preventing the generated gases from passing through to avoid their mixing. According to [101], the following reactions take place in AEC:

Cathode:

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \tag{36}$$

Anode:

$$2OH^-(aq) \rightarrow \frac{1}{2}O_2(g) + 2e^- \tag{37}$$

The most popular electrolyte is a 30% potassium hydroxide (KOH) concentrated liquid, but sodium hydroxide and sodium chloride may be used as well. Ceramic oxides like asbestos and potassium titanate, as well as polymers like polypropylene and polyphenylene sulfide, can be used to construct the diaphragm [134]. The most frequently used diaphragm in conventional AECs is 3-mm thick asbestos, however, it is beginning to be substituted with the alternatives due to health risks and since it prevents the AEC operating temperature to exceed 80°C. Steel with nickel coating serves as the anode, and steel with a catalyst coating serves as the cathode with a distance of 5mm between the two electrodes [132].

AEC has several benefits, such as producing hydrogen without the use of a precious metal catalyst and that it runs at relatively moderate temperatures, making it easier to manage. Its primary disadvantage is that the electrolyte liquid may leak, which could result in Ohmic loss and decreased efficiency [9, 134].

AEC is the most advanced process for producing hydrogen, and there is extensive research on using it to make "green" hydrogen. Firms are concentrating on raising production, enhancing performance, and lowering expenses. To reduce the price of power use, electrolyzer efficiency has grown recently. Current densities have also been enhanced to minimize cell surface area and capital costs. Other advancements include the utilization of ion exchange inorganic membranes as new, cutting-edge diaphragm materials to substitute asbestos. For large-scale hydrogen production, advanced AEC is designed with an operating temperature reaching 150°C. These electrolyzers can create hydrogen and oxygen that are 99.9% and 99.7% pure, respectively without the need for any extra purification tool even though catalytic conversion and adsorptive drying units can indeed enhance purity. One specific enhancement to advanced AEC is the zero gap design, which involves reducing the distance between electrodes to under 1 mm to decrease ohmic losses and enable higher current densities [132, 101].

AECs can function for around 30 years, however, they do require full maintenance every 7-15 years to substitute the electrodes, reactivate them, and change the diaphragms [132].

Recently, new pressurized AEC systems have been developed. These systems are more capable of adapting to fluctuations in power input, making them perfect for usage in combination with renewable energy sources and allowing them to compete with other technologies, such as PEM electrolysis [115]. Pressurized electrolyzers produce hydrogen at pressures between 0.6 and 3 MPa, whereas traditional atmospheric electrolyzers work at pressures as low as 0.6 MPa. Furthermore, in lab settings, pressures up to 20 MPa have been reported. The need for less energy to compress hydrogen to storage pressure levels is another benefit of pressurized electrolysis. However, due to the diaphragm's higher permeability at elevated temperatures and pressures, it can also lead to a decrease in the quality of the generated gases, negatively affecting the efficiency of the whole process [132].

4.4.2 Proton Exchange Membrane Electrolyzers

In the last ten years, PEM electrolysis has undergone substantial progress and is now widely used for hydrogen production [115]. Commercial PEM electrolyzers may produce hydrogen that is at least 99.99% pure without the requirement for extra purification apparatus for small-scale industrial uses [132]. They run between 50 and 80 °C, and their efficiency varies from 56% to 60% [49, 101, 104]. A thin (less than 0.2 mm), gas-tight polymeric membrane with an acidic character serves as the electrolyte. It has functional groups of the sulfonic acid class that carry protons through an ion exchange process. Some PEM electrolyzer designs may achieve pressures of up to 8.5 MPa, allowing the synthesis of oxygen at air pressure while producing hydrogen at 3.5 MPa eliminating the risks of handling pressurized oxygen [101].

At the anode, the water-splitting process generates protons and oxygen. These protons react with the cathodic electrons after passing through the membrane, creating hydrogen gas. The following reactions occur in a PEM electrolyzer [9, 101]:

Anode:

$$2H_2O(l) \rightarrow \frac{1}{2}O_2(g) + 2H^+(aq) + 2e^- \tag{38}$$

Cathode:

$$2H^+(aq) + 2e^- \rightarrow H_2(g) \tag{39}$$

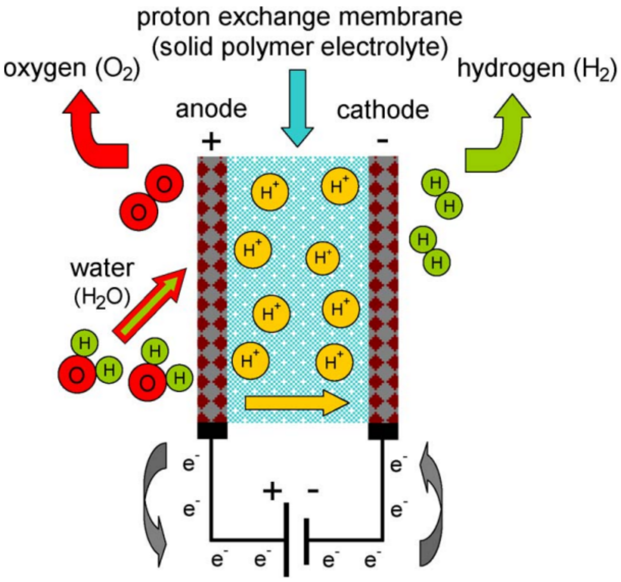


Figure 5: PEM Electrolyzer [101]

PEM has significant advantages over other kinds of electrolyzers. These benefits include the capability to scale up and down rapidly in reaction to variations in power input, a lower ohmic loss, high current density and ability to function at high pressure, purity of generated gases, performance at high voltages, and safety owing to the unavailability of caustic electrolyte. Given the acidic character of the electrolyte and the electrodes' metallic surfaces, PEM also produces hydrogen and oxygen at a higher rate than conventional methods. Its small gaseous permeability minimizes the possibility of flammable mixture generation, and also PEM can work at high pressure on the cathodic sites while the anode runs at air pressure. Furthermore, PEM can produce highly pressurized hydrogen for decentralized production and storage at refueling stations and are comparatively small, enabling possible use in populated areas. If properly designed, PEM can operate between zero-load and 160% of full load, permitting temporary overloading [132, 104].

The main disadvantage of PEM electrolysis is the significant initial investment required for the membrane and noble metal (Platinum and iridium) electrodes to function at high voltage and in an acidic medium. In comparison to AEC, it also has a shorter lifespan and a smaller hydrogen yield [132, 101].

Although the main research points are quite close to AEC, more work is anticipated for them to close the gap to AEC's expenses. Platinum and iridium elimination and reuse continue to be developed with PEM as these precious elements have the potential to restrict the use of PEM on a big scale [115].

4.4.3 Solid Oxide Electrolyzers

With the objective of lowering energy demand and, consequently, operational costs, SOEC was developed. SOEC Electrolyte is made of Yttria-stabilized zirconia (YSZ) that benefits from oxygen vacancies in the mixed oxide structure, which allows for excellent ionic conductivity even at high temperatures of operation. The anode is constructed from a combination of YSZ and perovskites intended to promote electrocatalysis through structural and electronic flaws, whereas the cathode is a cermet constructed of nickel and YSZ [101].

The required-to-operate temperatures of SOECs range from 650 to 1000 °C, and they utilize steam rather than liquid water. This type can be used When a high-temperature heat supply, such as nuclear reactors, geothermal energy, or solar thermal energy is provided. The system needs a high temperature intake to function effectively; the higher the temperature is, the less electrical energy is needed for the electrolysis. Theoretically, SOECs can contribute up to 40% of the energy required

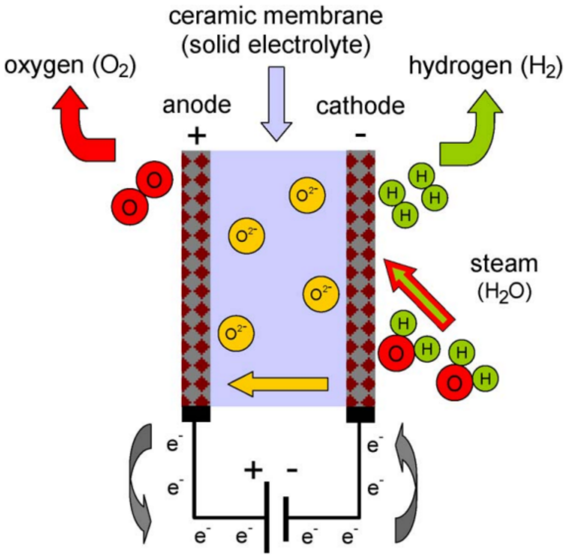


Figure 6: SOEC Electrolyzer [101]

to create hydrogen by steam electrolysis at 1000°C and also can cut the requirement for electricity by up to 25% [9, 132, 101, 104]. The reactions taking place in the SOEC are [101]:

Cathode:

$$H_2O(g) + 2e^- \rightarrow H_2(g) + O^{2-} \tag{40}$$

Anode:

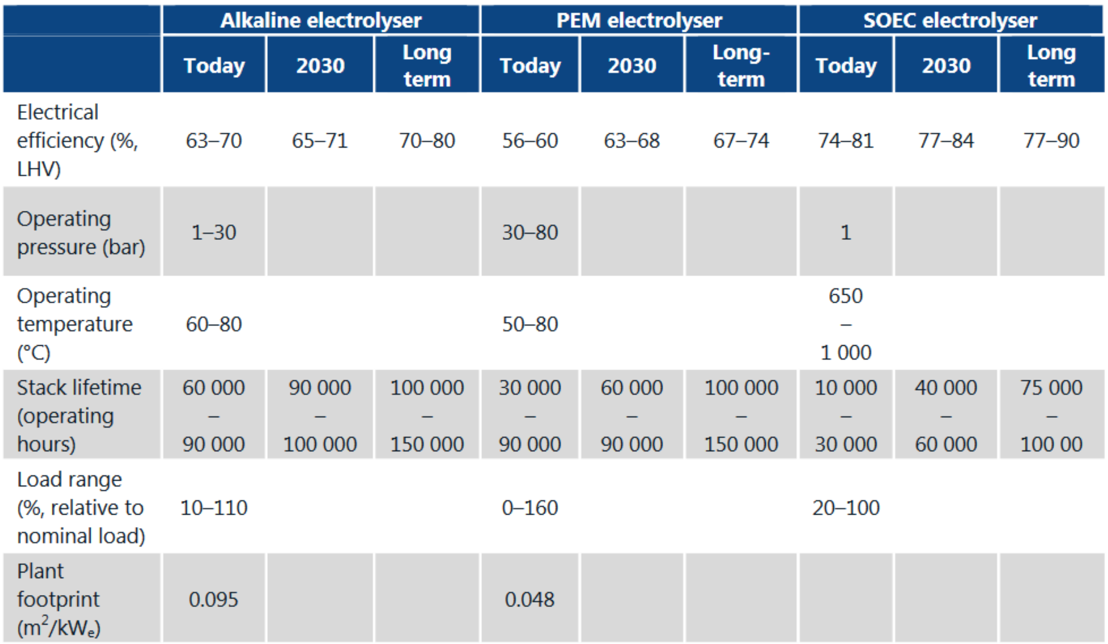
$$O^{2-} \rightarrow \frac{1}{2}O_2(g) + 2e^- \tag{41}$$

Owing to its solid electrolyte, SOEC is not prone to leaks, and its small design lowers resistive loss. Additionally, SOEC can function in reverse as a fuel cell, create syngas by co-electrolyzing steam and CO_2, and can also create ammonia by co-electrolyzing with air. In conjunction with hydrogen storage, SOEC can balance the grid and raise its overall usage rate [9, 115, 104].

On the other hand, SOECs suffer from degradation because of secondary and mechanical stress resulting from the high operating temperatures and also have greater capital costs due to the necessity for additional processing of the hydrogen-steam mix generated at the cathode. Given the impact of load variations on thermal stability, they are inappropriate when combined with fluctuating renewable energy [9, 101, 104].

Although SOEC is commercially accessible, AEC and PEM are more advanced and have a larger scale. For SOEC, research activities are concentrated on commercialization, boosting output, extending product lifespan, and lowering expenses. To rival the other conventional methods, SOEC still needs to make progress in those aforementioned areas [115].

The following table summarizes the most important elecrtolyzers characteristics for the present and future predictions for 2030 and the long-term.



	Alkaline electrolyser			PEM electrolyser			SOEC electrolyser		
	Today	**2030**	**Long term**	**Today**	**2030**	**Long-term**	**Today**	**2030**	**Long term**
Electrical efficiency (%, LHV)	63–70	65–71	70–80	56–60	63–68	67–74	74–81	77–84	77–90
Operating pressure (bar)	1–30			30–80			1		
Operating temperature (°C)	60–80			50–80			650 – 1 000		
Stack lifetime (operating hours)	60 000 – 90 000	90 000 – 100 000	100 000 – 150 000	30 000 – 90 000	60 000 – 90 000	100 000 – 150 000	10 000 – 30 000	40 000 – 60 000	75 000 – 100 00
Load range (%, relative to nominal load)	10–110			0–160			20–100		
Plant footprint (m^2/kW_e)	0.095			0.048					

Table 2: Comparison between the 3 electrolyzers' types at the present, 2030 and in the long-term. [104].

5 Hydrogen Storage

For the energy transition to renewable energy sources, the development of hydrogen storage technologies is important. There are various ways of storing hydrogen, including compressed gas at high pressure, cryogenic liquid at very low temperatures, cryo-compressed, and even underground [9, 115]. The most appropriate storage medium is subject to volume, duration, discharge speed, and location [104]. Research is interested in finding a cost-effective way to store hydrogen, and in this chapter, the major hydrogen storage methods are discussed.

5.1 Compressed Hydrogen

The most common and simple method of storing H_2 is to store it in its natural gaseous form under high pressure to reach lower volumes, where temperatures can be maintained at room temperature and pressure can reach 70–80 MPa [104, 116], which allows it to have a higher energy density. Normally, this pressurization process takes around 10 percent of hydrogen's energy content [122].

One advantage of storing hydrogen as a high-pressure gas is that it can be filled quickly and released at a high rate [116]. However, due to its low density, the energy content per weight of hydrogen is relatively low and amounts to only 15% of the energy density of gasoline even after applying high pressure [122]. It also requires more energy to compress hydrogen to the same pressure as helium and methane [117, 118].

The use of pressure vessels for hydrogen storage was first reported in 1880 when hydrogen was stored in wrought iron vessels at a pressure of 12 MPa [44, 119]. Pressure vessels are made with a central cylindrical section, two spherical domes, and polar openings [117]. Some metals, such as alloy or high-strength steels, are prone to embrittlement, which reduces the strength and durability of the material [117]. To avoid this issue, materials such as austenitic stainless steel, aluminum, and copper alloys are preferred for pressure cylinders due to their resistance to the effects of hydrogen at ambient temperatures [117]. The ideal characteristics of a high-pressure vessel for hydrogen storage are high tensile strength, low density, and the ability to either not react with hydrogen or allow it to diffuse [44].

Type I, II, III, and IV pressure tanks are available for storing hydrogen, respectively [119]. Type I tanks are typically utilized in industrial and commercial applications and are constructed of metals like carbon steel and low alloy steel. They can bear a maximum pressure of 50 MPa [119] and have a total volume of 2.5–50 m^3 at a pressure of 20–30 MPa [117]. However, they only have a relatively small hydrogen storage capacity of 1 weight percent [44]. Type II tanks have a strong load-bearing metal liner made of steel or aluminum to maintain gas sealing and restrict escape. The cylindrical portion of the liner has a fiber resin composite partly coiled around it. The structural load is split between the steel liner and the composite material, and the tank can resist an indefinite amount of pressure [119, 117]. Type III tanks have a thin metal liner surrounding them with a high-strength, stiff fiber resin composite that bears the majority of the pressure applied to the tank. Only around 20% of the weight is carried by the metal liner, and the vessel can bear pressures of up to 45 MPa. While weighing half as much as Type I tanks, it costs twice as much as Type II vessels [119, 120, 117]. Type IV tanks contain a fiber resin composite that completely encases a polymer liner or, in some situations, an ultra-thin metal liner. While only the tank boss and liner connection are made of metal, the polymer liner assures gas tightness. These tanks are the lightest of all kinds, but they are also the most costly [119, 120]. They can tolerate a storage pressure of a maximum of 100 MPa [117].

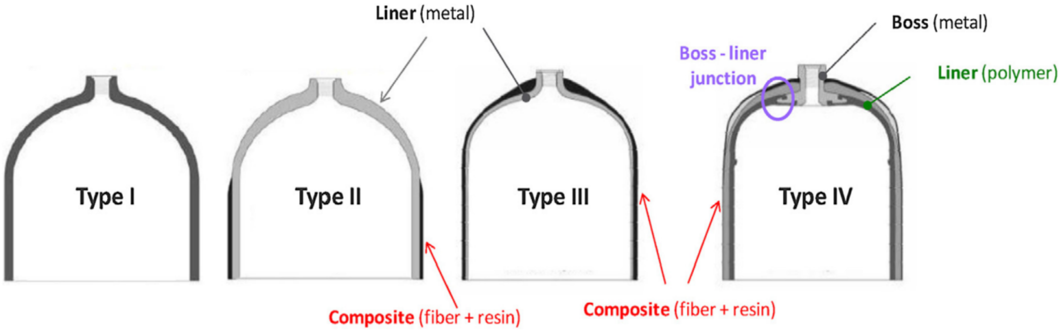


Figure 7: Tanks' 4 Types [119]

Long-term stationary storage employing geological methods such as salt caverns, drained oil and gas reservoirs, and aquifers has a 98% efficiency and costs roughly 0.6 usd/kgH_2 [104]. For large-scale storage, hydrogen gas can be pressurized and kept at pressures between 10 to 82.5 MPa [117], with the best seasonal storage pressure in salt caverns often being between 17.5 and 20 MPa and with a storage capacity of millions of cubic meters range [116]. The underlying concept of geological storage is injecting hydrogen gas below and keeping it under pressure, where it can subsequently be extracted as desired [117]. Pure hydrogen has only reportedly been kept in salt caverns thus far, which is still regarded as a very limited experience [21]. With hydrogen leakage of as little as 1% and no contamination difficulties, salt caverns are now the most plausible technique for storing compressed gaseous hydrogen for energy buffering [21].

The subsurface stored gas is separated into two components: a cushion and a working gas. Cushion gas is the underground storage reservoir's foundation gas, and its purpose is to keep the pressure at a suitable level to ensure the deliverability of the gas; the speed at which the gas can be released out of the reservoir. Cushion gas can be thought of as the baseline charge amount of the storage, similar to batteries, because it is supposed to remain forever in the reservoir and because it typically becomes stuck within the geological formations, it also becomes unrecoverable. Working gas, on the contrary, is the practical available storage space that can be charged and released continuously [117].

In addition to providing safe and secure storage, underground storage technologies also have a reduced chance to experience fires and are less prone to be affected by military or terrorist elements. Furthermore, with the minimal possible adjustments, underground storage can be seamlessly incorporated into city plans [117]. Moreover, compared to other available options, geological storage is the most cost-effective way to affordably store a significant quantity of hydrogen [121]. This method can enhance the usage of renewable energy sources for hydrogen production since it is adequate for long-term seasonal storage. H_2 can be kept underground in vast quantities after being produced using solar or wind power. When there is market demand, the conserved H_2 can then be delivered, allowing a continual process of supply and demand [116].

However, underground storage may face several difficulties, such as the need for geological criteria due to its low demographic and the difficulty in locating adequate subsurface storage locations close to utility sites [116]. Additionally, there are societal and legal barriers related to national rules, public widespread acceptance, and environmental concerns, as well as possible chemical interactions with hydrogen that could lead to gas contamination or loss [117, 121].

5.2 Liquefied Hydrogen

Liquid hydrogen is the name for hydrogen that can be held in a liquid state to boost its energy density [9]. It is non-corrosive, transparent, and liquefies to a boiling temperature of around -253 °C [123].

The technique of liquefaction involves cooling gas to cryogenic temperatures to transform it into a liquid. To do this, hydrogen atoms or molecules must be tightly bound to other elements [123]. Cryogenic refers to conditions with temperatures below -150 °C [124]. Cryogenic liquefaction is the method for turning a gaseous substance that is at air pressure into a liquid that is at cryogenic temperature. As a result, gaseous hydrogen is cooled to below -253 degrees Celsius via gases such as helium, neon, nitrogen, oxygen, and air at 1 atm or higher [9, 124]. A liquefaction process uses a mix of compressors, expansion engines, heat exchangers, and throttle valves. The Linde cycle and the Joule-Thomson expansion cycle are the two most widely utilized liquefaction methods. The gas is compressed as part of the Linde cycle process, and then it is cooled in a heat exchanger. When it ultimately enters a throttle valve, an enthalpic Joule-Thomson expansion creates liquid [9]. After being liquefied, hydrogen can be kept in enormous insulated tanks at the liquefaction unit [125]. In contrast to compressed H_2 (10-15% of H_2 energy), H_2 liquefaction at -253 °C is energy-intensive (40% of H_2 energy) [116].

Liquid hydrogen allows for significant hydrogen storage densities at atmospheric pressure. For instance, liquid hydrogen has a density of 70.9 g/L at 1 atm compared to compressed gas's density of 42 g/L [9]. Because liquid hydrogen has a larger energy density per unit volume than compressed hydrogen, it may be stored in large quantities in a little amount of space [116].

The biggest problem with liquid hydrogen storage is the energy requirement for cooling, which takes a lot of time and energy. Compared to the 10% energy loss experienced by compressed hydrogen, the energy content loss is projected to be 40% [44]. In addition, there are issues with hydrogen leakage and boil-off, which is when hydrogen evaporates from a liquid as a result of heat transmission [9]. Insulating the container can reduce boil-off without affecting the volumetric or gravimetric energy densities [116]. For storage quantities of 50 m^3, 100 m^3, and 20,000 m^3, respectively, the daily boil-off losses of discharging H_2 into the air are commonly evaluated at 0.4%, 0.2%, and 0.06% [30]. Due to this, liquid hydrogen is challenging to store for an extended period and is not appropriate for seasonal storage [119]. Therefore, short-term storage and delivery methods like truck delivery and international hydrogen shipment are more adequate for this storage approach [120].

Liquid hydrogen is transported and stored in cryogenic tanks for use in industrial and medicinal applications. To sustain the low temperature necessary for preserving hydrogen as a liquid, these tanks must be properly insulated [116]. It is possible to attain insulation by employing an internal pressure vessel and an outer protective jacket to shield the tank from accidents. To reduce thermal conductivity, the gap between the two layers can be coated with perlite or enveloped in strips of aluminum film [117, 119, 120]. In the case of a spill or tanker rupture, hydrogen at cryogenic temperatures has low adiabatic expansion energy, making it even harder to result in a catastrophic explosion [120]. Cryogenic hydrogen is generally employed for the transportation of gas using tanker trucks with a capacity of 60,000 liters or more [117]. Currently, research is concentrated on creating composite materials that are both lighter and tougher for cryogenic tanks [123].

Even though the system is gravimetrically and volumetrically practical, more study is required to address issues with hydrogen intake and discharge, high hydrogen liquefaction speed that results in significant energy loss, hydrogen boil-off, and vessel price [123].

5.3 Cryo-compressed Hydrogen

A novel technique called "cryo-compressed hydrogen storage" provides the pressurized storage of hydrogen at cryogenic temperatures [9]. The advantages of both compressed gaseous hydrogen storage and cryogenic liquid hydrogen storage are combined in this approach, resulting in lower boil-off loss and increased energy density [44]. Aceves et al. first presented this method, and it has demonstrated promising results in terms of storage and security [120].

The cryo-compressed technique entails a two-step cooling and compressing procedure. The energy density and storage capacity are improved by cooling the pressurized hydrogen gas. The system is typically cooled with nitrogen until it reaches its boiling point at -196 °C, which causes the volumetric density to jump three times over uncooled hydrogen. High volumetric and gravimetric storages are also made possible by this due to the higher physical density. In cryo-compressed storage, interior and exterior heat exchangers can regulate the storage pressure and temperature. Since the vessel and insulation are cooled down during the release of stored hydrogen, no extra cooling is required [9].

Vessels used for cryo-compressed hydrogen should be able to store hydrogen at cryogenic temperatures (-253 °C) and high pressures (at least 30 MPa) [44]. This technique increases the autonomy of the storage system by extending the duration before hydrogen must be boiled off [119]. The BMW Group has been investigating the application of cryo-compressed hydrogen storage for hydrogen cars with high energy and long-distance needs and has discovered that this process allows for high storage density (80 g/l) [119]. Cryo-compressed vessels are type III which is highly flexible in refueling since they can be loaded with either compressed gaseous hydrogen or liquefied hydrogen. Additionally, these tanks have insulation to reduce heat transfer from either the hydrogen or the outside surroundings [119].

Thanks to its double-layer construction and external vacuum container that guards against chemical and mechanical interference, cryo-compressed hydrogen storage provides high storage density (80 g/L), rapid and effective refilling, and a strong level of safety [9, 120].

In comparison to liquid hydrogen storage, which can survive for about seven times longer, cryo-compressed hydrogen vessels have a far shorter dormancy duration (maximum duration without losses if unused) of seven days, which is extremely short [9]. Furthermore, due to hydrogen's low volume density and the high price of pressure vessels resulting from the usage of composite materials like carbon fiber, the final cost of hydrogen increases and the tank size is relatively big. Using these vessels in heavily populated places raises additional questions regarding their safety. Due to these drawbacks, cryo-compressed hydrogen storage may not be the best option for the time being even though it is still essential to take into account when conducting research and development [44].

5.4 Hydrides

A hydride is defined as "any of a class of chemical compounds in which hydrogen is joined with another element" by Encyclopedia Britannica [126]. Ammonia (NH_3) and liquid organic hydrogen carriers (LOHC) are among the most often utilized compounds that store hydrogen chemically [123].

5.4.1 Ammonia

Ammonia (NH_3) is a nitrogen-hydrogen compound. It is a chemical that is frequently manufactured and has a sophisticated manufacturing, distribution, and transportation infrastructure. At ambient temperature, it is in a gaseous state, but it can turn into a liquid at -33 °C, which is not particularly difficult to achieve [123, 104].

Ammonia has many advantages over hydrogen in its original form. It can be stored in its liquid state at ambient pressure in cryogenic vessels at a temperature of approximately -33°C. Also, it has 1.7 times higher hydrogen density per m^3 than liquefied hydrogen, a developed global distribution infrastructure, and is significantly less expensive to transport than hydrogen. Additionally, it can be combined with water, kept at ambient temperature, and transformed into hydrogen without generating any negative waste. Ammonia may be combined with conventional fuels and burned effectively while emitting no CO_2 [115, 123, 104].

Around 7% to 18% of the energy in hydrogen is needed to transform hydrogen into ammonia, which is a substantial quantity. If ammonia is turned into pure hydrogen, an equal amount of energy is wasted. Because of its toxicity, ammonia should only be used in certain industries, and there is a chance that it could escape and cause acidification and air pollution [115, 104].

5.4.2 Liquid Organic Hydrogen Carriers

Organic substances known as liquid organic hydrogen carriers (LOHCs) can store significant quantities of hydrogen in a liquid state under ambient circumstances [9]. Utilizing LOHCs entails charging a "carrier" molecule with hydrogen, delivering it, and then recovering pure hydrogen by catalytic dehydrogenation at the endpoint [120, 104]. They typically have a gravimetric storage density of 6 wt% on average [123].

LOHCs are generally aromatic compounds that are dehydrogenated at hot temperatures of 300–350 C in the vicinity of platinum catalysts [9]. Benzene and cyclohexane, toluene and methylcyclohexane, naphthalene and decalin, N-ethyl carbazole and perhydro-N-ethyl carbazole, and dibenzyl toluene and perhydro dibenzyl toluene are some examples of the several types of liquid organic hydrogen carriers (LOHCs) that have been explored [9]. The relatively high content of hydrogen in these molecules is well recognized, as is their capacity to store hydrogen by chemical bonds with hydrogen-lean molecules, which can then be discharged via catalytic dehydrogenation [9]. Toluene and methylcyclohexane are both inexpensive choices for LOHC, but toluene is poisonous, whereas dibenzyltoluene is more costly but non-toxic [104].

Liquid organic hydrogen carriers (LOHCs) have several advantages, including the capacity to store hydrogen for extended periods without self-discharge, which makes them suitable for seasonal energy storage and delivering hydrogen to remote regions

[9]. These storage devices don’t emit carbon dioxide and are simple to operate in normal settings. Additionally, they are non-toxic and non-corrosive, and they do not require cooling to be transported conveniently as liquids [120, 104].

LOHCs have several disadvantages, such as the necessity for high temperatures and pressures during the hydrogenation and dehydrogenation operations, which are expensive and necessitate the use of various catalysts [9]. The energy-intensive conversion and reconversion procedures used by LOHCs use 35–40% of the energy of the hydrogen itself and have a low hydrogen storage capacity [120, 104].

6 Hydrogen Transportation

The development of a transportation infrastructure that is both effective and affordable will be crucial to the future success of the hydrogen sector. The distance, amount, and storage technique all affect how cost-effectively hydrogen is transported and distributed and the cost, energy consumption, and losses of hydrogen are significantly influenced by the manner of distribution [116, 120].

It is crucial to consider how hydrogen is being carried and stored. Hydrogen has a poor energy density, making long-distance transportation costly. Compression, liquefaction, or employing a hydrogen carrier like ammonia or LOHC are some solutions to this problem [115, 116].

Hydrogen can be delivered in gaseous, liquid, or hydride form using a variety of techniques such as shipping, vehicles, or pipelines. The location, distance, and desired usage of the hydrogen will all affect which method of delivery and storage is the most economical. For large distances, ships and pipelines are more economical options, while for shorter distances, trucks are an excellent option for moving liquid hydrogen or ammonia. The best option will depend on the particular circumstances, as each method has benefits and drawbacks of its own [115, 116].
Utilizing hydrogen as an energy carrier can be difficult due to embrittlement and safety issues, which also increase prices and potential dangers during the delivery process. Other challenges with hydrogen transportation include lowering prices, increasing effectiveness, maintaining purity, and limiting losses. The distribution of hydrogen requires major development because losses might reach 20% during transport, compared to 5-7% for methane and electricity [115, 30].

6.1 Pipeline Transportation

Pipelines are typically used to carry hydrogen, which is then widely distributed and used [9]. This approach is economical and efficient throughout lengths up to 2,000 kilometers. While Europe has over 5,000 km of hydrogen pipelines, with the longest ones in Belgium and Germany at 600 km and 400 km, respectively, the United States has about 2,500 km of hydrogen pipelines today. In contrast, there are 3 million kilometers of natural gas pipelines installed globally [115]. Hydrogen transportation through pipelines necessitates longer pipes and higher compression power but since hydrogen has smaller pressure losses than natural gas, recompression units can be placed further apart [24].

Transporting hydrogen through a pipeline has several benefits. With a lifetime of 40 to 80 years [104], it is the most economical and environmentally beneficial solution for large-scale distribution. Since most pipelines are buried below, there is less chance of mishaps or leakage, making pipeline transit safer and more dependable than other routes. Although the initial capital cost of constructing pipelines may be significant, maintenance and operating expenses are minimal. Furthermore, pipelines have a negligible adverse environmental impact and do not affect traffic on the roadways [9].

The construction of a hydrogen pipeline network is fraught with difficulties. Given its low density, hydrogen is more susceptible to losses than other fuels and demands significant pressure (about 1–2 MPa) to increase delivery speed. Also, Polymer materials, that are extensively used in gas pipes, are not suited for pressured hydrogen because of their large porosity. Aside from having a smaller size and a higher diffusion coefficient than natural gas, hydrogen is more likely to leak. To ensure safety, the parts of a hydrogen pipeline infrastructure must be built to stop leaks from valves, seals, and gaskets. Moreover, hydrogen can weaken pipeline materials, causing cracking and a loss of mechanical strength that might result in pipeline failure. All of these problems may affect how hydrogen is delivered and distributed. The high capital expenditures are an additional restriction on the delivery of hydrogen through pipelines [9, 104].

Most offshore pipes are capable of carrying pure hydrogen, and roughly 70% of inland pipelines in Europe might also be utilized, based on a project titled Re-Stream by DNV and Carbon Limits (2021) [127], with the other 30% possibly reusable with additional testing or revised standards [115]. Current high natural gas distribution pipelines may be adapted for the transportation of hydrogen, but this will need to be determined case-by-case and will rely on the quality of the hydrogen and the type of steel utilized [130]. Although hydrogen would demand triple as much volume to provide the same quantity of energy as natural gas, research findings in the Netherlands have indicated that the current natural gas system could be altered to distribute hydrogen [128, 129]. However, depending on the advancement of hydrogen use, supplemental transportation and storage capacity may be required. Hydrogen may need handling at a lower pressure or with the inclusion of an additional internal coating to be transported through a natural gas pipeline [115, 104].

It is also feasible to carry hydrogen through a pipeline using ammonia, which is less expensive but needs reconversion to hydrogen after use. In general, it is more economical to transfer hydrogen as a gas in pipes for lengths under 1,500 km, however over longer distances, it is cheaper to transport hydrogen as ammonia or through a LOHC by ship [115]. The United States now has 4,830 kilometers of ammonia pipelines. LOHCs can use conventional oil pipelines, but the need to send the LOHC back to its source for re-loading with hydrogen makes it difficult and costly, necessitating either truck transportation or a parallel pipeline that runs in the reverse directions [24].

One option that brings pure hydrogen to the market is blending it with natural gas and distributing it over a web of natural gas pipelines. Combining hydrogen with natural gas should reduce costs and reveal useful information for gradually switching the gas system to solely carry hydrogen [21].

Several extraction and purification processes have been employed to separate hydrogen from natural gas like pressure swing adsorption (PSA), membrane separation, and electrochemical hydrogen separation [9].

Based on the properties of the natural gas and the layout of the appliances, different amounts of hydrogen can be safely mixed into transmission lines. Blends lesser than 5-15% hydrogen typically only cause minor concerns, but blends containing 15% to 50% hydrogen usually necessitate more extensive adjustments to the equipment and pipeline [9]. It is still challenging to carry hydrogen blends through borders since different countries have different thresholds for blending hydrogen with natural gas. However, attempts are being made to regulate and unify those thresholds. Up to 20% hydrogen can technically be blended, according to studies, but the implications on pipes, in the long run, are unknown [115]. The maximum safe quantity of hydrogen that can be mixed has been set in several countries, including the Netherlands at 12%, the UK at 2 to 3%, and 5% in Germany with room to grow up to 20%. A 10% mixture is already being used in the US state of Hawaii [21].

The necessity for injection stations and a rise in running costs make integrating hydrogen into the natural gas network more expensive [115]. Additionally, a blend will diminish the energy content of the given gas because hydrogen has a lower energy density than natural gas. For instance, a natural gas pipeline with 3% hydrogen would convey around 2% less energy overall [24]. This energy loss can be very small compared to the impact of the blending and using 3% less natural gas in the system at such a scale.

6.2 Shipping Transportation

The accessibility of fossil fuels and renewable energy for the generation of hydrogen is constrained in some countries, such as Japan. Consequently, importing hydrogen by shipping is a viable alternative that can expand a country's energy imports, sparking a rise in interest in employing shipping for hydrogen delivery [116, 104].

There are various ways to transfer hydrogen in ships. Compressed hydrogen might be practical over shorter distances, but liquified hydrogen, ammonia, and LOHC seem to be the top choices for longer distances and bigger amounts [115].
A liquid hydrogen tanker vessel with a storage capacity of roughly 9,000 cubic meters and safety elements to reduce boil-off and maintain strict safety have been developed by Moss Maritime and Equinor. This is an important development for the transportation of liquid hydrogen in the ocean. Energy corporations are anticipated to become more involved in the creation, testing, and feasibility studies of specialist ships with suitable vessels for hydrogen transportation as the demand for hydrogen expands. Similar to LNG, hydrogen would need to be liquefied before sailing. The hydrogen that would boil off in the route (0.2% each day) would be used to fuel these ships. However, these ships would have to return empty except if a high-value liquid could be delivered on the return trip of the same ship [116, 104].

Ammonia uses chemical and semi-refrigerated liquefied petroleum gas (LPG) tankers, and it is the most advanced among hydrogen carriers of international shipping transportation. Today's shipping routes include transportation from Trinidad and Tobago and the Arab Gulf to Europe and North America. The expense of conversion and subsequent reconversion back to hydrogen prior usage would also have to be taken into account. LOHCs would be the most practical form to carry hydrogen by ship since oil product tankers could be employed. The supply lines would become more complicated due to the requirement for ships to travel back with the initial carrier [104].

Delivering hydrogen by shipping is cheaper than pipelines when the travel distance is longer than 1500 km. Shipping hydrogen in the form of ammonia or LOHC is the cheapest way. However, extracting hydrogen from those carriers makes the final cost higher, and the fact that carrier ships return to their original place empty, makes the whole process more complicated [116, 104].

6.3 Trucks Transportation

Trucks can carry hydrogen in a variety of forms, such as gas, liquid, or through a carrier like ammonia or LOHC. Normally, it is moved on trucks in tubes. Although this approach is well-known, it might not necessarily be the most economical choice for extended distances [115, 104].

Trucks hauling compressed hydrogen are primarily utilized for short trips of under 300 km. Gas is delivered in tanks composed of carbon and glass fibers. Due to regulatory restrictions on the pressure, size, and weight of the containers, it is uncommon to fill these tanks to their fullest limit of 1,100 kg of hydrogen at a pressure of 50 MPa. The maximum weight of hydrogen that can be transported on a truck in the US is 280 kg due to the pressure restriction for steel tubes which is significantly lower than the full capacity of the tanks. Nonetheless, the US Department of Transportation lately permitted the use of composite storage tanks with a higher pressure for transporting hydrogen [115, 104].

A truck can move about 5,000 kg of hydrogen when it is turned into ammonia or 1,700 kg of LOHC, but it will require a separate truck to deliver the carrier molecules back to the starting point after the hydrogen has been extracted [115, 104].

Trucks can carry liquid hydrogen, however, this is only feasible for trips shorter than 4,000 km. The Joule-Thompson effect, which was stated previously in the thesis, could cause the hydrogen to heat up and increase its pressure if the traveling distance is more than 4,000 km. The low temperature required to retain the hydrogen in liquid form is maintained by the insulation of these tankers, which are also referred to as cryogenic tanker trucks. They are frequently employed where there is a steady need for hydrogen and the decreased transport costs can cover the cost of liquefaction

[115, 104].

As discussed in the previous parts of the thesis, hydrogen storage and transportation applications are very well-connected and integrated together. A summary of storage and transportation methods is shown in figure 5 (Rail transport was not discussed in the thesis).

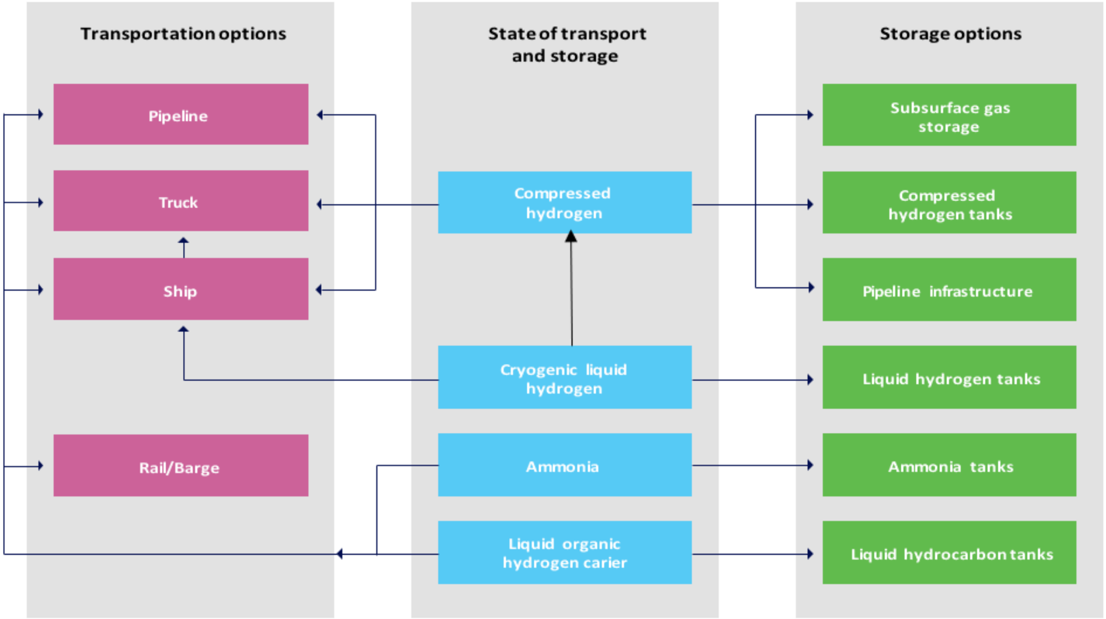


Figure 8: Overview of storage and transportation methods[115]

7 Summary

The present and future state of hydrogen production, storage, and distribution have been thoroughly investigated in this thesis. Hydrogen technologies in general are already being used in implemented in many different applications and sectors. The potential is only increasing, and the future of hydrogen technologies looks very promising as more research and development is conducted in the field of using hydrogen as an energy carrier and the importance of its role to reach carbon neutrality. Great effort is being done in studying hydrogen's unique properties and the effect they can have on the energy system in general. Safety measures are strictly considered, and it is one of the reasons why there is extensive research and development of materials used to produce, store and transport hydrogen.

Several hydrogen production technologies have been analyzed throughout this thesis. Hydrocarbon reforming seems to be the most common method to produce hydrogen nowadays, especially the SMR method since it is the most commercially mature process, followed by partial oxidation and auto-thermal reforming that combines both previous processes. Hydrocarbon reforming results in releasing a significant amount of carbon dioxide, even with CCS usage. Thus, it is not a sustainable way of producing hydrogen.
To find alternatives to conventional polluting methods, hydrogen production from biomass and water-splitting have been studied.
Thermochemical biomass technologies still release some amount of carbon dioxide and it doesn't solve this problem. Biological biomass is environmentally cleaner than thermochemical methods, with dark fermentation leading biomass technologies. However, the low hydrogen yield that comes from biomass is a serious issue, making it unreliable as the main source and maybe only fit for very small-scale production.
Water-splitting has the highest potential to lead hydrogen production technologies since it is a completely carbon-free process. Electrolysis is the most mature process and it is expected to be the main source of hydrogen production in just a few decades. Alkaline and PEM electrolyzers are commercially mature methods already and more research is being carried out to make them more economically and technologically competitive. Advanced Alkaline electrolyzers and PEM are also suitable to work with fluctuating renewable energy sources, making them the most promising hydrogen production methods.

Different means of hydrogen storage have also been analyzed, such as hydrogen gas compression, liquefying hydrogen, and carrying hydrogen in the form of a hydride (like ammonia and LOHC).
Liquefied cryogenic hydrogen efficiency is a major challenge that needs to be significantly improved to make it more widely used. However, it is still suitable for shipping in distances less than 1500 km.
The most promising and commercially ready ways of storage are compressed gas hydrogen and ammonia storage. Compressed gas hydrogen losses are around four times less than liquefied hydrogen and it can be used in pipelines, trucks, and un-

derground storage which gives it a clear advantage over other storage technologies. Ammonia is also very promising because it is widely produced and perfect for shipping applications, especially for long distances.

Hydrogen distribution is mainly conducted through road, shipping, and pipeline transport. Road truck transport of hydrogen is cheap and convenient for local and small distances distribution, while shipping is suitable for long-distance distribution of hydrogen especially if there is no pipeline network connecting the starting point with the destination. Using pipeline networks for distributing hydrogen is suitable for all forms of hydrogen except the cryogenic liquefied. It is also suitable for both long and short distances. However, the current natural gas pipeline network needs some modifications to be able to carry and transport hydrogen due to its unique properties.

In the meantime, there are barriers preventing hydrogen from being used in large-scale as an energy carrier. These barriers can be technological, economic, political, or social.
Although some green hydrogen technologies are already mature enough to be widely used, they are still not competitive enough with the conventional methods, some challenges related to efficiency and cost need to be addressed before the technology can be widely used. In addition, the existing infrastructure is more suitable for the traditional fossil-based energy system, and retrofitting the existing infrastructure or building a new one is very expensive and might be discouraging for big companies and governments. Strict policies and realistic strategic planning are essential to shift to a more sustainable energy system and hydrogen as an energy carrier represents a big part of it. Moreover, public acceptance is essential for large-scale usage of hydrogen.

Hydrogen technologies can have a huge role in a complete transition to renewable energy and carbon neutrality. More hydrogen production is essential for having a bigger renewable energy capacity since it offers seasonal storage required to give the system more flexibility. It is also a solution to the renewable fluctuation and variability problem, offering more reliability to the energy system and making a carbon-neutral energy system possible to achieve.

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