Hydrogen production: The future pillar of energy sector

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ABSTRACT

This chapter comprehensively explores Hydrogen Production Technologies, recognizing them as a set of key techniques that play a crucial role in the generation of the fundamental energy vector for the future of the energy sector. The growing importance of these technologies is evident, especially in the face of the imperative need to meet the climate goals set out in the Paris Agreement. In this context, the study presents a detailed classification of Hydrogen Production Methods, taking into account three fundamental parameters: the Primary Energy Source used, the Physical/Chemical Process employed and the Substrate consumed in the process. This approach revealed the existence of eleven distinct production methods, all of which were grouped and identified through a "Hydrogen Rainbow". In each of the colors of this rainbow, we explore the main aspects of relevance, deepening knowledge in this area.

Keywords: Hydrogen Production, Hydrogen Rainbow, Green Hydrogen.

INTRODUCTION

Since the Second Industrial Revolution, dating from the second half of the nineteenth century and characterized by the technological advents of Steam Engines and Internal Combustion Engines (ICMs), both consumers of fossil fuels for the execution of tasks that enabled the evolution of society, the significant increase in Greenhouse Gas (GHG) emissions into the atmosphere has been notorious.

In this context, GHGs are gases such as carbon dioxide (CO2), methane (CH4) and nitrous oxide (N2O), which absorb infrared radiation emitted by the Earth's surface and radiate it, keeping the atmosphere warm. It is worth mentioning that the Greenhouse Effect is a natural phenomenon and essential for the development and maintenance of life on planet Earth.

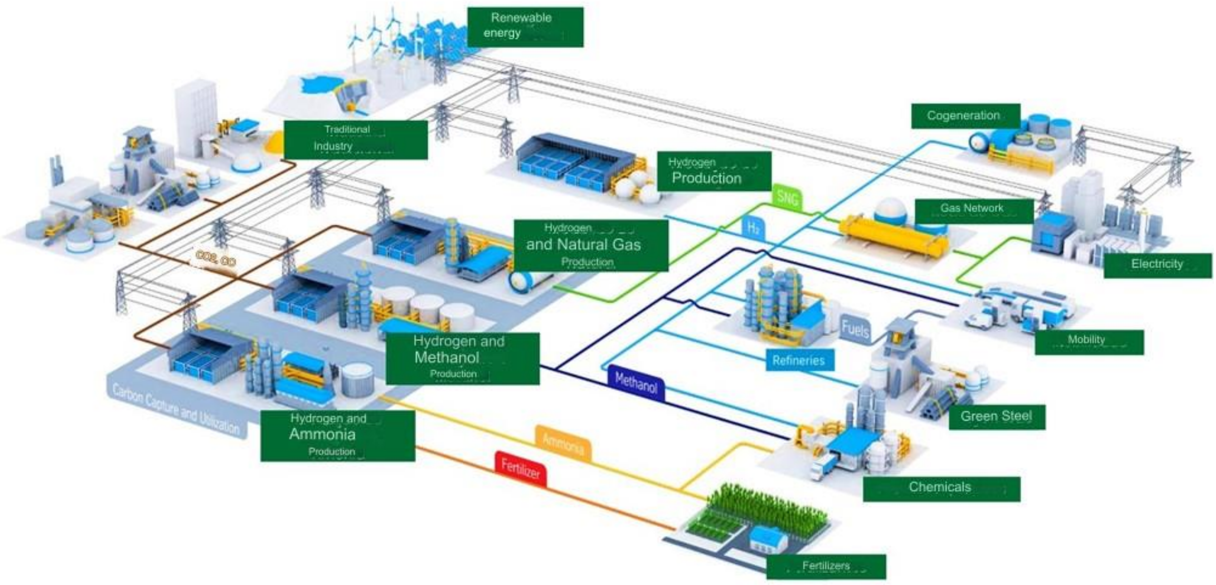
However, the use of fossil fuels, as well as other anthropological factors, such as deforestation and cattle ranching, have increased the atmospheric concentration of GHGs. In the pre-industrial era, CO2 had an average concentration of 280 parts per million (ppm) (ARTAXO, 2014), rising to 410 ppm according to the Sixth Report of the Intergovernmental *Panel on Climate Change (IPCC*) (GULEV et al., 2021), which also mentions average concentrations of 1866 parts per billion (ppb) of CH4 and 332 ppb of N2O. indicators that confirm, unequivocally, the influence of human activities on the planet's climatic conditions.

Since the 1970s, several climate conferences of global importance have been held periodically, with emphasis on the Paris Agreement in 2015, which established an approach to climate action, based on clear targets for reducing GHG emissions profiles for each country, with the aim of halting global warming at a maximum limit of 2 °C above pre-industrial levels. in addition to committing efforts to limit it to 1.5°C, considering that this would have a significant effect on reducing the risks and impacts of climate change.

Thus, Hydrogen emerges as an alternative to fossil fuels, since, in its molecular form (H2), it is a colorless and odorless gas, with a density of 0.08987 kg.m−3 at 0 °C and 1 bar, and an upper (PCS) and lower calorific value (PCI) of 141,880.0 kj.kg−1 and 119,960 kj.kg−1.

The low density combined with the high energy content give Hydrogen a wide range of applications still little explored in the global economy, such as: Agriculture, with the production of fertilizers from Ammonia; Chemical Industry, with direct use, such as processes with hydrogenation and combined with the production of methanol for application in fuels and steel; Urban Mobility, with direct supply in Fuel Cell Electric Vehicles (FCEVs) and with the production of synthetic fuels, such as Aviation Kerosene (QAV); Reelectrification, with the use of gas turbines and fuel cells. The list of applications of Hydrogen is illustrated in Figure 1.

Figure 1 – Hydrogen Value Chain and its Applications in the Economy



Source: Adapted from Thyssenkrupp (2023).

In view of this, it can be said that Hydrogen has uses similar to oil and its derivatives, and can therefore act as an energy vector in the context of a decarbonized global economy, especially with the drop in the Levelized *Cost of Energy* (LCOE) of Renewable Energy sources, which can compete, in terms of cost, with fossil fuels. but they still need more efficient forms of storage and distribution, finding in Hydrogen a promising solution for consolidation as the main energy alternative.

However, despite being very abundant, since it makes up 75% by mass and 90% in number of moles of the universe, most of the Hydrogen is only found in other compounds, such as water (H2O). Therefore, Hydrogen is not considered an energy source. Therefore, in order to enable the use of Hydrogen by society, it is necessary to understand the set of techniques, devices and knowledge that enable its use as a vector of the Global Energy Transition, comprising the entire technological chain, that is, Production, Storage, Distribution and End Use. Thus, in this chapter, the various methods of Hydrogen production will be addressed in the subsequent sections, highlighting the technology involved in each method, its levels of application and Greenhouse Gas emissions.

HYDROGEN PRODUCTION CHAIN

Currently, there is a great diversity of ways to produce hydrogen gas, due to the diversity of compounds that contain hydrogen atoms, as well as the various primary energy sources that can be used to extract these atoms and synthesize H2. This wide variety of technological routes in the production chain will be explored in this section, in which the main Hydrogen Production Methods will be discussed. In an initial analysis, it is important to emphasize that a "Hydrogen Production Method" is made up of five main aspects, namely:

a) **Primary energy source consumed**: It may or may not be renewable in nature, in addition to different profiles of CO2 emissions and other GHGs;

b) **Chemical/Physical Process employed**: It can range from traditional methods, such as Steam Reforming, to highly innovative approaches, such as Bioelectrohydrogenesis;

c) **Substrate:** It can range from long-chain compounds, such as oils or hydrocarbons, to diatomic compounds such as water (H2O), in which the main function is to provide protons for the formation of H2;

d) **Emissions**: It can vary in high, low, zero and even negative levels, that is, when a production method acts as a carbon sink;

e) **Co-products**: It can include common substances, such as oxygen gas, as well as complex and even dangerous compounds, such as nuclear waste.

Thus, in order to facilitate the understanding of the different Hydrogen Production Methods, the scientific community has developed a nomenclature associating each method with a color, resulting in the popularly known "Hydrogen Rainbow". It is important to note that, due to the level of innovation of many of the techniques used in hydrogen production, there is still no universal consensus on the colors associated with each method, varying according to the author and/or locality.

In this context, Table 1 presents eleven distinct methods of the "Hydrogen Rainbow", each associated with a color and detailed as to the five main aspects involved. This information was compiled from data from the Energy Research Company (EPE) and recent scientific articles, in addition to the CO2 emission profile associated with each method.

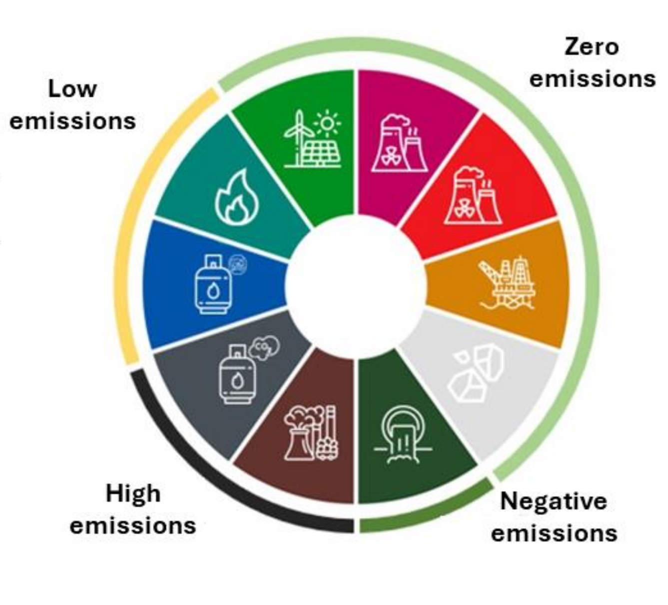
Table 1 – Hydrogen Production Methods: Main Aspects

Cor	Energia Primária	Processo	Substrato	Emissões	Coprodutos
	Térmica (Com emissões)	Gaseificação	Carvão Mineral	Alto	CO, Alcatrão, Amônia e etc
	Gás Natural sem CCUS	Reforma a Vapor	Gás Natural	Alto	CO, CO_2
	Gás Natural com CCUS	Reforma a Vapor	Gás Natural	Baixo	CO, CO_2
	Térmica (Sem emissões)	Pirólise	Gás Natural	Baixo	Negro de fumo
	Energias Renováveis	Eletrólise	Água Ultrapura	Nulo	Gás Oxigênio
	Energia Nuclear - Elétrica	Eletrólise	Água Ultrapura	Nulo	Gás Oxigênio
	Energia Nuclear - Térmica	Separação Catalítica	Água ou Metano	Nulo	Rejeitos nucleares
	Não há (Espontâneo)	Mecanismo Biológico	Hidrocarbonetos	Nulo	Não há
	Não há (Natural)	Craqueamento Hidráulico	Água Pressurizada	Nulo	Não há
	Energia da Biomassa	Mecanismo Biológico	Matéria Orgânica	Negativo	CO_2 e Biofilme

Source: Prepared by the author.

There are several technical, economic, social and environmental criteria that must be evaluated in each Hydrogen Production Method, such as Acquisition Costs (CAPEX), Operation and Maintenance (O&M) costs, among others. This variety of points of analysis enhances Hydrogen Technologies beyond purely technical-scientific factors, elevating the discussion to the real application. In this context, Figure 2 divides the Hydrogen Rainbow in relation to the Emissions Profile, in which it is possible to observe the predominance of scientific development in production methods with a zero/negative net emissions profile, such as Green Hydrogen and Moss Hydrogen.

Figure 2 – Hydrogen Rainbow: Emission Profiles



Source: Prepared by the author.

GASIFICATION

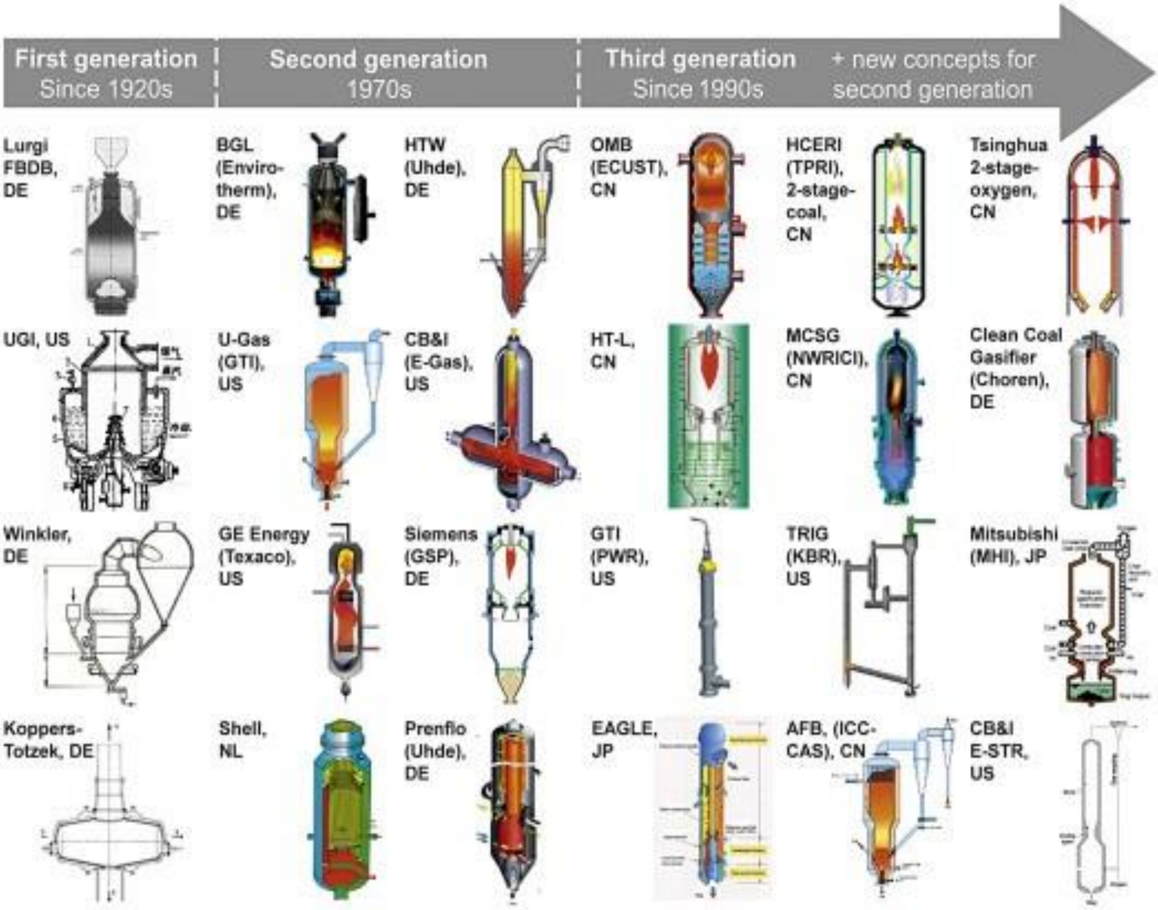
Analyzing Table 1, it is first observed the Brown Hydrogen, which is obtained from Gasification, that is, a thermochemical process created in the nineteenth century, which involves the thermal decomposition of coal in an environment with absent or controlled oxygen, using Thermal Energy from sources with a high level of CO2 emissions for the formation of the syngas. In this context, gasification reactors are a consolidated technology, subdivided into several types, as illustrated in Figure 3.

The term syngas refers to the mixture between Carbon Monoxide (CO), Carbon Dioxide (CO2) and Hydrogen (H2), that is, Hydrogen was produced with high direct emissions from the substrate gasification process (mineral coal) and indirect emissions in the generation of energy used in the process. It is worth mentioning that, for some authors and organizations, there is a subdivision between Brown Hydrogen and Black Hydrogen, in which coal and anthracite are used as substrates, respectively.

In summary, Brown Hydrogen is an extremely polluting option, with an estimated emission profile between 18 and 20 kgCO2eq (Kilogram of CO2 equivalent) per kilogram of Hydrogen produced, but, due to the low associated costs and technological maturity, 20% of all Hydrogen produced on the planet in 2020 used this method.

(International Renewable Energy Agency, 2022)

Figure 3 – Gasification Reactors: Evolution of Technology



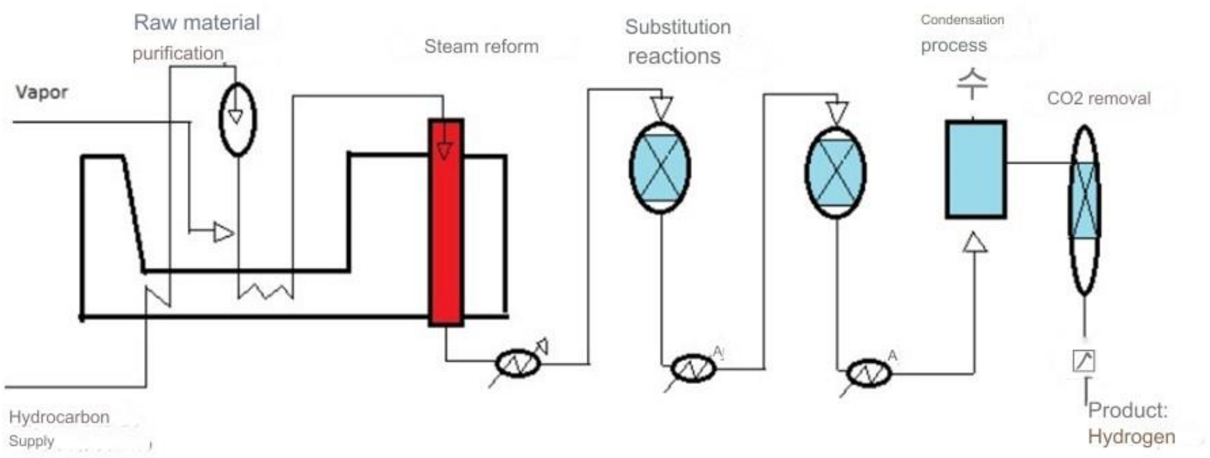
Source: Adapted from Wolfersdorf and Meyer (2017).

STEAM REFURBISHMENT

According to Table 1, both Grey Hydrogen and Blue Hydrogen are obtained through Natural Gas Steam Reforming, a technique used to convert hydrocarbons into syngas. This technique involves heating hydrocarbons, such as natural gas, in an environment with superheated water vapor, which causes the hydrocarbon bonds to break into smaller compounds, including hydrogen gas. It is important to highlight that Steam Reforming is a catalytic process that uses Natural Gas not only as a substrate, but also as a primary energy source for heating the water and the reactor. In other words, during the process, Natural Gas is used both as a raw material for the production of syngas and as a source of energy to promote the necessary chemical reactions.

Thus, both Steam Reforming and Gasification are thermochemical processes that involve chemical reactions for the production of syngas. However, the conversion techniques are distinct: Steam Reforming uses hydrocarbons as a feedstock, while Gasification uses biomass, coal or waste as feedstock. Figure 4 illustrates the Steam Reforming process for the production of Hydrogen. In view of this, the proximity of the Gray and Blue Hydrogen Production Methods is notorious, employing the same chemical/physical process (Steam Reforming) and the same substrate (Natural Gas), but the difference between the two methodologies consists in the Primary Energy Source.

Figure 4 – Steam Reforming: Flow Diagram of the process applied to Hydrogen production



Source: Ribeiro (2011).

In the case of Grey Hydrogen, Natural Gas without Carbon Capture, Utilization and Storage (CCUS) is used, that is, the GHGs resulting from the process are released into the atmosphere, resulting in a high emissions profile for Grey Hydrogen, estimated between 9 and 11 kgCO2eq per kilogram of Hydrogen produced. (International Renewable Energy Agency, 2022)

In Blue Hydrogen, Natural Gas with CCUS is used, that is, the GHGs resulting from the process are captured, compressed and stored in underground geological locations, such as depleted oil or gas reservoirs, which makes it a cleaner option compared to Gray Hydrogen, however, a relevant emissions profile is still observed, estimated between 4 and 5 kgCO2eq per kilogram of hydrogen produced. (International Renewable Energy Agency, 2022). It is worth mentioning that, according to data from the International Energy Agency (IEA), in 2019 the world production of Grey Hydrogen was about 71 million tons (Mt), which represents about 76% of the total world production of hydrogen that year. (International Energy Agency, 2021)

In addition, it is important to highlight the existence of other chemical processes for the production of Hydrogen from Hydrocarbons, as well as Steam Reforming, namely: Partial Oxidation, Autothermal Reforming, and Dry Reforming, both are reactions with specific industrial characteristics and applications.

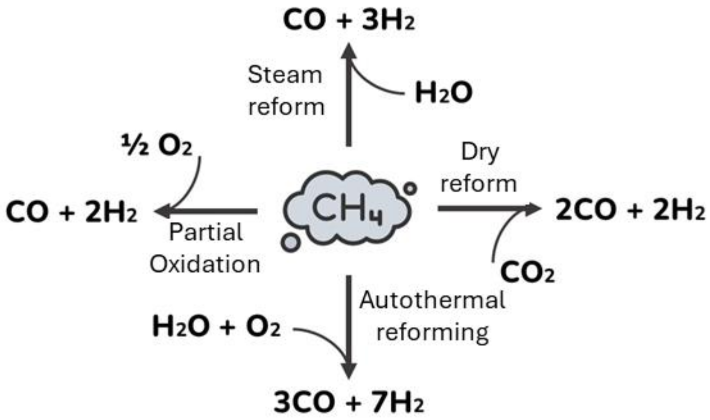
PARTIAL OXIDATION, AUTOTHERMAL REFORMING AND DRY REFORMING

In Partial Oxidation, hydrocarbon (Natural Gas) is mixed with oxygen in a controlled combustion environment rather than superheated water vapor. The reaction produces the syngas, containing a mixture of hydrogen and carbon monoxide (CO). Again, hydrogen can be purified and CO can be converted into CO2 through the *water-gas shift reaction*, which is most commonly used in petrochemical processes and ammonia production.

Autothermal Reforming, on the other hand, combines the Steam Reforming and Partial Oxidation reactions in a single reactor, using a mixture of water vapor and oxygen. This process is called "autothermal" because it does not require an external source of heat, since Partial Oxidation generates enough heat to promote steam reforming, combining the benefits of Steam Forming and Partial Oxidation, and ideal for applications that require high energy efficiency, such as in the synthesis of complex hydrocarbons.

There is also the Dry Reform, in which the hydrocarbon (Natural Gas) is mixed with CO2 at high temperatures, without the presence of water, producing the syngas mainly in situations with limited water availability or in remote and isolated locations. In this aspect, it is important to highlight that each hydrocarbon-to-hydrogen conversion reaction has advantages and disadvantages and the choice of technique used depends on specific characteristics in each application. Figure 5 summarizes the chemical equation of each reaction.

Figure 5 – Natural Gas Reforms: Main Chemical Equations



Source: Prepared by the author.

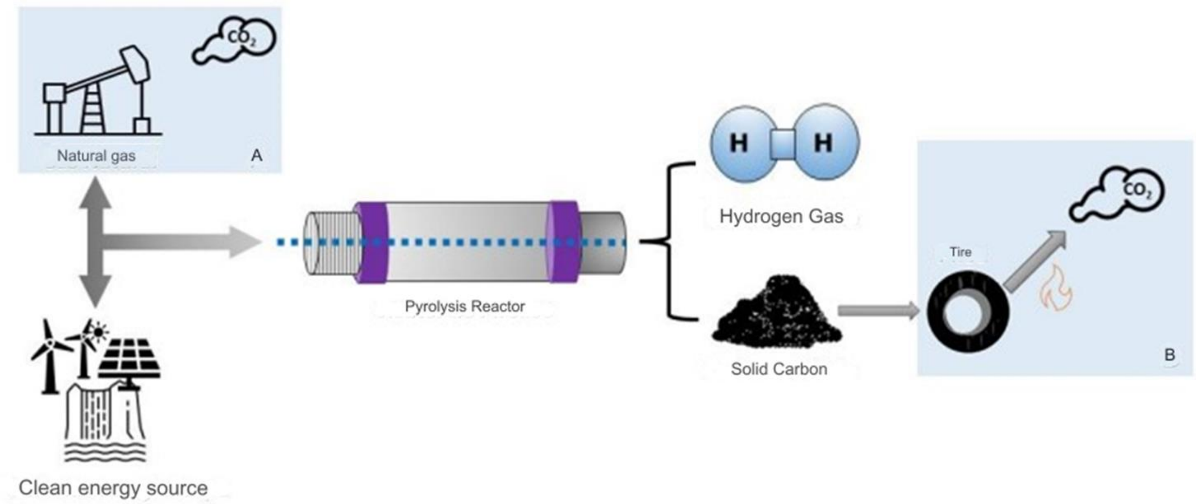
HYDROCARBON PYROLYSIS

In the above-mentioned chemical processes, i.e., Gasification and Hydrocarbon Reforming, the production of Hydrogen occurs together with the syngas. In view of this, in the context of the Energy Transition and, consequently, the search for alternative energy vectors to fossil fuels, Hydrogen can only be considered a viable option when it combines low production costs and low GHG emission profiles.

However, despite the low cost, the production of Hydrogen associated with syngas necessarily implies high emissions of CO2 and CO, which can be mitigated with CCUS, as is the case with Blue Hydrogen. Despite this possibility, CCUS techniques represent additional energy consumption, can have environmental impacts, and only partially eliminate greenhouse gas emissions. Therefore, the Hydrocarbon Pyrolysis process is a good alternative for the production of CO2-free Hydrogen, since the by-product of this technique is carbon (solid). In the rainbow illustrated in Table 1, Turquoise Hydrogen uses Pyrolysis applied to Natural Gas, which can also be obtained by biological processes (biomethane).

In this context, the thermal decomposition of methane, into carbon and hydrogen, occurs through pyrolysis at elevated temperatures (1,000 °C to 2,000 °C), resulting in a considerable energy deficit. To meet this consumption, in the case of Turquoise Hydrogen, it is essential to use an emission-free primary energy source. Analyzing the chemical equation of Turquoise Hydrogen, for each kilogram of methane, 250 grams of hydrogen and 750 grams of solid carbon, also known as carbon black, are produced, which has a high added value due to its industrial applications. Figure 6 illustrates the Turquoise Hydrogen Production Method.

Figure 6 – Turquoise Hydrogen: Process and Emissions in the Production Chain



Source: Energy Research Company (2022).

Finally, it should be noted that the Natural Gas Pyrolysis processes can be carried out in different ways, namely: Thermal Decomposition; Catalistic Decomposition and Plasma. The technological development of these techniques is of great relevance for the establishment of Turquoise Hydrogen as a technically, economically and environmentally viable route, since the development of Methane Pyrolysis reactors is recent and does not yet have extensive commercial application, with few tests on a pilot scale.

WATER ELECTROLYSIS

In the previous sections, the chemical/physical processes involved in the production of Brown, Gray, Blue and Turquoise Hydrogens were described, in which fossil fuels are used as substrates for the supply of hydrogen elements for the composition of the gas. In these processes, Natural Gas, consisting mainly of CH_4, is used as a substrate, that is, a chemical compound responsible for the donation of Hydrogen atoms to the composition of H2. In view of this, the chemical reactions involved in these techniques generally result in GHG emissions, thus not obtaining a significant environmental advantage from the use of Hydrogen compared to the direct use of fossil fuels as an energy vector.

In this context, it is important to remember that Hydrogen makes up 90% of the atoms in the Universe, making up the vast majority of chemical substances, far beyond the Hydrocarbons used in the previous sections, water (H2O) aggregates the largest share of Hydrogen on the planet. In addition, the breakdown of the water molecule for the generation of hydrogen gas does not release GHGs, thus having the main environmental contribution of Hydrogen as an energy vector. The process commonly related to the breakdown of the water molecule is Electrolysis.

Table 1 shows the Green and Pink Hydrogen effected by Electrolysis, both with a zero emission profile. The prominence of Green Hydrogen is notorious, especially after the Paris Agreement and the Russia-Ukraine conflict, which put European energy security at risk and boosted investments in Green Hydrogen in places with great potential for the production of Renewable Energy. However, there is little visibility for Pink Hydrogen, which also has a zero emissions profile, this is mainly due to the use of a primary source of nuclear energy, which, despite not emitting GHGs, has environmental problems related to the use of radioactive materials.

Electrolysis is a chemical process of oxidation reduction that occurs when an electric current is passed through a solution, where electrolytes are ionized. This physicochemical phenomenon is not spontaneous and requires energy to happen. During the electrolysis of water, the passage of electric current in the inert electrodes of the cathode and anode results in obtaining the gaseous compounds Hydrogen and Oxygen from the molecular compounds of the solution. The term "electrolysis" comes from the Greek "elektron," which means "electricity," and "lysis," which means "breakdown." (FELTRE, 2004)

Thus, the global reaction of the Water Electrolysis process can be described according to Equation 1.

$$2\mathrm{H2O}(l) + Energy \rightarrow 2\mathrm{H2}(g) + O2(g) \qquad (1)$$

The reduction and oxidation semi-reactions occurring at the cathode and anode, respectively, are determined by the electrolytes present in the aqueous solution and this can result in different types of Water Electrolysis, namely: Alkaline, Proton Exchange Membrane or Anions and Solid Oxide.

ALKALINE ELECTROLYSIS

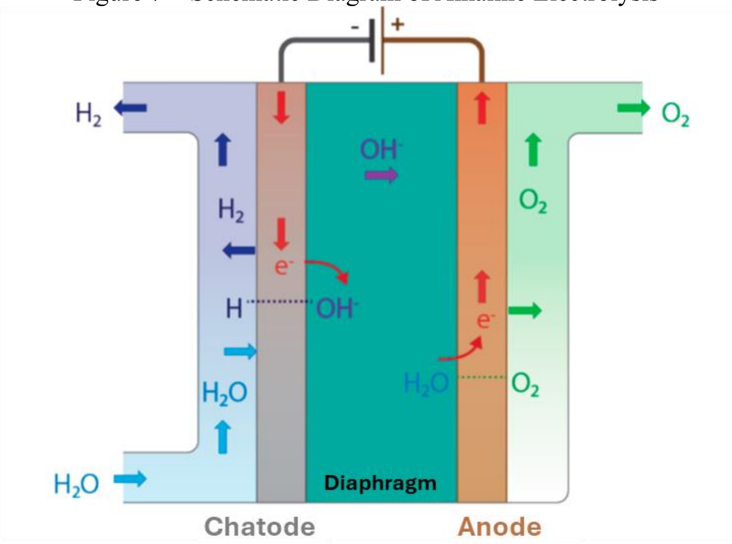
Since the discovery of the phenomenon of electrolysis by Troostwijk and Diemann in 1789, Alkaline Electrolysis technology has evolved significantly into large-scale hydrogen production, reaching *megawatt ranges*, and has become the most widespread commercial electrolytic technology worldwide. Alkaline electrolysis uses two electrodes, commonly metallic, immersed in a basic liquid solution of potassium hydroxide (KOH) with a concentration between 20 and 30%. A diaphragm separates the two electrodes and keeps the product gases separate to ensure efficiency and safety.

Thus, the anodic and cathodic semireactions are represented by Equations 2 and 3, and the process, which occurs in the range of 40 °C to 60 °C, is represented in Figure 7, also highlighting the materials involved in Alkaline Electrolysis.

$$2OH^{-}{}_{(aq)} \rightarrow H_2O_{(l)} + \frac{1}{2}O_{2(g)} + 2e^{-} \qquad (2)$$

$$2H_2O_{(l)} + 2e^{-} \rightarrow H_{2(g)} + 2OH^{-}{}_{(aq)} \qquad (3)$$

Figure 7 – Schematic Diagram of Alkaline Electrolysis



Source: Adapted from Gallandat, Romanowicz e Zuttel (2017).

Alkaline Electrolysis Cell *(AEC),* despite having reached a high level of development and applicability, still face some problems that make their large-scale application in the market unfeasible. Among these problems, the low partial charge range stands out, resulting from the cross-diffusion of the gases produced through the diaphragm, which reduces the efficiency of the electrolyzer by allowing the diffusion of oxygen at the cathode and hydrogen at the anode; the limitation of current density, due to high ohmic losses through the liquid electrolyte and diaphragm; and low operating pressure, which results from the inability to operate at high pressures with the liquid electrolyte.

PROTON EXCHANGE MEMBRANE ELECTROLYSIS

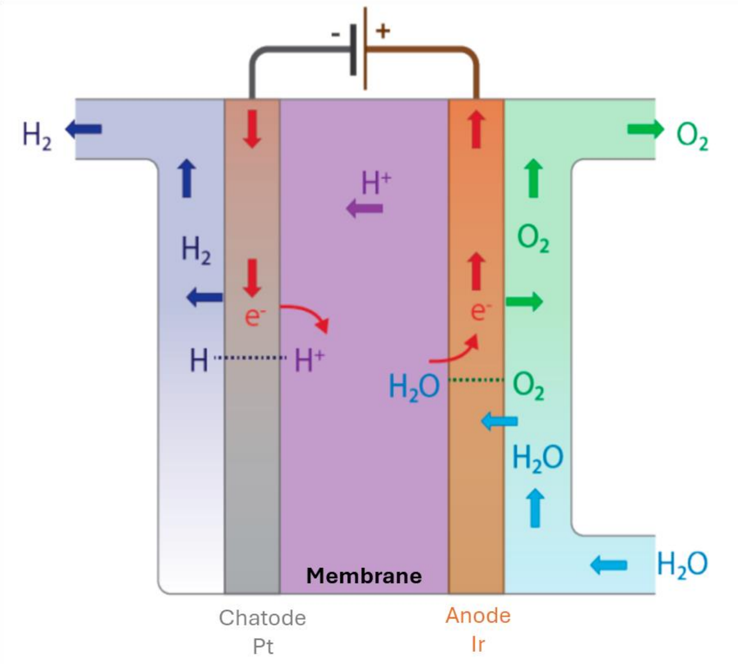
The scenario of overcoming the disadvantages of alkaline electrolyzers changed when General Electric, in the 1960s, developed the first water electrolyzer based on a solid polymer electrolyte concept. This concept introduced the proton exchange membrane or polymer electrolyte membrane (PEM), composed of a solid sulfonated polystyrene membrane that provides high proton conductivity, small gas cross-diffusion, compact system design, and high-pressure operation (CARMO et al., 2013).

Thus, the anodic and cathodic semireactions are represented by Equations 4 and 5, and the process, which occurs in the range of 20 °C to 100 °C, is represented in Figure 8, also highlighting the materials involved in PEM Electrolysis.

$$2H_2O_{(l)} \rightarrow 2H^+ + \frac{1}{2}O_{2(g)} + 2e^- \quad (4)$$

$$2H^+ + 2e^- \rightarrow H_{2(g)} \quad (5)$$

Figure 8 – Schematic Diagram of PEM Electrolysis



Source: Adapted from Gallandat, Romanowicz e Zuttel (2017).

The main obstacle of the PEM Electrolysis technology is the high cost of the components used, especially the platinum cathode and the material that composes the membrane, based on Perfluorosufonic Acid Polymer. Despite this, the marketing context of PEMEC (*Proton-Exchange Membrane Electrolysis Cell*) electrolyzers has been gaining a lot of notoriety in international scientific development forums. With a large financial contribution, this technology is expected to predominate in the electrolyzer market in the coming years. Some companies are already planning to launch commercial solutions in the 100 MW range for hydrogen production in 2023.

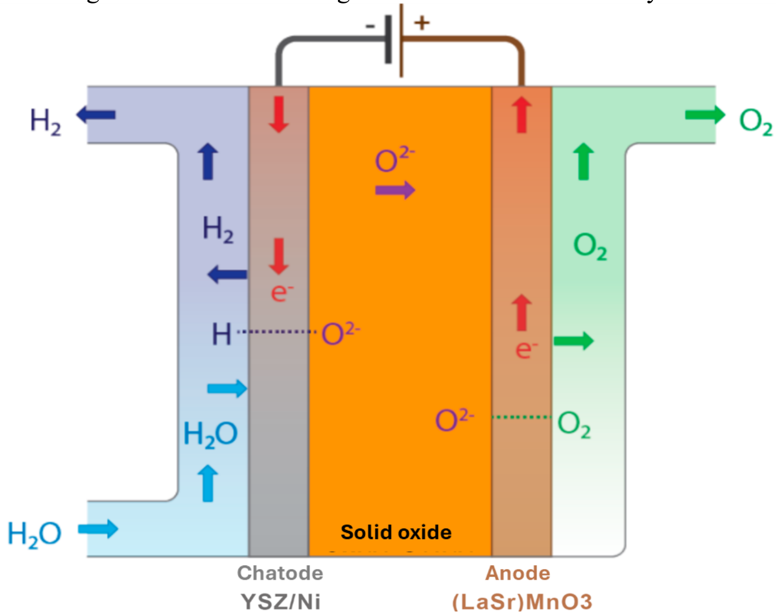
SOLID OXIDE ELECTROLYSIS

Solid Oxide Electrolysis is still in the pre-commercial stage, since, despite having the highest energy efficiency among electrolysis technologies, in addition to high-pressure operations, it still faces challenges such as: corrosion, sealing, thermal cycling and chromium migration, demanding the use of higher cost materials, making it impossible, for the time being, to use Solid Oxide electrolyzers on a large scale (SOEC, Solid *Oxide Electrolysis Cell*). Thus, the anodic and cathodic semireactions are represented by Equations 6 and 7, and the process is represented in Figure 9, also highlighting the materials involved in Solid Oxide Electrolysis.

$$O^{2-} \rightarrow \frac{1}{2} O_{2(g)} + 2e^- \quad (6)$$

$$H_2O_{(g)} + 2e^- \rightarrow H_{2(g)} + O^{2-} \quad (7)$$

Figure 9 – Schematic Diagram of Solid Oxide Electrolysis



Source: Adapted from Gallandat, Romanowicz e Zuttel (2017).

The chemical process occurs with the use of water vapor at elevated temperatures, ranging between 500°C and 800°C, which differentiates this technique from the other types of electrolysis discussed and indicates that the application should be focused on large-scale projects. The electrolyte used is Tritium Oxide Stabilized Zirconia (YSZ), which has high ionic conductivity and thermochemical stability at operating temperatures. The electrodes are composed of porous ceramics, with the cathode composed of YSZ and Metallic Nickel, and the anode composed of Lanthanum Manganite doped with Strontium.

Solid oxide electrolyzers are devices that can perform both the conversion of electricity into hydrogen, and the conversion of hydrogen into electricity. This reversibility characteristic is a major advantage over other electrolysis technologies, allowing the process to be adjusted according to the demand for electrical energy or hydrogen. In addition, SOECs have high energy efficiency and can operate at elevated temperatures, which makes it possible to use various types of fuels for electricity generation, such as biogas and natural gas.

BIOLOGICAL METHODS

As well as water and natural gas (hydrocarbons), there are several other compounds with hydrogen atoms in their chemical formula, which can act as donors in H2 production processes. Among these compounds, there is a great emphasis on Organic Matter, since its basic composition by essential molecules, namely: Carbohydrates, Lipids and Proteins, has a high number of Hydrogen atoms.

Thus, Biomass, when subjected to certain biological processes, configures the method known as Hydrogen Moss or Bio-Hydrogen, which has the great advantage of a negative net emissions profile, that is, it removes GHGs from the atmosphere during the production of Hydrogen, especially when compared to the absence of the application of these methods. In addition, it is also common to associate Bio-Hydrogen with lower energy consumption compared to other processes. In summary, there are three main bioprocesses, namely: Biophotolysis, which can be direct or indirect; Fermentation, subdivided into Photofermentation and Dark Fermentation and Microbial Electrolysis.

In Direct Biophotolysis, microalgae such as green algae (*Chlamydomonas reinhardtii*) or cyanobacteria (*Synechocystis*) convert water into hydrogen and oxygen in the presence of light during photosynthesis. Microalgae have simple nutritional requirements and are easily cultivated, they are also good fixers of CO2. All these factors indicate that direct biophotolysis has a great potential for the production of Bio-Hydrogen. However, direct biophotolysis has several limitations, including high sensitivity to O2, the need for light, and the production of the explosive H2-O2 mixture as a result of the process. (CAGALITAN; ABUNDO, 2021)

Indirect Biophotolysis differs from Direct Biophotolysis in that oxygen evolution occurs at a separate step of hydrogen production, eliminating the formation of explosive mixtures. The first step involves the photosynthesis of cyanobacteria, where CO2 and H2O are converted into organic substances and oxygen. Then, a light-independent reaction occurs in which the organic materials from the first step are broken down by the cyanobacteria into H2, CO2, and other compounds. However, hydrogen production by Indirect Biophotolysis is still quite low and this multi-step process requires a complex system that often leads to high investment and operational costs. (CAGALITAN; ABUNDO, 2021)

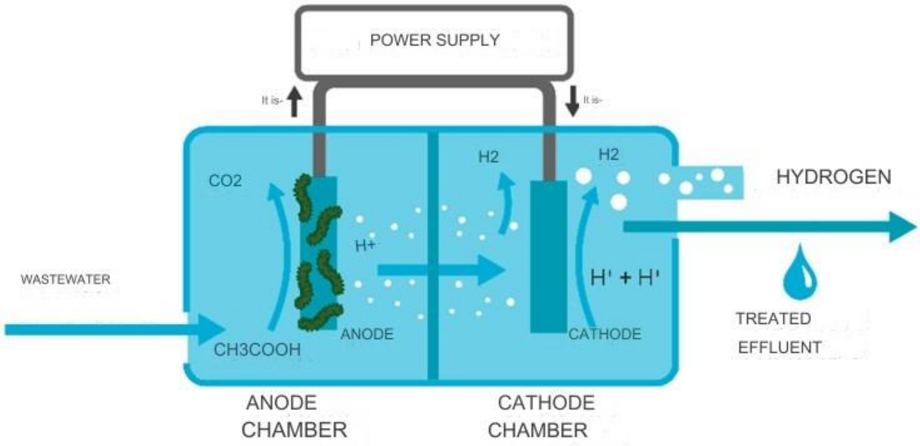
Fermentation is a biochemical process in which microorganisms produce alcohols, organic acids, hydrogen, carbon dioxide and other substances from the degradation of organic matter present in a substrate. In this sense, in Photofermentation, microorganisms use light energy to convert organic acids produced during anaerobic fermentation into H2 and CO2. Non-sulfur photosynthetic bacteria, such as those of the genera *Rhodobacter*, *Rhodobium* and *Rhodopseudomonas*, are examples of microorganisms capable of performing photofermentation. In Dark Fermentation, anaerobic fermenting bacteria, such as those of the genera *Clostridia*, *Escherichia*, *Citrobacter* and *Bacillus*, transform organic substrates into H2 and CO2 in the absence of oxygen and light. (CAGALITAN; ABUNDO, 2021)

Microbial Electrolysis is part of the field of Bioelectrochemical Technologies, that is, it uses oxidation reactions to generate high-value products, such as hydrogen. In this sense, a Microbial *Electrolysis Cell (MEC*) promotes both the production of hydrogen gas and the reduction of the organic charge of a substrate. ECMs are devices powered by the anaerobic digestion of exoelectrogenic bacteria, that is, capable of producing protons (H^+) and electrons (e^-) by oxidizing the organic matter present in a substrate, located in a chamber with an electrode (anode), also called an anodic chamber.

These electrons are collected by the anode and directed to another electrode (cathode), located in the cathode chamber, through an external electrical circuit. At the cathode, electrons are combined with protons in the absence of oxygen, producing hydrogen gas, this process consumes a small amount of electrical energy compared to the electrolysis of water. Figure 10 illustrates the process of Microbial Electrolysis. (LOGAN, 2008)

Although it is a promising alternative, the large-scale production of Moss Hydrogen still faces challenges, especially in relation to operating costs that are currently not competitive when compared to traditional hydrogen production routes.

Figure 10 – Schematic Diagram of Microbial Electrolysis



Source: Adapted from FUDGE et al. (2021).

However, biotechnology can be an ally to enable the processes associated with Bio-Hydrogen, regardless of the production route, some research aims to increase the yield and reduce the costs of the process, including the design of the reactors, the selection of microorganisms with greater productive capacity and the genetic and metabolic engineering to optimize the production routes of H_2. In addition, the use of alternative substrates, such as urban, agricultural or industrial waste, can be an interesting option to reduce the operating costs of the process.

NUCLEAR CATALYTIC SEPARATION, THERMOLYSIS, PHOTOCATALYSIS, HYDRAULIC CRACKING AND OTHERS

Table 1 shows the presence of a method called Red Hydrogen, which uses the high heat from nuclear reactors for the thermal decomposition of water or methane molecules (from natural gas or biological mechanisms, such as methanogenesis). This process is called Nuclear Catalytic Separation. In this aspect, a similarity is observed with Turquoise Hydrogen, due to the thermal decomposition of molecules and the production of hydrogen without the release of GHGs, generating oxygen gas as a by-product (when using water as a substrate) or carbon black (when using methane as a substrate), as well as in the Pyrolysis of Hydrocarbons.

However, the highlight of this method is the use of Nuclear Energy, similar to Pink Hydrogen, but with greater overall efficiency of the production stations, due to the possibility of using the waste heat from the reactors. However, despite the technological maturity of all the equipment involved in this technological route, there are still no pilot, demonstrative or even laboratory-scale projects, mainly due to the prioritization of Renewable Energies for the production of Hydrogen, due to competitive costs and the possibility of accidents in nuclear fission reactors.

In addition, there are two forms of Hydrogen production with a certain degree of spontaneity, namely: Gold Hydrogen and White Hydrogen. In the case of Gold Hydrogen, there is no need to use a primary energy source, since it arises spontaneously in depleted and/or deactivated oil and natural gas reservoirs, due to the action of anaerobic microorganisms, which produce hydrogen by digesting the remaining hydrocarbons in these places. White Hydrogen, on the other hand, is known as Natural Hydrogen, due to the fact that it does not need to employ a physical/chemical process, occurring naturally in caves submerged in deep rivers and in the soil. Recently, it has been the subject of potential surveys, verifying its existence on all continents. In Brazil, there are reserves in 6 states, namely: Ceará, Goiás, Tocantins, Roraima, Minas Gerais and Bahia, notably related to the São Francisco River Basin, due to the Hydraulic Cracking promoted by high geological pressures.

Finally, there are other chemical processes related, especially to Green Hydrogen, as alternatives to traditional Chemical Electrolysis, due to the high energy consumption, relatively low efficiency and the use of high-cost materials, thus, studies on thermal decomposition processes of the water molecule, that is, Thermolysis, and processes catalyzed by the presence of light, are highlighted. i.e. Photocatalysis. Thus, it can be said that Hydrogen Production Technologies are quite diverse, both in technological maturity and in aspects such as the emissions profile, the processes used, the substrates used, cost, scale and application possibilities.

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