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Green Hydrogen Generation and its Application as a Fuel: Advances and Perspectives

by
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ΤΜΗΜΑ ΜΗΧΑΝΟΛΟΓΩΝ ΜΗΧΑΝΙΚΩΝ

Παραγωγή πράσινου υδρογόνου και η χρήση του ως καύσιμο: πρόοδος και προοπτικές

Υπό
Αγγελιδάκη Ελπίδα Μαρία

Υπεβλήθη για την εκπλήρωση μέρους των απαιτήσεων για την απόκτηση του Διπλώματος Μηχανολόγων Μηχανικών του Πανεπιστημίου Θεσσαλίας

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Abstract

This thesis explores the production and utilization of green hydrogen as a sustainable fuel alternative. Considering the escalating climate crisis and global warming, there is an urgent need to implement strategies that significantly reduce carbon dioxide emissions. Green hydrogen emerges as a promising solution, as its combustion yields only water, rendering it an environmentally benign energy carrier. The study presents an in-depth examination of the principal methods employed for green hydrogen production, including thermochemical, electrochemical, biological, and hybrid processes. Emphasis is placed on water electrolysis, one of the most established techniques, whereby the application of electric current facilitates the decomposition of water molecules into hydrogen and oxygen. Furthermore, the thesis delves into the various hydrogen storage technologies, which are broadly classified into physical and chemical methods. Physical storage encompasses compression and liquefaction in high-pressure tanks, whereas chemical storage involves the absorption of hydrogen into solid materials and the formation of metal hydrides bonds. Subsequent sections highlight the key applications of green hydrogen in sectors such as transportation, including hydrogen-powered vehicles, aircraft, ships and industry, with a focus on its potential integration into large-scale facilities like refineries. The penultimate chapter outlines recent technological advancements and addresses the prevailing challenges that hinder the widespread deployment of green hydrogen. The final chapter offers a concise synthesis of the key findings and conclusions derived from this comprehensive investigation into the role of green hydrogen in the transition toward a cleaner and more sustainable energy future.

Key words: electrolysis, sustainable energy future, global warming, applications of green hydrogen, storage technologies.

Περίληψη

Η παρούσα Διπλωματική Εργασία πραγματεύεται την παραγωγή και τη χρήση του πράσινου υδρογόνου, ως καύσιμο. Δεδομένης της κλιματικής αλλαγής και της υπερθέρμανσης του πλανήτη, πρέπει να ληφθούν μέτρα για την μείωση των εκπομπών του διοξειδίου του άνθρακα. Το πράσινο υδρογόνο αποτελεί, λοιπόν, μια λύση ώστε να χρησιμοποιείται και ως καύσιμο, καθώς απελευθερώνει μόνο νερό. Αναλύονται λοιπόν, οι τρόποι με τους οποίους επιτυγχάνεται η παραγωγή του, όπως θερμοχημικοί, ηλεκτροχημικοί, βιολογικοί και υβριδικοί. Μία από τις πιο κύριες μεθόδους είναι η ηλεκτρόλυση, κατά την οποία μέσω ηλεκτρικού ρεύματος διασπάται το μόριο του νερού και παράγεται υδρογόνο. Στη συνέχεια παρουσιάζονται και αναλύονται οι τρόποι αποθήκευσης του υδρογόνου, οι οποίοι μπορούν να κατηγοριοποιηθούν σε δυο ομάδες, τους χημικούς και τους φυσικούς. Στους φυσικούς ανήκει η αποθήκευση σε μεγάλες δεξαμενές, ενώ στους χημικούς, η απορρόφηση σε υλικά και ο σχηματισμός δεσμών μεταλλικών υβριδίων. Επιπλέον, αναφέρονται κάποιες από τις εφαρμογές του πράσινου υδρογόνου, στα μέσα μεταφοράς, όπως τα αυτοκίνητα, τα αεροπλάνα και τα πλοία. Επίσης, γίνεται αναφορά στις δυνατότητες χρήσης του σε βιομηχανικές εγκαταστάσεις, όπως διυλιστήρια. Στο προτελευταίο κεφάλαιο παρουσιάζονται οι τελευταίες εξελίξεις, καθώς και κάποιοι προβληματισμοί, οι οποίοι δυσκολεύον την ευρεία χρήση του. Στο τελευταίο κεφάλαιο παρουσιάζονται συνοπτικά συμπεράσματα από την μελέτη για τη χρήση του πράσινου υδρογόνου.

Λέξεις-κλειδιά: Πράσινο υδρογόνο, Παραγωγή υδρογόνου, Αποθήκευση υδρογόνου, Ηλεκτρόλυση, Καθαρή ενέργεια, Πράσινη μετάβαση.

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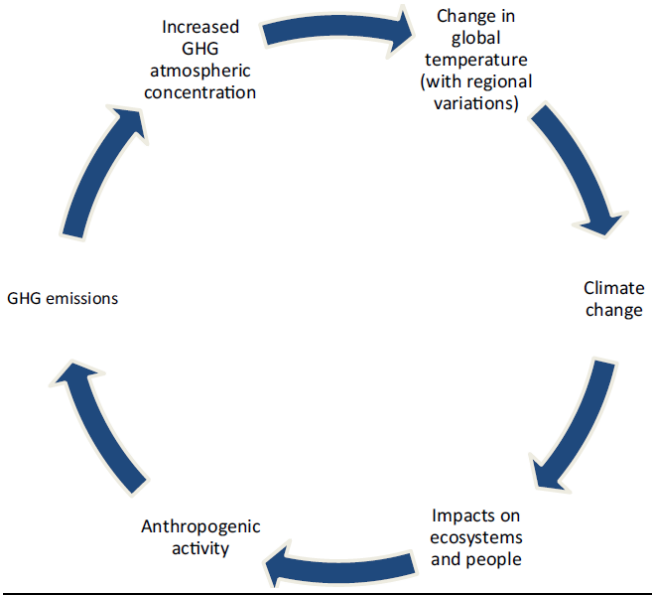
Chapter 1: INTRODUCTION

Since climate change plays a significant role globally, a change was necessary. Beginning from the meaning of climate change. Climate change is a long-term change in the weather patterns that affect the Earth's local, regional and global climates and are consist of natural and human causes. Some evidence for Rapid Climate Change is the rising global temperature, the warmth of the ocean, the shrink of the ice sheets, the rise of sea levels and the extreme events that are increasing in frequency. These changes that were observed in the mid-20th century are driven by human activities. According to NASA and the National Oceanic and Atmospheric Administration (NOAA), the earth's surface temperatures in 2016 were the warmest since modern records in 1880, temperatures were 1.78 degrees Fahrenheit (0.99 degrees Celsius) warmer than the mid-20th century mean. For example, fossil fuel burning increases the greenhouse gas levels and results in raising Earth's average temperature. Since the pre-industrial period (between 1850 and 1900) human activity has increased Earth's global temperature. With the warning of the previous, on 12 December 2015, in Paris, 196 Parties at the UN Climate Change Conference adopt the Paris Agreement for the well- known net zero. The ascendancy of this agreement was set up on 4 November 2016 and the most important purpose was to limit global warming to 1.5ºC, through economic and social transformation, based on the best available science. The Paris agreement constitutes a landmark in the climate change process because it is an institution that brings together all nations for the common good.[1]

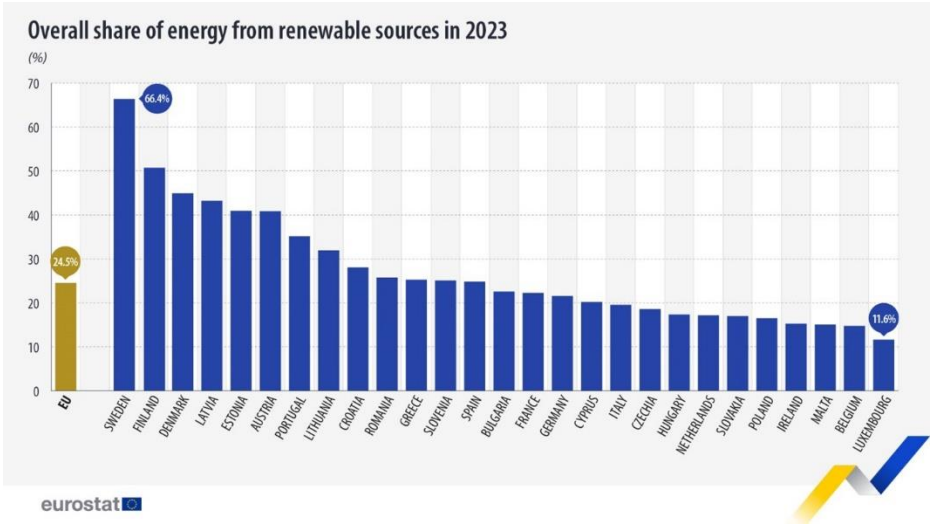


- **Figure 1**: path of climate change. [2]

The challenges of the immediate measures led to another method of energy, Renewable Energy Sources (RES). The exact definition of RES in energy from sources that are naturally replenishing but flow limited. Some of the dominant sources are biomass, hydropower, geothermal, wind and solar.[2]

It's essential to point out that despite the continued reliance on fossil fuels while showing a diverse but still relatively small role for renewable sources in the U.S. energy mix, the breakdown of U.S. primary energy consumption by source for the year 2023, totaling 93.59 quadrillion British thermal units (BTUs). Petroleum remains the dominant source, accounting for 38% of total energy use, closely followed by natural gas at 36%. Coal, nuclear electric power, and renewable energy each contribute 9%. A closer look at the renewable energy segment, which totals 8.24 quadrillion BTUs, reveals that biomass constitutes the largest share (60%) of renewables. Within biomass, biofuels (32%) and wood (23%) are the most significant contributors, with smaller portions coming from biomass waste (5%). Other notable renewable sources include wind (18%), solar (11%), hydroelectric (10%), and geothermal (1%). This data highlights the continued reliance on fossil fuels while showing a diverse but still relatively small role for renewable sources in the U.S. energy mix.[3]

From data that was extracted in December 2024, 24,5% of energy consumed in renewable energy, especially the 10.8% was used in transport. In the diagram below, it is observed that Sweden ranked first among EU countries, with two-thirds of its gross final energy consumption coming from renewable source.



➢ **Figure 2**: Europe's energy from Renewable Sources in 2023. [3]

1.1 Motivation

The increasing severity of climate change, resource depletion, and environmental degradation has made it clear that the current energy paradigm is unsustainable. We are at a pivotal moment in history, where our decisions today will determine the quality of life for future generations. Motivated by a deep concern for our planet and an unwavering belief in the power of innovation, I have chosen to focus my research on green energy, particularly green hydrogen, as a vital pathway to a more sustainable and resilient future.

My interest in green hydrogen stems from its transformative potential. It not only addresses the urgent need to reduce greenhouse gas emissions but also offers a means to decentralize and diversify energy systems. This can empower nations, communities, and individuals, reducing dependence on fossil fuels and fostering energy security.

Moreover, the global shift toward renewable energy is not just a technical challenge, it is a moral imperative. The consequences of inaction are already visible: rising sea levels, extreme weather events, loss of biodiversity, and humanitarian crises linked to environmental stress. I believe that through focused research, technological advancement, and a shared vision, we can contribute to reversing this trajectory.

This thesis represents both a scientific endeavor and a personal commitment. It is driven by a sense of responsibility to contribute meaningfully to the global energy transition and to support the development of solutions that can safeguard our planet. My work is inspired by the belief that sustainable energy is not only possible but essential and that green hydrogen is a key part of that solution.

1.2 Introduction to Literature Review

The most widely discussed method of green hydrogen production in the literature is water electrolysis, which involves splitting water into hydrogen and oxygen using electricity sourced from renewable energy systems such as solar, wind, or hydropower. Studies by Shiva Kumar and Hankwon Lim (2022) provide an extensive overview of alkaline and PEM (Proton Exchange Membrane) electrolysis technologies, focusing on their efficiency, operational conditions, and scalability for industrial use. Other electrochemical and hybrid systems are also gaining attention, especially for their potential to integrate renewable energy surpluses and optimize grid stability.

Alternative production methods such as biomass gasification, microbial electrolysis, and thermochemical processes have also been examined. Obiora et al. (2024) reviewed the

prospects and challenges of hydrogen production from biomass, underlining the need for waste-to-energy integration and sustainability in fuel generation. Hybrid methods, like plasma-assisted reforming and microbial-electrochemical approaches, have been highlighted for their innovative contributions to increasing hydrogen yields and energy efficiency.

Hydrogen storage is a critical component of the hydrogen value chain. The literature categorizes storage technologies into physical storage, including high-pressure gaseous hydrogen and cryogenic liquid hydrogen and chemical storage, such as metal hydrides and adsorbent materials. Usman (2022) provided a comparative review of these methods, emphasizing their energy density, safety concerns, and technological maturity.

Advanced materials such as MOFs (Metal-Organic Frameworks), carbon nanotubes, and complex hydrides like $NaAlH_4$ and $LiBH_4$ are frequently studied for their high hydrogen uptake and reversibility. However, limitations such as low thermal conductivity, degradation over multiple cycles, and cost remain significant barriers to commercial deployment.

In the field of **t**ransportation, hydrogen fuel cells have received widespread attention. Aminudin et al. (2023) reviewed the technological progress of fuel cell electric vehicles (FCEVs), highlighting efficiency improvements, cost reductions, and the development of hydrogen refueling infrastructure. Hydrogen-powered aircraft and shipping are also areas of active research and development, particularly for long-range, heavy-duty applications.

Industrially, green hydrogen is being explored for refining, ammonia production, and steelmaking, where it can displace carbon-intensive processes. For example, the REFHYNE project in Germany demonstrated the feasibility of integrating a 10 MW electrolyzer in a refinery setting, contributing to the decarbonization of oil refining processes.

From a policy standpoint, international cooperation and regulatory frameworks are crucial for scaling up hydrogen technologies. The European Commission's hydrogen strategy, along with national initiatives from countries such as Japan, Germany, and the USA, provides valuable direction for research funding, infrastructure development, and commercialization pathways.

Economic incentives, including subsidies and carbon pricing, are often cited in the literature as necessary mechanisms to close the cost gap between green and grey hydrogen. Additionally, public-private partnerships and investment in workforce training are consistently recommended strategies to support the long-term viability of the hydrogen economy.

1.3 Thesis Organization

This thesis is structured to provide a comprehensive overview of green hydrogen as a sustainable energy vector, starting from its fundamental properties to its real-world applications and recent developments. Each chapter is designed to build on the previous one, leading to a holistic understanding of the potential and challenges of hydrogen in the global energy transition.

Chapter 2: Hydrogen – Physical and Chemical Properties, and Production Methods

This chapter introduces hydrogen as a chemical element, detailing its physical and chemical properties, such as its atomic structure, reactivity, energy content, and behavior under different conditions. The second part of the chapter presents the various hydrogen production methods, classified into gray, blue, and green hydrogen. Emphasis is given to green hydrogen, which is produced via electrolysis using renewable energy sources, positioning it as the most environmentally friendly option.

Chapter 3: Hydrogen Storage Methods

Efficient and safe storage is a critical component of the hydrogen value chain. This chapter explores the main hydrogen storage techniques, including compressed gas storage, liquid hydrogen storage, and solid-state storage using metal hydrides and chemical carriers. The advantages, limitations, and technical challenges of each method are analyzed, with special attention to their suitability for different applications and scales.

Chapter 4: Applications of Green Hydrogen

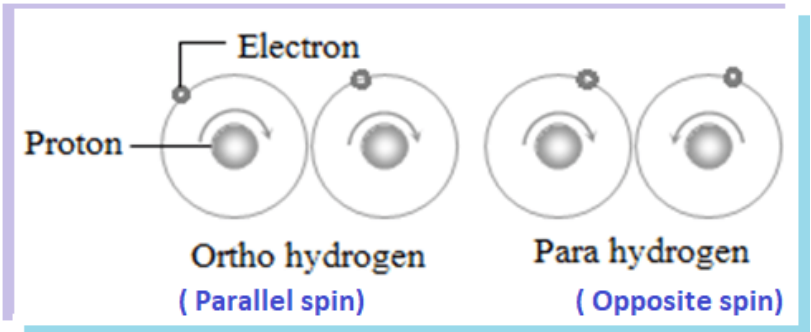
This chapter focuses on the diverse and expanding applications of green hydrogen across sectors. It includes its use in fuel cells for transportation, industrial processes (such as steelmaking and ammonia production), residential heating, and grid energy storage. The role of hydrogen in supporting the decarbonization of hard-to-abate sectors and in enabling sector coupling is also discussed.

Chapter 5: Recent Developments and Future Outlook

The final chapter presents the latest technological, industrial, and policy developments in the green hydrogen sector. It includes a review of current pilot projects, investments, innovations in electrolysis technology, and international hydrogen strategies. It also discusses ongoing challenges, such as costs, infrastructure, and public acceptance and offers a perspective on future directions and research opportunities.

Chapter 2: HYDROGEN

Hydrogen, denoted by the chemical symbol **H** and possessing an atomic number of **1**, is the simplest and most abundant element in the universe, while making up 75% of the mass of all visible matter in stars and galaxies [4]. As the first element in the periodic table, each atom of hydrogen consists of a single proton and one electron, and it naturally exists as a diatomic molecule (H_2) under standard temperature and pressure, because the atomic arrangement of a single electron is highly reactive [4]. The mass of the atom is concentrated in its nucleus, since the proton is more than 1800 times more massive than the electron. However, hydrogen rarely can have both a proton and a neutron and this form is called deuterium or heavy hydrogen and is an isotope. Other isotopes are tritium with two neutrons and one proton, but these isotopes are unstable and decay radioactively. Another segregation is about proton's spin and there are two categories the ''orthohydrogen'' and the ''parahydrogen''. The orthohydrogen is dominant at room temperature in normal hydrogen, while at very low temperatures becomes unstable and converts into parahydrogen and during this process, releases heat.



- **Figure 3:** ortho and para hydrogen. [13]

Overall, hydrogen is characterized as a colorless, odorless, tasteless, and highly flammable gas, notable for its low density and high diffusivity. The most known chemical reaction is the burn with oxygen to form water; indeed, the name hydrogen is derived from Greek words meaning ''maker of water''.

From a chemical standpoint, hydrogen exhibits a high degree of reactivity. It readily forms covalent bonds with nonmetals and ionic hydrides with certain metals. It also plays a crucial role in reduction reactions, particularly in reducing metallic oxides to pure metals. Moreover, the ability of hydrogen to engage in hydrogen bonding is a significant feature influencing the structural and functional behavior of water and various biological

macromolecules. Hydrogen occurs in three isotopic forms: **protium (^{1}H)**, **deuterium (^{2}H or D)**, and **tritium (^{3}H or T)**. Protium, the most prevalent isotope, has no neutrons, whereas deuterium contains one neutron and is commonly used in nuclear reactors as a moderator in the form of heavy water (D_2O). Tritium, with two neutrons, is a radioactive isotope utilized in nuclear fusion technologies and in applications such as self-luminous paints. Due to its fundamental properties and widespread presence, hydrogen is a subject of extensive research and holds significant promise in the development of sustainable energy systems, particularly in fuel cell technologies and clean energy transitions.

- **Physical Properties of Hydrogen**

Hydrogen, the lightest and most abundant element in the universe, possesses several unique physical characteristics that significantly influence its handling, storage, and utilization, particularly as a fuel source. This chapter discusses its physical state, sensory characteristics, toxicity, density-related measures, and leakage behavior under various conditions.

- ***State of Hydrogen***

Hydrogen exists in three primary states, gaseous, liquid, and solid, depending on environmental temperature and pressure. At standard atmospheric pressure, hydrogen transitions to a liquid at 20 K (−253 °C) and to a solid at 14 K (−259 °C). These values denote some of the lowest boiling and melting points among known substances, surpassed only by helium. Due to these cryogenic requirements, the liquefaction and solidification of hydrogen involve considerable technical and energy-related challenges.

The extremely low boiling point of hydrogen limits its convenience as a liquid fuel under ambient conditions. Unlike hydrocarbon fuels, which remain liquid at room temperature and atmospheric pressure, hydrogen must be stored either under high pressure or at cryogenic temperatures. Consequently, storage solutions must be engineered to maintain either high compression or thermal insulation.

- ***Sensory Characteristics***

Pure hydrogen is a colorless, odorless, and tasteless gas. This property complicates leak detection, as hydrogen escapes unnoticed under normal sensory conditions. Additionally, unlike natural gas, hydrogen cannot be odorized using sulfur-based compounds such as mercaptans due to their detrimental effects on fuel cell catalysts.

- ***Toxicity and Asphyxiation Potential***

Hydrogen is non-toxic but acts as an asphyxiant by displacing oxygen in confined environments. Oxygen concentrations below 19.5% can lead to adverse physiological effects,

including impaired judgment, unconsciousness, and ultimately, death. Although hydrogen diffuses rapidly and rises due to its low molecular weight, which mitigates the risk of prolonged asphyxiation in open environments, safety protocols must be enforced in enclosed spaces to prevent accidental buildup.

- ***Density and Related Measures***

Hydrogen's extremely low atomic weight results in a correspondingly low density. At 20 °C and 1 atm, its vapor density is approximately 0.08376 kg/m³, while its liquid density at the boiling point is 70.8 kg/m³. For comparison, methane and gasoline are significantly denser in both gaseous and liquid forms.

Hydrogen's specific gravity (relative to air) is approximately 0.0696, indicating that it is much lighter than air. Its expansion ratio, defined as the volume increase from liquid to gaseous state atmospheric conditions is 1:848. This high expansion ratio underscores the challenges of storing hydrogen efficiently and safely.

- ***Leakage Behavior***

Hydrogen molecules, being the smallest of all elements, exhibit high diffusivity and permeability through many conventional containment materials. This characteristic increases the risk of leaks, particularly through seals and joints not specifically engineered for hydrogen service. Despite its leakage potential, hydrogen exhibits favorable dispersion behavior. Once leaked, it rises and diffuses rapidly, especially in open air, reducing the likelihood of hazardous accumulation. Nonetheless, dedicated leak detection systems and proper ventilation are imperative components of hydrogen infrastructure to ensure safe operation.

- ***Energy of Hydrogen***

Hydrogen is a highly promising energy carrier due to its exceptional energy content per unit mass, clean combustion profile, and versatility in both combustion and electrochemical energy conversion systems. This chapter presents an overview of the energy properties of hydrogen, comparing it to conventional fuels, and discusses its implications in energy systems design and sustainability.

- ***Energy Content***

Hydrogen possesses the highest specific energy of any known fuel. The **higher heating value (HHV)** of hydrogen is approximately **141.86 kJ/g (61,000 Btu/lb.)**, while its **lower heating value (LHV),** which excludes the latent heat of water vaporization is **119.93 kJ/g (51,500 Btu/lb.)**. These values significantly exceed those of hydrocarbon fuels such as methane, propane, gasoline, and diesel. For instance, the LHV of gasoline is approximately 44.5 kJ/g, making hydrogen more than twice as energy-rich by weight. This superior gravimetric energy

density renders hydrogen particularly attractive in applications where weight is a critical parameter, such as aerospace propulsion and fuel cell electric vehicles (FCEVs). It is for this reason that hydrogen has long been employed as a primary fuel in space missions.

- ***Energy Density***

Despite its high specific energy, hydrogen's **volumetric energy density** is comparatively low due to its low density in gaseous form. At ambient pressure and temperature, hydrogen has an LHV-based energy density of just 10,050 kJ/m³ (270 Btu/ft³), which is significantly less than methane and liquid hydrocarbons. This low volumetric energy density necessitates either high-pressure compression (e.g., up to 700 bar) or liquefaction to make hydrogen viable for mobile and compact applications. The high energy density of liquid hydrogen, while beneficial, requires cryogenic storage at −253 °C, posing significant engineering challenges. Additionally, hydrogen can be stored in metal hydrides or other solid-state materials, but these systems typically involve increased mass and lower energy efficiency.

Table 1: Presentation of energy densities of hydrogen under various storage conditions

STORAGE STATE	ENERGY DENSITY(LHV)
Gaseous @ 1 atm, 15 °C	10,050 kJ/m³ (270 Btu/ft³)
Gaseous @ 200 bar, 15 °C	1,825,000 kJ/m³ (48,900 Btu/ft³)
Gaseous @ 690 bar, 15 °C	4,500,000 kJ/m³ (121,000 Btu/ft³)
Liquid	8,491,000 kJ/m³ (227,850 Btu/ft³)

- ***Energy Conversion and Use***

Hydrogen may be utilized through combustive or electrochemical processes. In traditional internal combustion engines, hydrogen combustion yields water vapor as the sole product, without carbon dioxide, carbon monoxide, or particulates. However, under high-temperature conditions, small amounts of nitrogen oxides (NO_x) may still form due to atmospheric nitrogen involvement. Alternatively, when hydrogen is used in fuel cells, such as proton exchange membrane fuel cells (PEMFCs), it reacts electrochemically with oxygen to generate electricity, producing only water and heat as by-products. This process offers significantly higher efficiencies compared to combustion up to 60% in fuel cells, compared to 25–30% in internal combustion engines.

The reaction involved in a hydrogen fuel cell can be summarized as:

Anode Reaction:

$$H_2 \longrightarrow 2H + 2e^-$$

Cathode Reaction:

$$\frac{1}{2}O_2+2H+2e^- \longrightarrow 8H_2O$$

Overall Reaction:

$$H_2+\frac{1}{2}O_2 \rightarrow H_2O$$

This clean conversion pathway makes hydrogen a central component of decarbonization strategies in the transportation, industrial, and power generation sectors.

- ***Energy Storage Considerations***

Given its properties, hydrogen serves as an effective medium for renewable energy storage, addressing the intermittency of sources such as solar and wind. Surplus electrical energy can be converted to hydrogen via electrolysis, stored, and later reconverted to electricity through fuel cells or turbines when demand rises. This capability supports the development of a resilient, low-carbon energy infrastructure.

2.1 Methods of production

Before presenting the various hydrogen production methods, it is important to refer to the different types of hydrogen, which are commonly distinguished by color labels. These color codes are not literal but rather symbolic, and they are used to indicate the production method and the associated environmental impact of each type. Hydrogen is categorized based on its production methods and the corresponding environmental impact. Its versatility, combined with the fact that it emits only water vapor when used as fuel, positions it as a promising option for a low-carbon future. However, it is important to note that not all hydrogen is produced equally in terms of sustainability. Among the various types, green hydrogen stands out as the most environmentally sustainable, as it is generated through electrolysis powered by renewable energy sources. The most widely recognized method for producing green hydrogen is through electrolysis, a process in which water is split into hydrogen and oxygen using electricity derived from renewable energy sources such as wind, solar, or hydropower. This method results in zero greenhouse gas emissions and relies on water, one of the most abundant resources on Earth. Further details regarding the production process will be provided in the following sections. Another notable type of hydrogen is blue hydrogen, which is produced through the reforming of natural gas (methane). Although it is not as environmentally clean as green hydrogen, blue hydrogen represents a significant transitional step toward a lower-carbon future, while represents a practical transitional pathway for executives in sectors such as the chemical and industrial industries, where natural gas infrastructure is already well established. It facilitates

the reduction of greenhouse gas emissions and supports enhanced environmental stewardship, all while preserving existing operational frameworks. Furthermore, the adoption of blue hydrogen can be viewed as a strategic measure, positioning organizations for a smoother transition to more sustainable hydrogen production methods in the future. Brown hydrogen is regarded as the least environmentally sustainable variant, as it is derived from fossil fuels such as coal and oil. In comparison, grey hydrogen is produced through the process of steam methane reforming (SMR), which remains the most widely utilized method within the hydrogen production sector, accounting for over 90% of global hydrogen output. Pink hydrogen is generated using nuclear energy, with nuclear reactors supplying the electricity necessary for electrolysis. Finally, turquoise hydrogen is obtained via high-temperature methane pyrolysis, presenting a promising alternative to traditional SMR by potentially lowering energy requirements and producing solid carbon as the sole byproduct. [5]

2.1.1 Water Electrolysis

To address the emerging challenges associated with the transition to a sustainable energy system, green hydrogen has emerged as a viable and forward-looking solution. It is primarily produced through the electrolysis of water, a process that splits water molecules into hydrogen and oxygen using electricity. While electrolysis is the most recognized method, alternative approaches such as gasification and molecular conversion also exist. Electrolysis is particularly effective when powered by renewable energy sources, especially wind and solar, due to their broad geographic availability and decentralized nature. The integration of renewable energy with electrolysis offers a significant advantage: excess electricity generated during periods of low demand can be converted into hydrogen and stored. This stored hydrogen can later be utilized to help balance fluctuations between energy production and consumption.[6]

Historical Background

Water electrolysis is a well-established process with a history spanning around 200 years. The identity of its original discoverer is still debated, as various sources offer differing claims. However, historical accounts by Trasatti (1999) and De Levie (1999) suggest that the first recorded observation occurred in 1789, when Dutch scientists Adriaan Paets van Troostwijk and Jan Rudolph Deiman noticed that electric discharges could split water into two gases, what they referred to as “combustible air” and “life-giving air,” now known as hydrogen and oxygen. A decade later, in 1800, English scientists William Nicholson and Anthony Carlisle further advanced this understanding by demonstrating that water could be decomposed using direct

current. It was not until 1834 that Michael Faraday formulated the fundamental laws of electrolysis, providing the scientific foundation for the eventual development of industrial electrolyzers (Kreuter and Hofmann, 1998). Also, in 1902 more than 400 industrial electrolyzers were in operation and in 1939, the Norwegian company Norsk Hydro built the first big electrolysis plant with a capacity of 10,000 m^3 H_2/h. [7]

Thermodynamics

The overall equation of the water splitting is:

$H_2O \rightarrow \frac{1}{2}O_2 + H_2$ (1.1)

$\Delta H(T) = \Delta G(T) + T\,\Delta S(T)$,

where $\Delta H(T)$ is the total amount of energy, which is to be supplied to an electrolysis cell so as to split water molecules, according to the first equation (1.1). $\Delta G(T)$, the change of Gibbs free energy represents the electrical energy and the $T\,\Delta S(T)$ represents the appropriate amount of heat.

The minimum applied cell potential for the start of the process is represented by the reversible voltage Vrev, which is given by the following type:

$$Vrev = \frac{\Delta G}{n*F} = 1.23\ V,$$

with ΔG of 237.22 kJ/mol (at standard conditions of 1 bar and 298 K), n the number of electrons (2 because two electrons moved) transferred in reaction (1.1) and the Faraday constant F of 96,487 C/mol the reversible voltage calculates as 1.23 V.

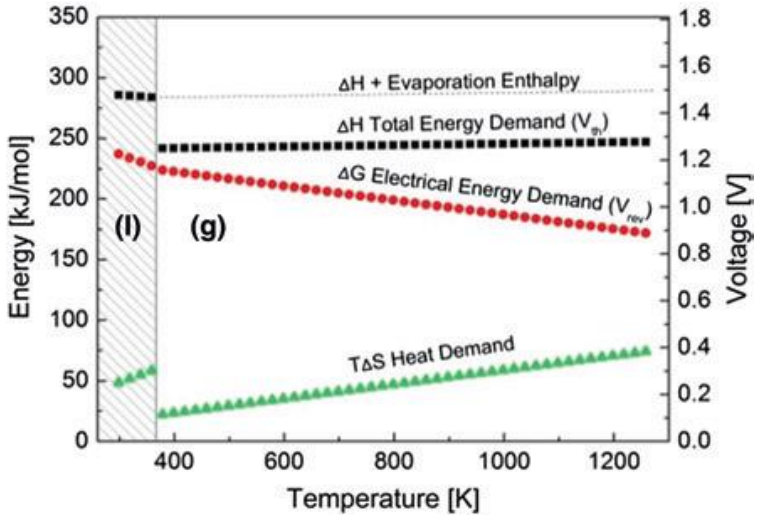
The thermo-neutral voltage Vth, defined by Eq. (1.2), is related to enthalpy change associated with the water splitting reaction.

$$Vth = \frac{\Delta H}{nF} = \frac{\Delta G}{nF} + T\frac{\Delta S}{nF} = 1.48\ V$$

With ΔH of 285,84 kJ/mol and a temperature T of 298 K a thermo-neutral voltage of 1.48 V is obtained. [9] [7]

- If the voltage Ecell, which is applied to the electrolysis cell, is higher than Vrev but lower than Vth water splitting just takes place by absorbing heat from the environment as the cell dissipates the heat associated with the change in entropy irreversibly.
- If Ecell = Vth, the Joule heat generated within the electrolysis cell equals the heat consumption of the endothermic electrolysis reaction and therefore no heat exchange with the environment would be required.

- If Ecell > Vth the electrolysis cell produces surplus heat due to joule heating and must be properly cooled to reduce degradation of the system.



- **Figure 4**: Water electrolyzer thermodynamics and cell voltage as a function of operation temperature. [Data for calculation taken from Dorf (2004)] [7]

The previous diagram of energy and voltage according to temperature depicts the temperature dependence of the particular energy demands and the corresponding cell voltages for water electrolysis. At 373 K, when water vapors, there is a discontinuity of the total energy's curve (ΔH). As a result, steam as feedstock rather than liquid water requires less energy. Also, from the diagram, the electrical energy demand continuously decreases with increasing temperature. Expect from the influence of the temperature, pressure on the cell voltage is also estimated with a form of the well-known Nernst Equation:

$$\Delta V = V - V^{\circ} = -\frac{RT}{nF} ln1/\sqrt{P}$$

where R is the ideal gas constant (8.314 J/mol K) and P is the overall pressure within the electrolysis cell assumed to be equal at both electrodes.

Electrolyzer Efficiency

The efficiency of an electrolyzer system is generally defined as:

$$nsys = \frac{EnergyOutput}{Energy\ Input} \rightarrow \frac{Heating\ Value\ H2}{Electrical\ Energy\ Input}$$

and includes the overall energy demand of all components of the system.

The energy output in hydrogen production is typically represented by its heating value, which can be expressed as either the higher heating value (HHV = 3.54 kWh per standard cubic meter, with 1 scm referring to a standard cubic meter) or the lower heating value (LHV = 3 kWh/scm).

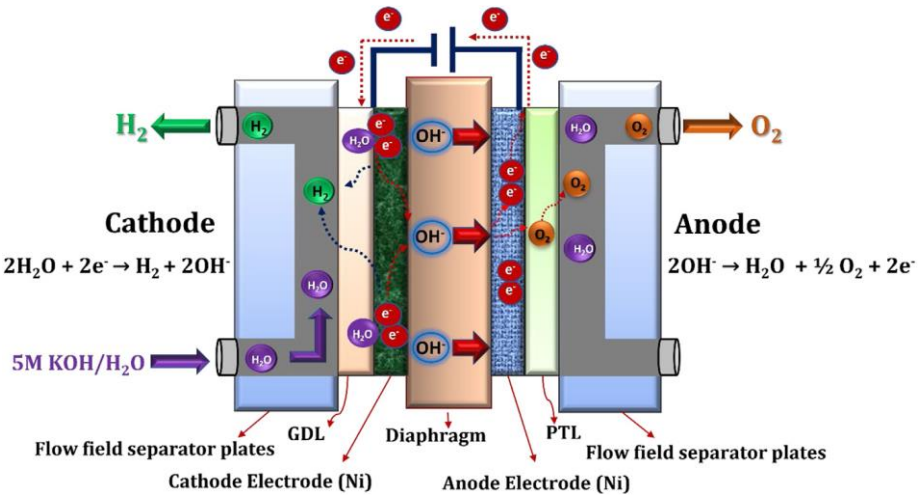
**scm=standard cubic meter, a cubic meter of gas under standard conditions, defined as an atmospheric pressure of 1.01325 bar and a temperature of 15 °C.*

Since liquid water is commonly used as the input material in electrolysis, the energy needed to evaporate water must be considered. For this reason, the HHV is more appropriate for calculating overall system efficiency.

In standard water electrolysis systems, the primary energy input is electrical, unless the operating voltage drops below the thermodynamic threshold (Vth). The efficiency calculation also depends on the scope of the electrical input considering whether it applies to a single electrolytic cell, a cell stack, or the complete electrolyzer system, which includes auxiliary components necessary for operation.

Furthermore, the utilization rate of the system significantly influences energy conversion efficiency. Operating the electrolyzer at less than 50% of its rated power typically leads to a 10–30% decline in efficiency. This issue becomes especially relevant in applications involving fluctuating power supply, such as those in Power-to-Gas systems that rely on variable renewable energy sources.

2.1.2 Alkaline Electrolysis



➢ **Figure 5**: Schematic illustration of alkaline water electrolysis working principle. [9]

Alkaline water electrolysis is an electrochemical process that splits water into hydrogen and oxygen gases using electrical energy. This process involves two separate half-cell reactions: the hydrogen evolution reaction (HER) occurring at the cathode and the oxygen evolution reaction (OER) occurring at the anode. During alkaline electrolysis, at the cathode, two moles of water molecules in the alkaline solution are reduced to generate one mole of hydrogen gas (H_2) and two moles of hydroxide ions (OH^-). The hydrogen gas is released from the cathode surface, while the hydroxide ions migrate through a porous separator under the influence of the electric

field towards the anode. At the anode, the hydroxide ions are oxidized to produce half a mole of oxygen gas (O_2) and one mole of water (H_2O), as illustrated in Figure 5.

Cell Components of Alkaline Water Electrolysis

The primary components of an alkaline water electrolysis cell include diaphragms or separators, current collectors (also referred to as gas diffusion layers), separator plates (bipolar plates), and end plates. Commonly, asbestos, Zirfon, or nickel-coated perforated stainless-steel diaphragms are employed as separators. Nickel mesh or foam is typically used as the gas diffusion layer, while stainless steel or nickel-coated stainless-steel serves as bipolar and end plates, respectively.[9]

2.1.3 PEM electrolysis

In the proton exchange membrane (PEM) water electrolysis process, water is electrochemically split into hydrogen and oxygen gases. At the anode, water molecules are oxidized to produce oxygen gas (O_2), protons (H^+), and electrons (e^-). The oxygen gas is released from the anode surface, while the protons migrate through the proton-conducting membrane to the cathode. Meanwhile, the electrons travel through the external circuit to the cathode side. At the cathode, the protons and electrons recombine to form hydrogen gas (H_2). The basic principle of PEM water electrolysis is illustrated in Figure 6.

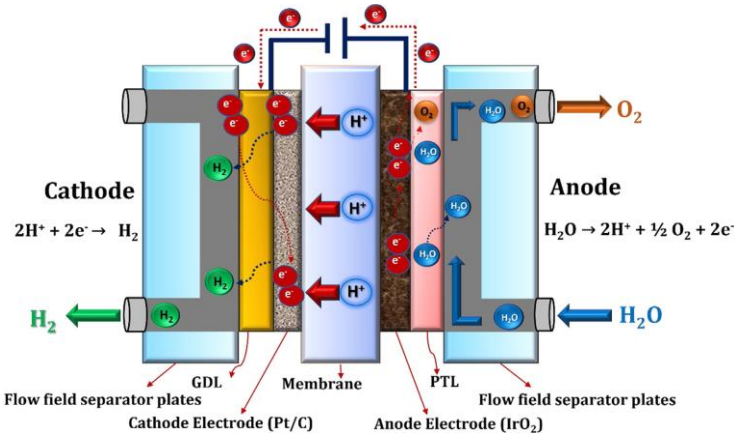
Cell Components of PEM Water Electrolysis

The main components of a PEM water electrolysis cell include the membrane electrode assembly (MEA), which consists of the proton exchange membrane and the anode and cathode electrode materials, as well as gas diffusion layers, separator plates (bipolar plates), and end plates. Common proton exchange membranes include Nafion®, Fumapem®, Flemion®, and Aciplex®, with Nafion® (specifically Nafion® 115, 117, and 212) being the most widely used due to its high proton conductivity, excellent mechanical strength, high current density capabilities, and chemical stability.

State-of-the-art electrode materials for PEM electrolysis are noble metal-based electrocatalysts, notably iridium dioxide (IrO_2) for the oxygen evolution reaction (OER) at the anode, and carbon-supported platinum (Pt) for the hydrogen evolution reaction (HER) at the cathode. However, these noble metals are expensive and scarce, with iridium being rarer than platinum.

For instance, a 10 MW PEM electrolyzer operating at 1 A/cm² requires approximately 15 kg of iridium with catalyst loadings of 2–3 mg/cm². At the August 2021 iridium price (~196,119 USD/kg), this catalyst cost exceeds 2.9 million USD (Metalary, 2021).

Porous titanium or titanium mesh and carbon cloth are typically used as gas diffusion layers for the anode and cathode, respectively. Bipolar and end plates are often made from titanium coated with platinum or gold, designed with various flow field configurations. Among these, straight parallel flow field designs have shown superior performance in PEM electrolyzers. Nevertheless, these plates are costly and contribute approximately 48% of the total cell cost (IRENA, 2020b). Thus, developing cost-effective cell components, especially electrode materials and separator plates, remains a critical challenge.[9]



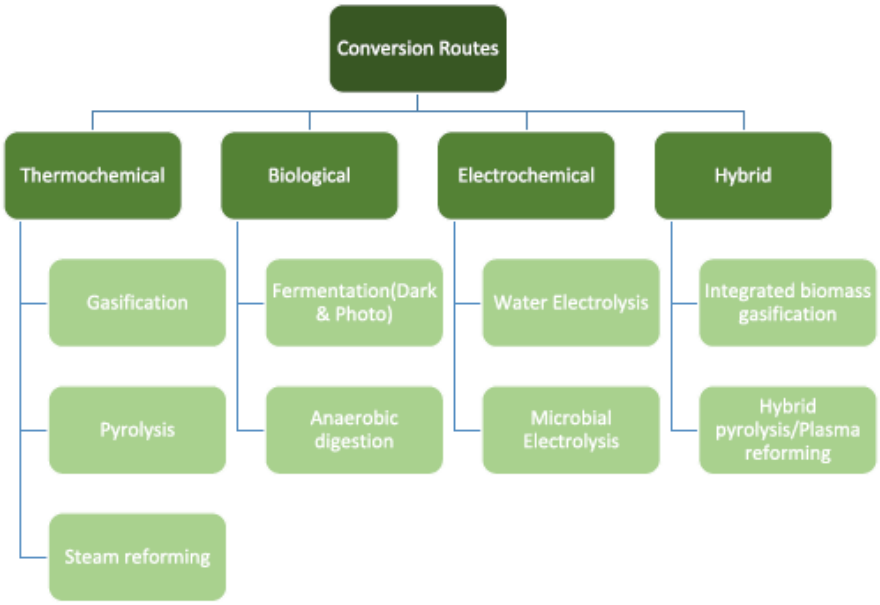
➢ **Figure 6**: Schematic view of PEM water electrolysis working principle. [9]

2.2 Biomass Gasification

Another way to produce hydrogen is the biomass gasification, which is a thermochemical conversion. Biomass includes wastes and residues from agricultural activities, animal wastes and livestock operation residues, forest remnants, various types of wood and wood wastes, oceanic plants and organic wastes from municipalities. In this chapter, biological, electrochemical and hybrid methods will be discussed.

2.2.1 Thermochemical Processes

To begin with the biomass to hydrogen conversion route, like the diagram depicts:



➢ **Figure 7**: Organizational chart for hydrogen production routes. [10]

Biomass is converted into hydrogen-rich syngas through gasification, a process that does not involve burning. This method includes heating biomass (organic or carbonaceous feedstock), steam and oxygen to temperatures exceeding 700 °C in a controlled environment and as a result CO, hydrogen, CO2, nitrogen, water and higher hydrocarbon are produced. Reaction between the produced CO and water to produce hydrogen is known as water-gas shift reaction. Hydrogen can be removed from the gas stream using adsorber or specific membranes in order to remove the CO2 and then is led to pressure swing adsorption (PSA) to give the final product. Gasification at higher temperatures contributes to quicker and more efficient reactions and as a result it becomes the preferred method for biomass to hydrogen conversion. Wet biomass resources such as sewage sludge and algae can be processed through co-hydrothermal gasification, a method that operates in under an hour using pressurized water as both the solvent and reaction medium under high-temperature conditions. This technique is particularly effective because elevated temperatures accelerate reaction rates, positioning gasification as a leading approach for hydrogen generation from biomass.

Research on this method indicates that maximizing hydrogen output requires careful optimization of process parameters, namely temperature, catalyst concentration, and reaction time. For instance, a substantial hydrogen yield of 40 wt.% was achieved under conditions of 426.36 °C, a catalyst loading of 2.3 wt.%, and a reaction time of 70.22 minutes. These findings highlight the importance of process fine-tuning to enhance the efficiency of biohydrogen production and support the transition toward cleaner energy systems.

In addition to its efficiency, gasification offers environmental advantages by converting waste biomass into hydrogen and useful byproducts, while simultaneously reducing greenhouse gas emissions. However, to ensure its long-term viability, a comprehensive evaluation of its environmental impact is essential. From an economic perspective, the viability of biomass gasification is challenged by its relatively high production cost, ranging from $1.21 to $2.42 per kilogram, with pyrolysis presenting similar costs at $1.21 to $2.19 per kilogram [10]. Therefore, improving hydrogen yield and exploring ways to lower operational temperatures are crucial for increasing both the sustainability and cost-effectiveness of biomass gasification, with particular emphasis on energy conservation.

However, the high production costs associated with biomass-based hydrogen ranging between $1.21 and $2.42 per kilogram for gasification and $1.21 to $2.19 per kilogram for pyrolysis pose a significant challenge to the economic viability of these processes. Enhancing hydrogen output and developing strategies to reduce reaction temperatures are key measures for improving the overall efficiency and sustainability of biomass gasification, particularly in terms of energy conservation.

Another thermochemical method is pyrolysis, combustion with steam reforming, hydrothermal liquefication and supercritical water reforming.

- **Pyrolysis**: This process entails heating biomass in an oxygen-free environment, leading to the release of gases such as hydrogen, methane, and carbon monoxide. An important environmental benefit of this approach is its potential for carbon neutrality, as the carbon dioxide emitted during pyrolysis can be balanced by the CO_2 uptake of plants during their growth cycle. In addition to offering a renewable pathway for hydrogen generation, pyrolysis also supports waste minimization by transforming biomass residues into useful by-products. Nevertheless, its commercial viability is currently limited by production costs, which range between $1.21 and $2.19 per kilogram. Therefore, advancing large-scale implementation is critical to improving the economic performance of this technology.
- **Combustion with Steam Reforming:** Biomass can be combusted to provide the energy needed for steam reforming of hydrocarbons or bio-oil, yielding hydrogen-rich gases. This hybrid approach combines combustion and catalytic reforming to optimize hydrogen output.
- **Hydrothermal Liquefaction and Supercritical Water Reforming:** In this method, wet biomass is processed in supercritical water (above 374°C and 22 MPa), which enhances the

breakdown of organic compounds into hydrogen and other gases. It is particularly suitable for biomass with high moisture content.[10]

2.2.2 Biological Processes

Expect from the thermochemical methods there are also the biological processes, such as fermentation and digestion by certain organisms. These organisms, such microalgae and cyanobacteria, break down the water molecules and produce biohydrogen. Initially, fermentation consists of dark fermentation and photo-fermentation.

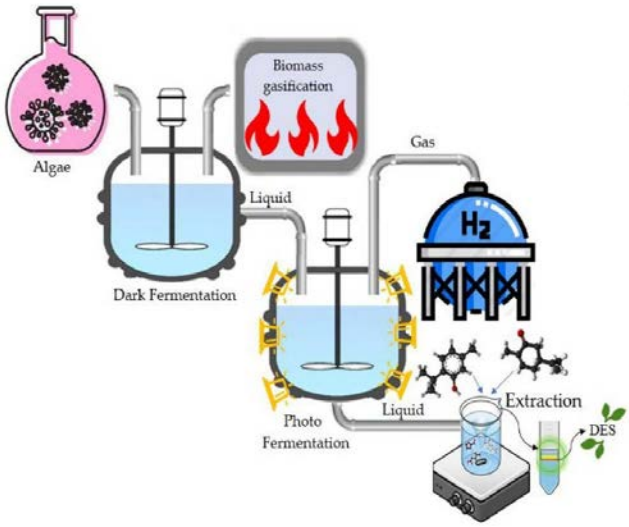
Dark fermentation is a light-independent biological process with significant potential for generating biohydrogen from biomass rich in organic content. This method involves the use of anaerobic microorganisms, both facultative and obligate, which decompose complex organic substrates into simpler compounds under oxygen-free conditions. Several operational factors, including temperature, pH levels, inoculum type, and hydraulic retention time play a crucial role in determining the overall hydrogen yield. Recent developments in this field have introduced the use of inorganic nanoparticles, such as iron and nickel, to improve process efficiency. These materials enhance enzyme activity and electron transfer mechanisms, leading to increased hydrogen production rates. Compared to photo fermentation, dark fermentation is considered more efficient in terms of energy consumption, making it a more sustainable and economical option.

In dark fermentation systems, the substrates utilized can range from organic waste and raw biomass to purified sugars. The microbial communities employ various metabolic pathways, with multiple enzymes facilitating the conversion of these substrates into hydrogen. Current research is focused on improving the hydrogen production rate and enhancing the process efficiency, allowing for greater yields from the same quantity of organic material. Conversely, photo fermentation relies on light energy to activate photosynthetic pathways in specific microorganisms. This process can produce hydrogen with a purity of approximately 58.90% and achieve a maximum energy conversion efficiency of 10.12%, as described by the following reaction:

$$16ATP + N_2 + 16H_2O + 10H^+ + 8e^- \rightarrow 16ADP + 2NH_4^+ + 16Pi + H_2$$

Adenosine diphosphate: Adenosine diphosphate (ADP) is a crucial molecule in cellular energy metabolism, playing a vital role in transferring and providing energy to cells.

Adenosine triphosphate: Adenosine triphosphate (ATP) is the primary energy-carrying molecule in cells, often called the "energy currency" of the cell



- **Figure 8**: Dark and photo-fermentation. [10]

Although photo fermentation can yield high hydrogen output, its dependence on sunlight limits its practicality and consistency under variable environmental conditions, especially when compared to the more robust nature of dark fermentation.

In the field of bacterial processes, anaerobic digestion plays an important role, where hydrogen gas can be produced through the anaerobic degradation of biomass by microorganisms, a process that may subsequently lead to the formation of methane or biogas. This method of anaerobic digestion represents an environmentally friendly and clean approach to energy generation, offering a sustainable alternative to fossil-based fuels. The underlying mechanism involves the microbial fermentation of organic substrates, resulting in the release of biogas.

In a study conducted by Malolan et al. (2020), the co-digestion of cow dung and chicken manure was shown to be effective for biogas production, achieving a 29% hydrogen yield on the tenth day of the process. Moreover, the use of microalgal biomass derived from digestate water further enhanced the generation of both hydrogen and methane. These results underscore the viability of anaerobic digestion as a cost-efficient and environmentally sustainable technology for biohydrogen production, while also promoting integrated waste management through a closed-loop system.

Furthermore, the application of bacterial inocula and biochar has been shown to improve hydrogen yields and facilitate the treatment of food waste leachate. Nonetheless, maintaining optimal environmental conditions, including temperature, pH, and substrate concentration is

critical for maximizing the conversion efficiency of fermentable materials into hydrogen fuel, thereby supporting its development as a renewable and sustainable energy source.

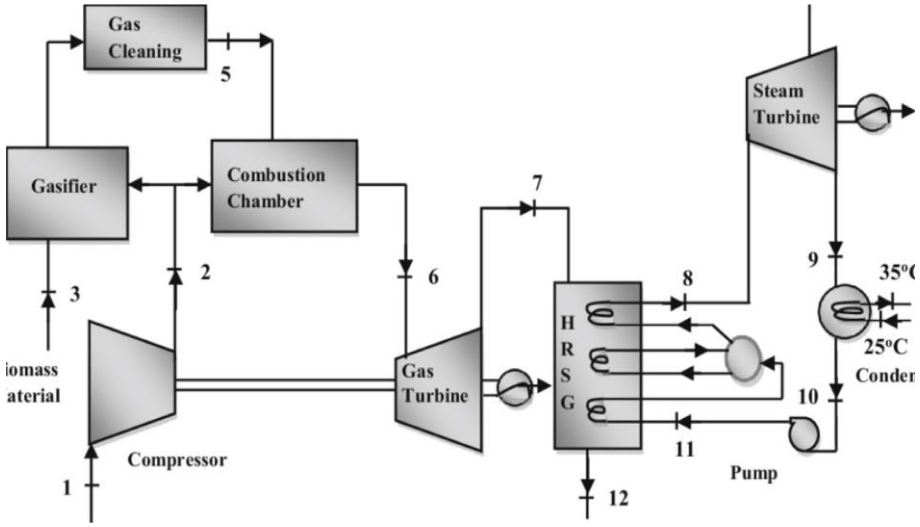
Furthermore, there are the electrochemical processes with the most known among them is water electrolysis, which is analyzed previously. However, microbial electrolysis is also important. This method has received increasing attention from the research community over the last decade due to its innovative approach to biohydrogen production. It relies on the catalytic activity of specific microorganisms to facilitate the conversion of organic matter into hydrogen. During this process, active bacterial species assist in the liberation of protons, electrons, and carbon dioxide from organic substrates. This biological mechanism is harnessed in Microbial Electrolysis Cells (MECs), a novel technology that enables the transformation of dissolved organic compounds in wastewater into storable chemical energy, particularly in the form of hydrogen gas.

In MEC systems, a small external voltage is applied in conjunction with the biological energy generated by microbial metabolism. This supplementary input is necessary to overcome the thermodynamic barrier associated with electrolysis. Exo-electrogenic microorganisms play a central role in this process by metabolizing substrates such as acetate and glucose, ultimately yielding high-purity hydrogen gas. However, the efficiency of this technology is currently constrained by limited hydrogen generation rates. To address these limitations, ongoing research efforts are directed toward enhancing hydrogen production efficiency through various strategies. These include the genetic improvement of microbial strains, optimization of reactor designs, and the selection of the most effective microbial consortia. In a notable study, Zhen He et al. proposed an enhancement to the microbial electrochemical system by integrating a dynamic membrane onto the anode electrode. This modification significantly improved system performance, resulting in increased current density, lower effluent turbidity, enhanced wastewater treatment, and greater energy recovery, in comparison to conventional systems lacking membrane integration.

2.2.3 Hybrid Processes

Finally, there are hybrid processes, which include gasification with gas shift reactors for water with steam methane reforming. A review of the literature highlights the

promise of thermochemical conversion methods for sustainable hydrogen production from biomass derived from responsibly managed forests**.** Among the various approaches, the highest biomass-to-hydrogen conversion efficiencies were achieved through integrated systems combining biomass gasification with water–gas shift reactors and steam methane reforming**.** These hybrid techniques enable enhanced hydrogen yields by maximizing the conversion of biomass-derived gases into hydrogen-rich streams.



- **Figure 9**: Integrated Biomass Gasification Cycle. [10]

- **Integrated Biomass Gasification**

Integrated biomass gasification is a thermochemical process that converts biomass into hydrogen and other byproducts using heat, steam, and oxygen under controlled conditions, without direct combustion, like figure 10 depicts. This method is a well-established route for hydrogen production from biomass and can be incorporated into existing forest product manufacturing facilities. Recent studies have explored the integration of high-temperature electrolysis with biomass gasification for synthetic methane production. Moreover, ongoing research is investigating the synergy between biomass gasification and renewable energy sources, such as solar and wind power, to assess potential technological advancements and address implementation challenges.

Decision matrices have proposed the use of biomass gasification in conjunction with direct wind energy or wind-electrolyzer systems, although their economic and technical feasibility remains underexplored. These strategies aim to improve syngas and fuel yields while laying the groundwork for renewable fuel production.

Two potential future research directions include:

- Direct integration of intermittent wind power with the electrical grid and indirectly heated biomass gasifiers, and
- The replacement of an electrolyzer in a directly heated biomass gasification system to co-generate fuel and power using local wind energy.

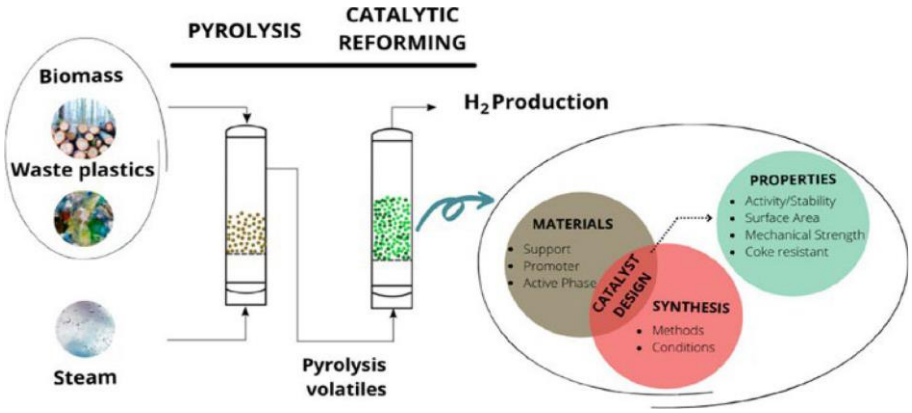
- **Hybrid Pyrolysis/Plasma Reforming**

An emerging approach for sustainable hydrogen production is the integration of pyrolysis and plasma-assisted reforming, which leverages the benefits of both methods to increase hydrogen yield. This hybrid technique utilizes cellulose pyrolysis followed by plasma-assisted reforming, optimizing the conversion of waste biomass into hydrogen.

A novel two-stage pyrolysis–plasma/catalysis process has demonstrated higher hydrogen and total gas yields compared to conventional pyrolysis–catalysis systems without plasma activation. The process performance depends on several parameters, including the catalyst type, reforming temperature, steam concentration, and discharge power, investigated using a coaxial dielectric barrier discharge plasma reactor.

Experimental results indicate that non-catalytic plasma reforming is favored at lower temperatures, while higher hydrogen selectivity and yields are obtained at elevated temperatures under catalytic conditions.

There is still a lack of reliable data regarding power consumption rates and accurate cost estimates for biomass-based hydrogen production. Further studies are essential to identify the most efficient and economically viable production pathways.



➢ **Figure 10**: Hybrid Pyrolysis/Plasma Reforming process route. [10]

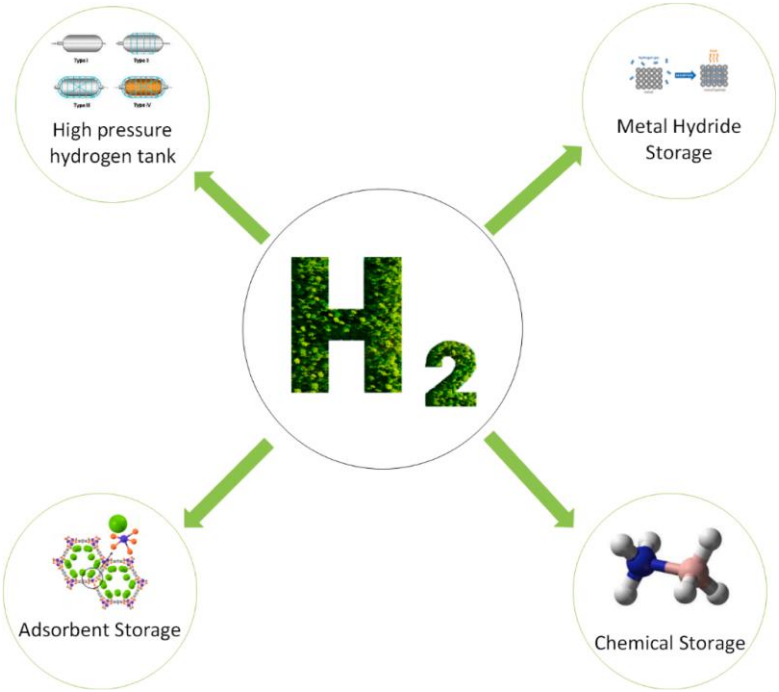
2.2.4 Hydrogen Purification

Concerning the hydrogen purification, polymers such as polysulfone (PSF) and cellulose acetate (CA) are commonly employed in the fabrication of hydrogen separation membranes and are readily available in commercial markets. In addition to polymer-based systems, dense metal membranes are also utilized for hydrogen separation applications.

A novel and promising approach in this domain is electrochemical hydrogen separation (EHS). This technique presents a significant advantage over conventional separation methods, as it enables the simultaneous compression and purification of hydrogen in a single operational step. Furthermore, EHS is characterized by lower energy requirements, negligible pollutant emissions, quiet operation, and a reduced environmental footprint.

Another established method is pressure swing adsorption (PSA), which can produce hydrogen with purities ranging from 98% to 99.999%. The integration of such technologies facilitates the efficient separation and purification of hydrogen, particularly when derived from biomass sources, thereby enhancing the overall performance of hydrogen production systems.

2.3 Methods of Storage



- **Figure 11**: H_2 storage [11]

H_2 is a desirable fuel, not only for its positive impact on the environment but for its high energy density which is seven times bigger than gasoline's. As a result, new methods of storage are

necessary to be found. Hydrogen storage technologies are highly dependent on the scale of storage and the specific operational conditions under which they are implemented. For large-scale applications, options such as underground hydrogen storage have been explored [6],while small-scale solutions often involve solid-state hydrogen storage systems. Nevertheless, the long-term and mid-term storage of hydrogen remains a subject of ongoing research, primarily due to the complex interactions between hydrogen and the materials involved. Current understanding of these interactions is still evolving. The most widely adopted approaches for large-volume hydrogen storage include the use of subsurface geological formations, such as underground caverns, depleted oil and gas reservoirs, aquifers, and abandoned mines.[11]

So, there are four categories of H_2 storage. Firstly, the high-pressure hydrogen tank, the metal hydride storage, the adsorbent storage and finally the chemical storage. This chapter will introduce and analyze the previous categories. Only the first category belongs to physical methods, because the other three belong to chemical methods. This separation of physical and chemical is general.

2.3.1 High Pressure Hydrogen Tank

To begin with the three main physical forms of hydrogen, which are the Compressed-Gaseous H_2 (CGH_2), Cryo-Compressed H_2 (CCH_2) and Liquid H_2 (LH_2). CCH_2 technology or cold/cryogenic compression can thermodynamically be considered a combination of compression and liquefication. A cryogenic tank must be structurally capable of containing cryogenic fluids to endure internal pressures. Compared to hydrogen storage at 700 bar under ambient conditions, the cryo-compression process requires fewer high-strength materials. Standard practice includes vacuum insulation and the use of durable materials to contain pressure, which are generally neither rare nor hazardous.Cryo-Compressed hydrogen storage tanks offer notable advantages for automotive applications, including high thermal durability and elevated storage density. However, hydrogen's cooling energy is often lost during venting and discharge. This study proposes a novel venting technique that incorporates a throttling valve to improve the efficiency of cryo-compressed hydrogen storage. The research investigates different operational conditions, such as initial and release pressures and various filling levels, during parking, discharging, and driving scenarios. Results show that using a throttling valve with a release pressure of 2 MPa can extend parking time by up to 55%. In cases where the tank has a high filling density and is parked for extended durations, the recovery of cooling capacity significantly prolongs storage time. Simulations of hydrogen storage pressures under driving

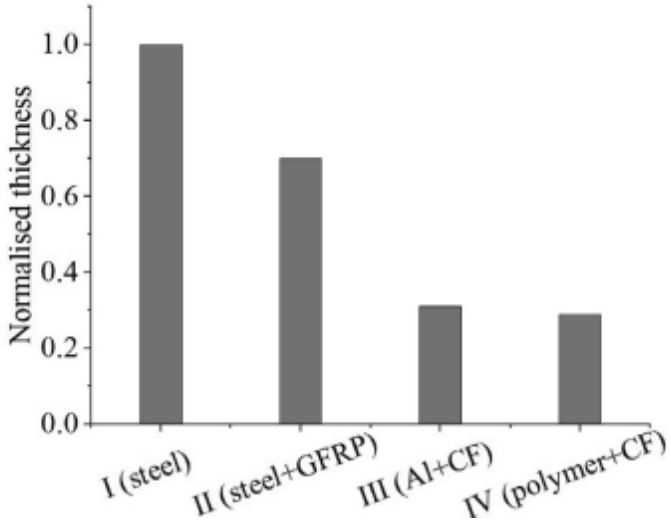
conditions demonstrate that throttling reduces the maximum operating pressure, leading to decreased investment requirements. Cryogenic hydrogen storage systems operate based on dynamic modeling principles and are engineered to accommodate both liquid hydrogen and hydrogen compressed up to 350 bar. To enable frequent and reliable refueling regardless of the tank's initial conditions, a dual flow refueling system is implemented. The thermodynamic state of the hydrogen during refueling depends on temperature: it is classified as a supercritical fluid when the temperature exceeds 120 K, and as a subcooled liquid when it falls below 100 K. Maintaining adequate internal pressure during storage requires the integration of an in-tank heating element. As hydrogen is withdrawn from the supercritical state, it undergoes phase transitions, first forming a two-phase mixture and eventually becoming a superheated gas. Efficient hydrogen delivery is ensured when the minimum pressure threshold is achieved and the heating element is adequately rated to sustain the required thermal load. The allowable duration for storing cryogenic hydrogen within the tank is influenced by both the internal storage pressure and the system's maximum permissible pressure. Notably, hydrogen cannot be extracted from the tank if evaporative losses remain below 64% of the theoretical storage capacity. This limitation underscores the importance of optimizing storage conditions to minimize energy loss and maximize fuel utilization. The incorporation of cryogenic pressure vessels within high-pressure hydrogen storage systems enables the storage of high-density hydrogen while minimizing evaporative losses, which are commonly observed in traditional liquid hydrogen systems. These vessels require less carbon fiber material, thereby offering increased storage capacity relative to structural weight. Their lightweight construction and rapid refueling capability make them well-suited for a broad range of applications, from short daily commutes to extended travel. Typically, cryogenic hydrogen storage is employed for longer-distance applications, whereas compressed hydrogen is more appropriate for shorter trips.

As the scale of cryo-compressed hydrogen storage systems increases, both thermal endurance and overall performance improve. Storage vessels with slender geometries and large capacities can attain higher system energy densities. In such configurations, simplified insulation designs with minimal thickness can provide adequate thermal endurance, particularly when optimized volume-to-surface area ratios are achieved. Nevertheless, the physical constraints of the available design space may influence vessel and insulation geometry, requiring a balance between cost-effectiveness, vehicle integration, and system efficiency. Compared to conventional liquid hydrogen tanks, the studied cryo-compressed vessels demonstrate thermal endurance that is five to ten times greater, while also significantly reducing evaporative losses.

These advantages highlight their potential for enhancing the practicality and performance of hydrogen storage systems in mobility applications.

The second and the most known way of storage is CGH_2, which has reached commercial maturity for both stationery and mobile applications. In contrast to liquid hydrogen (LH_2) storage, CGH_2 systems can utilize natural subsurface formations with limited porosity, such as salt caverns, as both containment structures and storage media. These underground formations, which may also include rock caverns and depleted oil or gas reservoirs, are primarily employed for large-scale stationary CGH_2 storage at pressures typically ranging from 50 to 200 bar. This pressure range results in a relatively low volumetric hydrogen density, approximately 10 g/L. Salt cavern-based storage offers several key advantages, including minimal hydrogen loss, substantial storage capacity, and lower capital investment compared to constructing purpose-built storage vessels. However, the feasibility of this approach is constrained by the limited availability of suitable natural or engineered geological formations, which are unevenly distributed globally. Furthermore, only select locations may meet the required geological and environmental criteria, thus restricting its broader implementation. When hydrogen stored in these caverns needs to be distributed, the development of transmission and distribution pipeline networks becomes necessary. This requirement further reduces the flexibility of this approach in adapting to emerging hydrogen supply and demand hubs, while the infrastructure development itself is both capital intensive and time consuming. An alternative CGH_2 storage method involves the use of pressurized tanks. These tanks are categorized into four types based on design and material composition. Type I and Type II tanks, due to their significant weight, are generally used for stationary storage. In contrast, Type III and Type IV tanks are more suitable for mobile applications. Type IV tanks, in particular composed of advanced composite materials, such as carbon fiber with a non-metallic liner, are capable of withstanding pressures between 700 and 1000 bar. This allows for an increase in volumetric hydrogen density to approximately 40 g/L at 700 bar. Analytically, **Type I tanks** are constructed entirely from metals, most commonly steel or aluminum alloys. These tanks are the most straightforward to manufacture, making them the most cost-effective among the five types. They can be produced in large capacities and typically operate at pressures around 200 bar. However, due to the inherently high density of metallic materials, Type I tanks are considerably heavy. As a result, their use is generally limited to stationary hydrogen storage in industrial settings or applications on large-scale platforms such as submarines, where space and weight constraints are less critical. **Type II tanks** are similar in design to Type I but incorporate an additional layer of

reinforcement. Specifically, the cylindrical body of the tank is wrapped with high-strength filaments such as carbon fiber or glass fiber. This wrapping allows Type II tanks to operate at higher pressures, typically around 300 bar, while maintaining structural integrity. Like Type I, these tanks are primarily used in stationary applications due to their weight and design characteristics. **Type III and Type IV tanks** have been developed to address the need for lightweight hydrogen storage solutions in automotive and other mobile applications. Both types feature full composite wrappings, usually made from high-performance carbon fibers such as Toray T700S or T800S. The key distinction between them lies in the liner material: Type III tanks employ a metallic liner, while Type IV tanks use a polymer-based liner. The liner serves primarily as a gas barrier, while the outer composite layer bears the mechanical load.



- **Figure 12**: Comparison of the overall thickness of different types of hydrogen tanks.[12]

For Type III tanks, the liner is often made from aluminum alloys such as AA6061 or AA7000, which offer favorable machinability and enhanced mechanical properties following heat treatment. Thanks to the high tensile strength (approximately 4900 MPa) and low density (1.80 g/cm³) of carbon fibers like T700S, both Type III and Type IV tanks are capable of withstanding much higher internal pressures than their metal-based counterparts. Additionally, they are significantly lighter, with reduced wall thickness. In fact, to endure the same internal pressure, the wall thickness of Type III and Type IV tanks is less than half that of Type I tanks, as demonstrated in Figure 13. Consequently, these advanced composite tanks enable the compression of hydrogen to higher densities, allowing more gas to be stored in smaller and lighter vessels, an essential feature for applications in lightweight and fuel-efficient vehicles[12].**Type V hydrogen tanks** represent the most advanced category of hydrogen storage vessels, being

constructed entirely from composite materials without any internal liner. These fully composite tanks are approximately 20% lighter than Type IV tanks and are engineered to tolerate even higher internal pressures, reaching up to 1000 bar. Despite their promising performance characteristics, Type V tanks are still in the developmental stage. Their widespread commercial application is currently limited due to the high cost associated with advanced composite materials, which poses a significant economic barrier to large-scale adoption. Despite their superior performance in portable scenarios, the relatively low storage density and high production cost of Type IV tanks make compressed hydrogen transport by road or ship economically unfeasible for large-scale or long-duration applications. Moreover, CGH_2 tanks are not easily scalable, which limits their utility to smaller and short-term hydrogen storage solutions.

Finally, the liquified H_2 is analyzed. Liquid hydrogen (LH_2) storage involves the conversion of hydrogen gas into its liquefied form to significantly enhance its volumetric energy density, making it more suitable for storage and transportation. This storage approach requires three essential components: a liquefaction unit to cool and condense the hydrogen gas into a liquid, a cryogenic storage tank to hold the liquid hydrogen, and a regasification system to convert it back to the gaseous phase for end use. One of the primary advantages of LH_2 storage is its high volumetric density, exceeding 60 g/L at 1 bar. However, this method faces two major challenges that hinder its broad commercialization: the extremely high energy demand associated with the liquefaction process and the inherent hydrogen losses due to boil-off, which typically range from 1% to 5%. Consequently, LH_2 storage remains in the late stages of development as efforts continue to improve its efficiency and economic feasibility [13].

Hydrogen Liquefaction Processes

Hydrogen liquefaction is a critical process for long-distance storage and transportation due to the increased volumetric energy density of liquid hydrogen (LH_2). Several liquefaction technologies have been developed and evaluated to reduce energy consumption and improve efficiency. The four primary hydrogen liquefaction processes are:

1. **Conventional Claude Cycle**:
   The Claude cycle is a well-established process involving isentropic expansion through turbines for cooling, along with regenerative heat exchange. While reliable, this method exhibits relatively high energy consumption, typically around 10–13 kWh/kg of LH_2, making it less favorable for large-scale deployment without optimization.
2. **Modified Claude Cycle with Turbine Energy Recovery**:

This improved version integrates a turbine-based energy recovery system and operates in a closed-loop with mixed refrigerants for pre-cooling. It significantly reduces energy consumption, achieving values near 6 kWh/kg of LH_2. The process is scalable and cost-effective for large plants and shows promise for commercial implementation.

3. **Dual-Cycle Cryogenic Process**:

   A more advanced configuration uses two independent cryogenic cycles to enhance liquefaction efficiency. Turbo-compressors are used, and the process can handle high liquefaction capacities (e.g., 100 tons per day). This method achieves high performance with lower power consumption (as low as 3.258 kWh/kg LH_2), making it a leading option for next-generation liquefaction facilities.

4. **Hybrid Mixed-Refrigerant Cycle**:

   This process uses a combination of precooling with mixed refrigerants followed by a cryogenic cycle for final liquefaction. It is particularly suitable for scaling-up and offers improved thermodynamic performance. Energy analysis shows favorable results, including a coefficient of performance (COP) of 0.1797 and process rational efficiencies exceeding 50%.

Hydrogen liquefaction, as mentioned before, is primarily considered for applications involving long-distance transportation, such as intercontinental hydrogen shipping. Nevertheless, there is also a need for small-scale liquid hydrogen (LH_2) storage in specific scenarios, including on-board storage for fuel cell vehicles and aviation applications. Based on its intended application, LH_2 storage can generally be categorized into two main types: stationary storage and mobile storage. Stationary storage refers to the on-site containment of liquid hydrogen at locations such as production facilities, end-user installations, or hydrogen-powered energy generation sites. In contrast, mobile storage includes the storage of LH_2 during transportation, whether by truck or ship, as well as its use for fueling vehicles and aircraft during operation. Cryogenic infrastructure, including storage tanks, pipelines, and refrigeration systems is specifically engineered to maintain the extremely low temperatures required for liquid hydrogen (LH_2) storage and transportation. However, heat ingress is inevitable during both storage and transmission, which becomes especially critical for long-duration storage or long-distance transport. This heat leakage causes the evaporation of liquid hydrogen, a phenomenon known as boil-off. Compared to its gaseous form, liquid hydrogen offers a significantly higher volumetric energy density, allowing a greater quantity of hydrogen to be stored within a fixed volume. Nonetheless, the generation of boil-off gas (BOG) increases the internal pressure of the storage or transport system. If this pressure is not properly managed, it can lead to serious safety hazards, including the risk of explosion. Although releasing small amounts of hydrogen into the atmosphere poses minimal environmental risk and is a simple disposal method, this approach results

in energy loss. Therefore, in order to improve safety and minimize waste, many hydrogen producers opt to capture and recycle the boil-off gas rather than venting it directly to the environment. Boil-off in liquid hydrogen storage systems is attributed to several contributing mechanisms, including the conversion of ortho-hydrogen to parahydrogen (a spin isomer transition), heat access from the external environment, thermal stratification, sloshing induced by mechanical motion, and flashing, which results from sudden phase transitions due to pressure or temperature fluctuations. A comprehensive explanation of each mechanism is provided below.

- ***Ortho- to Para-Hydrogen Conversion***

As previously discussed in Section 2, the conversion of ortho-hydrogen to parahydrogen is an exothermic process that contributes to hydrogen boil-off during storage. This transformation poses a significant challenge to the long-term storage and transportation of liquid hydrogen. To minimize associated energy losses, appropriate catalysts are introduced during the hydrogen liquefaction stage to accelerate the conversion process. Achieving a higher concentration of parahydrogen prior to storage reduces the amount of heat released from this isomeric transformation, thereby lowering the extent of hydrogen evaporation over prolonged periods.

- ***Heat Exchange with the Surrounding Environment***

Another major factor contributing to boil-off is thermal pressure from the external environment. Since liquid hydrogen must be stored at extremely low temperatures (~−253 °C), well below ambient conditions, efficient cryogenic insulation is essential. Nevertheless, complete elimination of heat transfer is unachievable, and some degree of thermal loss is inevitable. The rate of boil-off gas (BOG) generation is influenced by both the quality of the insulation and the surface-to-volume ratio of the storage vessel. For instance, a 50 m^3 cryogenic tank may experience BOG rates of approximately 0.4% per day, whereas a significantly larger 20,000 m^3 tank may exhibit rates as low as 0.06% per day. Effective thermal management strategies are therefore critical for enhancing the efficiency of liquid hydrogen storage systems. Two main approaches are typically employed. First, to reduce the surface-to-volume ratio and consequently, the thermal exposure large-scale spherical or cylindrical adiabatic tanks are commonly utilized. Second, the selection of insulating materials plays a crucial role, with a focus on low thermal conductivity materials to minimize heat transfer into the tank. To mitigate heat transfer into cryogenic hydrogen storage systems, advanced insulation techniques are employed. A double-wall structure with a vacuum layer is commonly used to suppress heat transfer through both convection and conduction. Additionally, multilayer

insulation (MLI) and variable-density multilayer insulation (VD-MLI) are implemented to minimize radiative heat transfer. To further improve storage efficiency, some systems incorporate a vapor-cooled shield (VCS), which utilizes self-evaporation to absorb incoming thermal energy, thereby enhancing overall thermal performance.

- ***Sloshing***

Sloshing refers to the internal motion of liquid hydrogen within the storage tank, often caused by vehicle acceleration, deceleration, or mechanical vibrations during transport. This phenomenon not only contributes to increased boil-off rates but may also compromise the structural integrity of the tank wall. The intensified movement results in additional heat transfer to the liquid through the dissipation of kinetic energy and expands the contact area between the liquid and vapor phases, thereby accelerating evaporation.

- ***Flashing***

Flashing occurs when liquid hydrogen is transferred from a high-pressure environment to a lower-pressure tank. This sudden pressure drop induces partial vaporization of the liquid hydrogen, contributing to immediate boil-off and increasing the complexity of managing system pressure stability during transfer operations.

- ***Thermal Stratification and Overfilling***

When thermal leakage occurs within the storage tank, the evaporated hydrogen initiates natural convection, driven by buoyancy effects, which in turn raises the internal pressure. Due to the density difference between the liquid and vapor phases, a relatively stable liquid-vapor interface can form. If the tank is overfilled, or if thermal stratification becomes pronounced, pressure control and boil-off management can become increasingly difficult, posing operational and safety challenges.

Materials selection for cryogenic application

Materials used in liquid hydrogen (LH_2) storage systems must satisfy a range of stringent criteria, including resistance to hydrogen embrittlement and permeation, mechanical integrity, thermal durability, and resilience to fire and elevated temperatures. Hydrogen embrittlement is a critical issue, characterized by the deterioration or cracking of metallic materials upon exposure to hydrogen, which can occur under both cryogenic and ambient conditions. This phenomenon is

influenced by variables such as temperature, pressure, and the intrinsic strength of the alloy. Although the primary mechanism involves hydrogen atoms infiltrating the metal lattice at the atomic scale, the resulting effect is macroscopic degradation, often manifesting as a reduction in the structural strength of materials like steel. Notably, hydrogen embrittlement is less severe with liquid hydrogen than with gaseous hydrogen, due to the reduced rate of hydrogen diffusion at lower temperatures. Stainless steels are the most employed materials for liquid hydrogen storage applications due to their favorable balance of strength, corrosion resistance, and low-temperature performance. Different stainless-steel grades exhibit unique properties based on their alloying elements. For example, 316L stainless steel, which contains molybdenum (Mo), offers enhanced resistance to chloride-induced corrosion, making it particularly suitable for use in marine or coastal environments. Meanwhile, 321 stainless steels, alloyed with titanium (Ti), demonstrates superior resistance to intergranular corrosion and retains high strength at elevated temperatures, making it appropriate for heat-intensive applications.

To further enhance the hydrogen embrittlement resistance of stainless steels, various surface modification and protection techniques have been investigated. These include surface coatings, cathodic protection, ion implantation, and laser shot peening, all of which aim to extend the material's lifespan and reliability in hydrogen-rich cryogenic conditions. A major limitation in adopting lightweight composite materials for liquid hydrogen storage is hydrogen permeation, which continues to pose a significant barrier to their widespread application.[13]

2.3.2 Metal Hydride Storage

The next category of storage is metal hydride materials. Prior to assessing the applicability of distinct metal hydride systems for various uses, it is imperative to remember and compare their principal material characteristics. The two foremost metrics in the comparison of hydrogen-storage technologies are the gravimetric storage capacity and the volumetric energy density. The gravimetric storage capacity (expressed in weight percent, wt. %) is defined as the ratio of the mass of hydrogen absorbed at maximum uptake to the mass of the hydride material. The volumetric energy density (expressed in kWh/dm^{-3}) is given by:[14]

$$\mathrm{Ved} = \frac{\mathrm{mH2}*\mathrm{LHV}}{\mathrm{VMH}} \quad (2.1)$$

where:

- M_{H2} denotes the mass of hydrogen absorbed at saturation,

- LHV is the lower heating value of hydrogen (approximately 120 MJ kg^{-1}), and
- V_{MH} represents the volume of the hydride material.

Among interstitial hydrides, gravimetric capacities typically lie in the range of 1–2 wt.%, whereas complex hydrides can exhibit markedly higher values. For example, lithium borohydride ($LiBH_4$) attains a theoretical maximum gravimetric capacity of 18.5 wt. %. To delineate the operational pressure and temperature domains of different hydride materials, one employs pressure–concentration-isotherms (PCI; also referred to as pressure–composition–temperature or PCT diagrams) alongside van 't Hoff plots. The van 't Hoff relationship is described by:

$$\ln\left(\frac{Peq}{P0}\right) = -\frac{\Delta H}{R*T} + \frac{\Delta S}{R} \quad (2.2)$$

Where,

- Peq is the equilibrium pressure,
- P_0 is the reference pressure (typically 1 bar),
- ΔH and ΔS are the reaction enthalpy and entropy of the ad-/desorption, respectively
- R is the universal gas constant, and
- T denotes the absolute temperature

While ΔS remains relatively uniform across most hydrides owing principally to the entropy change of the hydrogen gas phase ΔH varies substantially. Low-temperature hydrides, characterized by smaller reaction enthalpies, permit hydrogen uptake and release near ambient conditions. Consequently, strategies such as elemental substitution or alloying to reduce ΔH, are of significant interest for enhancing the practical performance of metal hydride storage systems.[14]

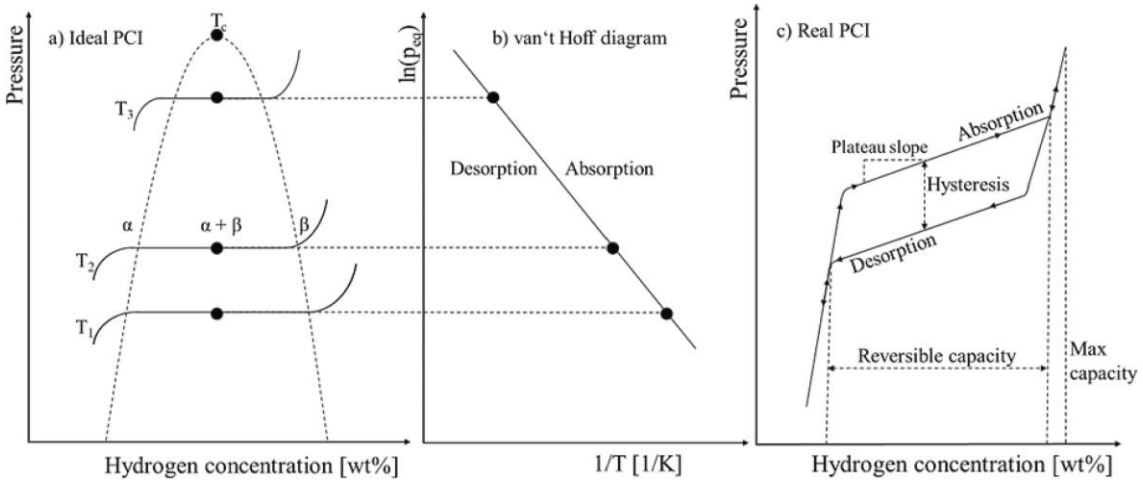
The equilibrium pressure (Peq), as defined by the Van't Hoff equation, corresponds to the pressure at the midpoint of the plateau region in a pressure–concentration isotherm (PCI) curve (see Fig. 13a). For the hydrogen absorption reaction to proceed, the pressure of the surrounding hydrogen gas must exceed the equilibrium pressure at the given temperature. In contrast, during hydrogen desorption, the ambient hydrogen pressure must be lower than the equilibrium pressure.

As indicated by Equation (2.2), the equilibrium pressure increases with temperature. Since the absorption process in most metal hydrides is exothermic, the heat released during hydrogen uptake

leads to a rise in temperature. This temperature increase consequently elevates the required hydrogen pressure for continued absorption. In the absence of an effective thermal management system, this self-heating effect can inhibit the reaction, significantly prolonging the refueling time.

Similarly, during the desorption process, an adequate heat supply is necessary to maintain the temperature required to achieve the desired hydrogen pressure for release. In real-world conditions, the isotherms depicted in PCI diagrams do not exhibit perfectly flat plateaus; instead, they show a slope and hysteresis between the absorption and desorption branches (see Fig. 13c). Certain hydride materials, such as TiFe, may even exhibit multiple plateau regions corresponding to different phase transitions.

The gradient of the pressure plateau with respect to the hydrogen content and the presence of hysteresis must be carefully considered when defining the operational range. These factors significantly influence the reversible hydrogen capacity, which is critical for achieving efficient and practical hydrogen storage performance.



- **Figure 13**: a) Ideal PCI at different temperatures with the corresponding b) van't Hoff plot and c) real PCI with hysteresis and plateau slope.[14]

Most interstitial hydride materials are capable of operating under ambient or near-ambient conditions, typically within a temperature range of 0–100 °C and a pressure range of 1– 40 bar. This operational flexibility represents a major advantage over conventional compressed gaseous hydrogen (CGH_2) storage, which typically requires 200–1000 bar, and liquid hydrogen (LH_2) storage, which necessitates cryogenic conditions at approximately 20 K. [10]

Elemental hydrides (e.g., MgH_2) and complex hydrides also function at relatively low pressures; however, they require substantially higher operating temperatures, generally within the range

of 100–400 °C, depending on the specific material. One of the most frequently cited drawbacks of metal hydride-based hydrogen storage, in comparison to CGH_2 and LH_2, is the prolonged refueling and discharge times, which arise from slow reaction kinetics. Kinetic behavior varies significantly across different hydride materials and is influenced both by intrinsic material properties and external operating conditions. For interstitial hydrides in particular, the reaction rate is seldom limited by intrinsic kinetics. Instead, the rate-limiting factors are often associated with thermal management issues, specifically the efficiency of heat transfer or contaminants present within the hydride material.

Recent research efforts aimed at improving kinetic performance have focused on two principal approaches:

1. Enhancement of material properties, such as through partial elemental substitution, or the incorporation of dopants and catalysts, to promote faster hydrogen absorption and desorption.
2. Improvement of thermal conductivity, which is essential for effective heat transfer during operation. Strategies include the use of high-conductivity support structures (e.g., aluminum foams) and optimized container designs, incorporating features such as cooling channels and heat transfer ribs.

As previously noted, the presence of impurities can adversely affect the kinetics of metal hydrides. Therefore, tolerance to contamination is another critical parameter in material selection. Common contaminants in hydrogen gas, originating from various production and purification methods include O_2, H_2O, CO, CO_2, N_2, NH_3, and a range of hydrocarbon compounds. The presence of impurities in hydrogen gas can result in various adverse effects on metal hydride materials. These effects include:

- **Poisoning**, which leads to a permanent reduction in hydrogen storage capacity,
- **Retardation**, characterized by a significant decrease in reaction kinetics,
- **Undesired chemical reactions**, such as **corrosion**, and
- **Inert gas blanketing**, which inhibits hydrogen diffusion and reaction.

The lifetime of a metal hydride material is primarily assessed by its long-term cyclic stability, defined as the material's ability to retain its hydrogen storage capacity over multiple absorption–desorption cycles. Through repeated hydrogen cycling, metal hydrides are subject to both

physical and chemical degradation mechanisms, which cumulatively result in a gradual loss of usable capacity over time. Although metal hydrides are generally considered safer than high-pressure gaseous hydrogen systems, due to the reduced risk of explosion, certain safety considerations remain. Several hydride materials are pyrophoric and may ignite upon exposure to air, particularly in the event of container failure or rupture. Additional hazards arise from the toxicity of some compounds and the potential for accidental inhalation of fine hydride powders, necessitating appropriate handling protocols and containment strategies during system operation and maintenance.

This chapter focuses on the synthesis, activation, handling, and property enhancement of selected metal hydride materials. The selection criteria for these materials are based on their promising performance as reported in the literature, as well as their relevance in commercial or demonstration-scale applications. To ensure a representative overview, materials from different hydride classes are included.

Among the elemental hydrides, magnesium and magnesium hydride (Mg/MgH_2) are selected due to their well-documented storage potential. From the interstitial hydrides**,** TiFe**,** $TiMn_2$**,** and $LaNi_5$ are examined as representative compounds of the AB**,** AB_2**,** and AB_5 subgroups, respectively. Within the class of complex hydrides**,** sodium alanate ($NaAlH_4$)**,** a widely studied material in the alanate family is chosen. Finally, lithium borohydride ($LiBH_4$) is included owing to its distinction as the metal hydride material with the highest theoretical gravimetric hydrogen capacity. Tailoring the performance characteristics of metal hydride alloys through material modification techniques is a common approach to improve storage performance.

The most promising enhancement strategies include:

- Doping**,** particularly with catalytic additives to improve kinetics,
- Alloying or elemental substitution, depending on the specific property targeted,
- Reduction of particles or grain size, often achieved through mechanical ball milling,
- Application of severe plastic deformation (SPD) to refine microstructure,
- Thermal treatment (annealing) to enhance phase stability and performance consistency.

These strategies aim to optimize hydrogen sorption kinetics, capacity, thermal conductivity, and overall cycling stability of the hydride materials under practical operating conditions.

This chapter outlines the synthesis methods, activation procedures, handling considerations, and property enhancement strategies for selected metal hydride materials. The materials were chosen based on their relevance in current literature and existing commercial or demonstration-scale applications. They represent a range of hydride classes: MgH_2 (elemental hydride), TiFe, $TiMn_2$, $LaNi_5$ (interstitial hydrides of AB, AB_2, and AB_5 types), and $NaAlH_4$ and $LiBH_4$ (complex hydrides from the alanates and borohydrides groups, respectively).

Magnesium Hydride (MgH_2)

Synthesis methods for MgH_2 include mechanical milling, chemical vapor deposition, plasma metal reactions, melt spinning, chemical reduction, electrochemical deposition, and thin film techniques. A straightforward method involves the direct hydrogenation of magnesium at temperatures above 400 °C under elevated hydrogen pressure. Activation is often necessary due to the formation of a passivating oxide layer upon air exposure, which hinders hydrogen absorption. It typically involves thermal cycling in a hydrogen atmosphere (400–450 °C) or mechanical activation (e.g., ball milling in hydrogen). Handling requires strict exclusion of air and moisture, as reoxidation of the surface degrades performance.

Enhancements focus on:

- **Catalytic doping** with transition metals or alloys (e.g., Ni, Fe, Ti, $TiMn_2$, $ZrMn_2$), which lowers the dehydrogenation temperature and activation energy.
- **Carbon-based additives** (e.g., CNTs, graphene) that improve cycling stability.
- **Nanoscaling** (3–50 nm particles) achieved through high-energy ball milling or chemical methods, which increases diffusion rates and kinetics.
- **Nanoconfinement** in porous scaffolds (e.g., carbon aerogels, CMK-3, SBA-15) to inhibit particle agglomeration during cycling.
- **Hybrid hydride mixtures** (e.g., MgH_2-AlH_3-$NaAlH_4$) to improve both kinetics and capacity.

Titanium Iron (TiFe)

TiFe alloys are produced via arc or induction melting from high-purity raw materials under inert atmospheres. Alternative methods include electrochemical reduction and high-energy mechanical alloying, though these remain cost- and energy-intensive. Activation is a key step, often involving repeated hydrogenation/dehydrogenation cycles at 400–450 °C and ~65 bar. Enhanced activation can be achieved via ball milling, severe plastic deformation, or alloying

with elements such as Mn, Pd, or Zr. Handling is sensitive to oxidation; the formation of TiO_2 significantly inhibits hydrogen diffusion. Exposure to air must be minimized.

Enhancements include:

- **Elemental substitution** (e.g., Mn, V, Co, Zr) to improve activation, plateau pressure, and cycling stability.
- **Surface treatments**, such as Pd coating, to restore activity after air exposure.
- **Hybrid hydride additions** (e.g., $TiMn_2$) to combine beneficial properties.

Titanium Manganese ($TiMn_2$)

$TiMn_2$ alloys are typically synthesized through arc or induction melting, followed by annealing at ~1000 °C for 24–72 hours. The resulting non-stoichiometric Laves phases ($TiMn_x$, x = 0.75–2) are hydrogen-active. **Activation** is simple and usually does not require thermal or mechanical treatments. However, performance can be enhanced through annealing and ball milling. Handling must occur under inert conditions due to Mn's high oxygen affinity.

Enhancements focus on:

- **Elemental substitution** (e.g., Zr, Cr, V, Ni, Al, Cu, Fe) to reduce plateau pressure, improve reversibility, and lower hysteresis.
- **Optimization of composition**, such as Hydralloy C5, to tailor kinetics and storage performance for specific applications.

Lanthanum Nickel ($LaNi_5$)

$LaNi_5$ is produced via arc, induction, or electron-beam melting. An alternative method involves the reduction of La_2O_3 and Ni using CaH_2, followed by chemical separation.

Activation is rapid and requires only low-temperature hydrogen cycling (<100 °C, <100 bar). Mechanical treatments such as ball milling can negatively affect capacity due to over-stabilization of hydride phases but can be partially reversed by annealing. Handling is less sensitive to air exposure compared to other hydrides. $LaNi_5$ exhibits a self-restoring surface mechanism, often attributed to in-situ Ni regeneration.

Enhancements include:

- **Partial substitution** of Ni with Al, Mn, or Co to reduce plateau pressure and improve cycling life.
- **Substitution of La** with Ce, Pr, Nd, or mischmetals to improve stability, although at the cost of higher plateau pressures.

Sodium Alanate ($NaAlH_4$)

$NaAlH_4$ is synthesized by ball milling NaH and Al powders under hydrogen atmosphere (130 °C, 90 bar). High-energy reactive ball milling offers a one-step alternative. Recycled aluminum can also be used as a cost-effective precursor. Activation and handling require inert conditions due to $NaAlH_4$'s pyrophoric and toxic nature.

Enhancements focus on:

- **Doping with Ti-based catalysts** (e.g., $TiCl_3$) to enable reversibility at moderate temperatures (~100 °C) and pressures (100 bar).
- **Other dopants**, such as $ScCl_3$ and $CeCl_3$, which further improve kinetics and cyclic stability.
- **Carbon-based and MOF-based additives** (e.g., CNTs, graphene, MIL-125(Ti)) to enhance hydrogen uptake and reversibility.

Lithium Borohydride ($LiBH_4$)

$LiBH_4$ is produced through various chemical routes, including direct hydrogenation of Li and B, or cation exchange from $NaBH_4$ in solvents like THF. Practical synthesis methods aim to lower costs and simplify production. Handling is critical, as $LiBH_4$ ignites in humid air and poses safety risks.

Enhancements are aimed at overcoming its high desorption temperature and poor reversibility:

- **Metal doping** (e.g., with Fe, Ti, Ni) to destabilize the hydride and lower desorption energy.
- **Cation/anion substitution** (e.g., $LiZn_2(BH_4)_5$, $LiBH_3F$) to tune thermodynamics.
- **Catalyst addition** (e.g., $TiCl_3$, ZnF_2) to reduce the dehydrogenation temperature to below 100 °C.
- **Nanostructuring and nanoconfinement**, achieved through MFPVD or embedding in porous matrices, to improve kinetics and cycle stability.

2.3.3 Adsorbent Storage

In physisorption-based hydrogen storage, hydrogen molecules are adsorbed onto the surface of solid materials through van der Waals forces, rather than forming chemical bonds as in many metal hydrides and complex metal hydrides. This form of storage is fully reversible, allowing for rapid adsorption and desorption cycles, which translates into fast refueling capabilities without significant technical barriers. The enthalpy of adsorption and desorption is relatively low, typically between 1 and 10 kJ/mol, which simplifies the thermal management during operation. Furthermore, this process does not involve any chemical transformations, thus eliminating hydrogen losses due to byproduct formation. Candidate materials for physisorption storage include microporous carbons, metal-organic frameworks (MOFs), and zeolites, all known for their high surface areas, a critical requirement since physisorption is inherently a surface phenomenon. Carbon-based adsorbents, especially activated carbons, can be engineered to exhibit high surface areas. Zhou et al. reported that activated carbon can achieve a hydrogen uptake of approximately 5 wt.% at 77 K and 30–60 bar. Single-walled carbon nanotubes (SWCNTs) have also shown promising storage capacities, with Zhao et al. reporting 1.73 wt% at 77 K and 10 MPa. However, at room temperature, Liu et al. found that various carbon nanotubes (SWCNTs and MWCNTs), even with post-treatment, exhibit storage capacities below 1.7 wt.% at 12 MPa**.** Zeolites, which are microporous crystalline aluminosilicates, also offer notable surface areas for adsorption. For instance, CaX zeolite has demonstrated a hydrogen uptake of 2.19 wt.% at 15 bar and 77 K, while NaX zeolite showed 2.55 wt.% at 77 K and 40 bar. However, performance significantly declines in ambient conditions; Du and Wu reported a drop to 0.4 wt.% at 20 °C and 40 MPa. Similarly, USY zeolite has shown a maximum capacity of 0.4 wt.% at 30 °C and 50 bar, as reported by Chung. Among all physisorption materials, metal-organic frameworks (MOFs) stand out for their exceptionally high surface areas and structural tunability. For example, MOF-210 has a recorded surface area of 6240 m^2/g, and a hydrogen uptake of 7.9 wt.% at 77 K and 80 bar**.** MOF-5, according to Li et al., has a storage capacity of 4.5 wt.% at 77 K and near ambient pressure, which reduces to 1.0 wt.% at room temperature and 20 bar. Farha et al. reported that NU-100, with a surface area of 6143 m^2/g, can store up to 9.0 wt.% at 56 bar and 77 K. However, as noted by Langmi et al., the storage capacities of MOFs at room temperature generally remain below 1 wt%. Additionally, the low thermal conductivity of MOFs approximately 0.3 W/(m·K) poses challenges for heat dissipation during rapid cycling.

Chapter 3: Applications of Green Hydrogen

Green hydrogen, produced via the electrolysis of water using electricity from renewable energy sources, presents a promising solution for decarbonizing various sectors of the economy. Its versatility allows for integration into multiple applications, ranging from energy systems to industrial and transportation infrastructure. The primary areas of application are outlined below:

- *Electric Power Generation*: Green hydrogen can be converted into electricity through fuel cells or combustion in gas turbines, offering a clean and efficient power source suitable for residential, commercial, and industrial use.
- *Transportation*: As a zero-emission fuel, green hydrogen is suitable for use in a wide range of transport modes, including passenger vehicles, buses, heavy-duty trucks, trains, and marine vessels. Hydrogen-powered fuel cell vehicles emit only water vapor, offering a sustainable alternative to conventional internal combustion engines.
- *Renewable Energy Storage*: Green hydrogen serves as an energy storage medium that supports the intermittency of solar and wind power. Surplus electricity generated from renewables can be used to produce hydrogen, which is then stored and later reconverted to electricity during periods of high demand or low generation.
- *Industrial Applications*: Many industries, including steel manufacturing, chemical production, and oil refining, utilize hydrogen as a key input. Replacing fossil-derived hydrogen with green hydrogen in these processes can significantly reduce associated carbon dioxide emissions.
- *Synthetic Fuel Production*: Green hydrogen can react with captured CO_2 to produce synthetic fuels such as methane, methanol, ammonia, and other hydrocarbons. These can be employed in sectors such as transport and energy or used as feed stocks in chemical industries.
- *Heating Systems*: Green hydrogen can be applied in thermal energy systems for space and water heating in residential, commercial, and industrial buildings. It can either be burned in hydrogen-compatible boilers or used in fuel cell-based combined heat and power (CHP) systems, contributing to the decarbonization of the heating sector.
- *Aviation*: Ongoing research is investigating the use of green hydrogen as a sustainable aviation fuel. Although still at an early stage of development, it offers the potential to drastically lower the carbon footprint of the aviation industry.

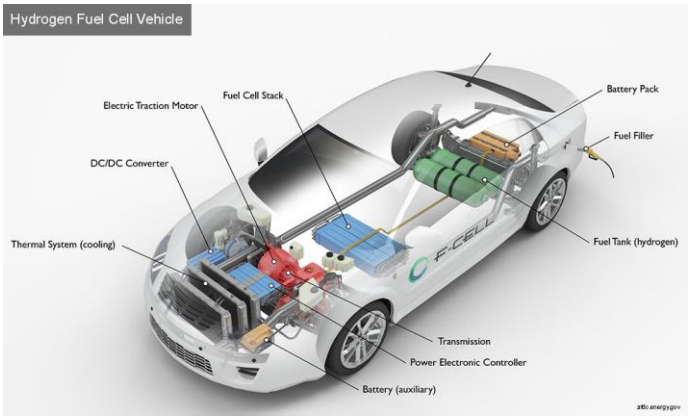
- *Agriculture*: Green hydrogen can facilitate sustainable fertilizer production by serving as a precursor in the synthesis of ammonia, thereby mitigating the environmental impacts of traditional ammonia manufacturing methods.
- *Hydrogen Infrastructure (Grids)*: The establishment of hydrogen pipeline networks, akin to natural gas distribution systems, can enable the transport and distribution of green hydrogen to diverse end-users. These grids support the integration of renewable energy, improve system efficiency, and promote the scalability of hydrogen technologies across sectors.

3.1 Green Hydrogen in Transportation

Green hydrogen is gaining recognition as a transformative and sustainable energy carrier in the transportation sector, offering a zero-emission alternative to conventional fossil fuels. Hydrogen fuel cell electric vehicles (FCEVs)**,** including cars, buses, trucks, trains, and ships leverage hydrogen's high energy density, which enables extended driving ranges and rapid refueling times. These advantages position hydrogen as a particularly viable solution for heavy-duty and long-distance transport, where battery-electric vehicles often face challenges related to weight limitations and limited range. The replacement of diesel and gasoline fuels with green hydrogen can significantly contribute to reducing air pollution and greenhouse gas emissions, particularly in hard-to-electrify segments of the transportation industry. As advancements in hydrogen technologies and infrastructure progress, the deployment of hydrogen across diverse transportation modes holds the potential to redefine mobility and promote a low-carbon, clean energy future. Despite its potential, the infrastructure for transporting green hydrogen remains underdeveloped. Currently, hydrogen is often distributed via existing natural gas pipelines, which are not optimized for hydrogen and result in energy losses during transport. Furthermore, long-term use of these pipelines for hydrogen distribution may lead to material degradation due to hydrogen embrittlement, increasing the risk of cracking and leakage. In the short term, blending hydrogen with natural gas offers a partial mitigation strategy, but upgrading and expanding dedicated hydrogen infrastructure will be essential for safe, efficient, and large-scale deployment.

3.1.1 Automobiles

- ***What are FCEVS?***



➢ **Figure 14**: Parts of hydrogen Fuel Cell Vehicle. [15]

Fuel Cell Electric Vehicles (FCEVs) are a class of electric vehicles that utilize compressed hydrogen gas as a fuel source. They operate using a fuel cell system, which serves as a high-efficiency energy converter, directly transforming hydrogen into electricity through an electrochemical reaction. This generated electricity powers the vehicle's electric motor, enabling propulsion without combustion and producing only water vapor as a by-product. [15]

- **Hydrogen Fuel Cell Vehicle Technology**

Hydrogen fuel cell vehicles (HFCVs) represent an advanced and environmentally friendly alternative to conventional internal combustion engine vehicles. These vehicles utilize hydrogen gas as the primary fuel, which is electrochemically converted into electricity through a fuel cell system, powering an electric motor. This technology produces zero tailpipe emissions, with water as the only by-product. Hyundai, Toyota, and Honda, some of the prominent automobile manufacturers, announced a high level of FCEV production in 2020. Hyundai Nexo accounted for 63% of total sales in 2019, Toyota Mirai accounted for 32%, and Honda Clarity Fuel Cell accounted for less than 5%.

- **Fuel Cell Technology and Its Role in HFCVs**

At the core of HFCVs lies fuel cell technology, which enables the electrochemical conversion of hydrogen into electrical energy. The basic fuel cell consists of three key components: an anode, a cathode, and an electrolyte membrane.

When hydrogen gas is introduced to the anode, it undergoes oxidation, where hydrogen molecules are split into protons (H^+) and electrons (e^-), a reaction facilitated by a platinum catalyst, as the following equation:

$$H_2 \rightarrow 2H^+ + 2e^-$$

The protons pass through the electrolyte to the cathode, while the electrons flow through an external circuit, generating an electric current that powers the vehicle's electric motor. At the cathode, O_2 from the ambient air reacts with the protons and electrons to form water:

$$O_2+4H+4e^-\rightarrow 2H_2O$$

This continuous electrochemical reaction ensures a steady supply of electricity for vehicle propulsion. Fuel cells represent a diverse group of electrochemical energy conversion devices, with several types developed for various applications. Common fuel cell technologies include proton exchange membrane fuel cells (PEMFCs), solid oxide fuel cells (SOFCs), phosphoric acid fuel cells (PAFCs), alkaline fuel cells (AFCs), molten carbonate fuel cells (MCFCs), and batteries, among others.

These fuel cells are categorized based on their operating temperatures:

- Low-temperature fuel cells: AFCs and PEMFCs
- Medium-temperature fuel cells: PAFCs
- High-temperature fuel cells: MCFCs and SOFCs

Each type is either currently used in commercial applications or is under active research and development. Table 2 presents the relationship between operating temperature and output power across different fuel cell technologies.[16]

PEMFCs are highly versatile and demonstrate strong potential for deployment across various energy scales. They are already used in automotive, portable, and stationary power generation applications, and their applicability is expected to expand further in the future. However, a key challenge facing PEMFC technology is the issue of hydrogen storage. The need for large, external hydrogen storage systems limits the feasibility of PEMFCs in portable electronics. Additionally, when PEMFCs are integrated into residential energy systems, the risk of hydrogen leakage poses a safety concern that must be carefully managed.

- **Electrochemical Principles of Hydrogen Fuel Cells**

The chemical reactions in hydrogen fuel cells are governed by redox (reduction–oxidation) principles, involving the transfer of protons and electrons within the cell. The anode facilitates the oxidation of hydrogen, while the cathode supports the reduction of oxygen. At the anode, hydrogen dissociates into protons and electrons under the action of a platinum catalyst. The protons move through the proton exchange membrane (PEM), while electrons are directed through an external circuit to generate usable electric power. At the cathode, the oxygen molecules combine protons and electrons to produce water:

$O_2+4H+4e^- \rightarrow 2H_2O$

The overall chemical reaction in a hydrogen fuel cell is:

$2H_2+O_2 \rightarrow 2H_2O$

This reaction illustrates that water is the sole emission, highlighting the fuel cell's environmental sustainability and clean energy potential.

Table 2: Major type of fuel cell

	PEMFCs	AFCs	PAFCs	MCFCs	SOFCs
Electrolyte	Polymeric membrane	Potassium hydroxide	Phosphoric acid	Molten carbonate	Ceramics
Change carrier	H^+	OH^-	H^+	CO_3^{2-}	O^{2-}
Operating temperature	-40-120ºC (150-180°C in high temp PEMFCs)	50-200 ºC	150-220 ºC	600-700ºC	500-1000 ºC
Electrical efficiency	Up to 65-72%	Up to 70%	Up to 45%	Up to 60%	Up to 65%
Primary fuel	H2, reformed H2, methanol in direct methanol fuel cells	H2 or cracked ammonia	H2 or reformed H2	H2, biogas, or methane	H2, biogas, or methane
Primary applications	Portable, transportation, and small-scale stationary	Portable and stationary	Stationary	Stationary	Stationary
Shipments in 2019	934.2 MW	0 MW	106.7 MW	10.2 MW	78.1 MW

- **Design and Architecture of Hydrogen Fuel Cell Vehicles**

Fuel cell electric vehicles (FCEVs) consist of multiple subsystems that support the operation of the fuel cell stack, collectively referred to as the Balance of Plant (BOP). These components are essential for regulating fuel and air supply, managing temperature and humidity, and controlling power output.

- ***Balance of Plant (BOP)***

The Balance of Plant (BOP) comprises all auxiliary systems required for the efficient operation of the fuel cell stack, including fuel processing**,** fuel circulation**,** humidification**,** thermal management, and power control systems. In automotive applications, the compact design constraints make BOP integration particularly challenging. Consequently, reducing the size, weight, and cost of BOP systems is a major design priority.

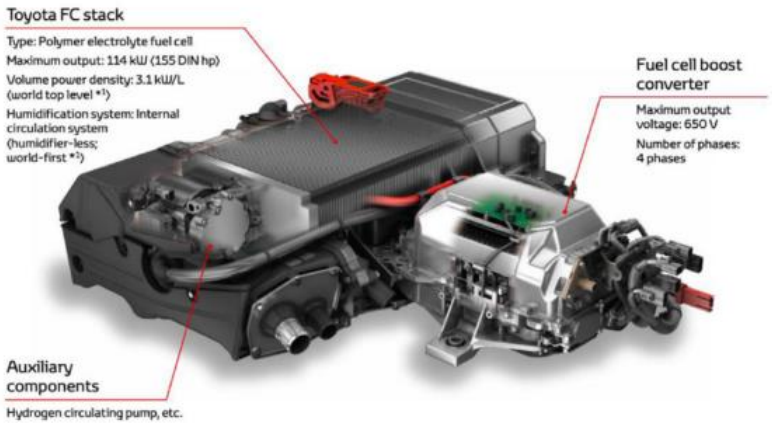
Thermal management in FCEVs aims to remove the excess heat generated by the fuel cell stack and maintain the system's temperature close to ambient conditions. This is more complex than in internal combustion engine (ICE) systems, as fuel cells operate at significantly lower temperatures.

The air supply system is comparatively simpler, given the abundance of ambient air. However, it contributes significantly to system cost approximately 10–21% and requires compression to reach PEMFC operating pressures of 1.5–2 atm**.** This ensures reduced polarization losses during load conditions and supports consistent reactant delivery. Moreover, air quality plays a crucial role in fuel cell performance; contaminants can accumulate in the catalyst layer or membrane, impairing overall efficiency.

Humidification systems are also vital for maintaining the hydration and ionic conductivity of the proton exchange membrane (PEM). These systems contribute roughly 2–7% of the total system cost. Despite water generation within the fuel cell, localized membrane drying, particularly near the intake, is common under high-temperature or low-humidity conditions (e.g., 80 °C ambient air). This makes the integration of humidifiers essential in passenger vehicles. Additionally, thinner PEMs, which exhibit reduced ohmic resistance, can also mitigate humidification requirements.

- ***Fuel Cell Stack***

The fuel cell stack is composed of multiple individual cells connected in series to achieve the desired power output and voltage, as a single fuel cell typically produces only around 0.9 V. Manifold systems are used to distribute fuel and oxidant to all cells within the stack. However, scaling up to stack level introduces complexities in water, heat, and fuel management, as interactions between cells can impact overall performance.



➢ **Figure 15**: Toyota Mirai fuel cell stack. [15]

Each cell's current, heat transfer, and reactant flow are interdependent. As all cells share the same current path, variations in local resistance can degrade stack performance. Design challenges also arise in the distribution of reactants and coolants. When a manifold supplies multiple cells**,** variations in flow resistance can lead to uneven reactant distribution, causing local fuel starvation, reduced cell performance, and eventual material degradation. Similar issues are observed in coolant distribution, where inadequate cooling in specific regions can result in localized overheating and reduced durability. An example of a fuel cell stack configuration used in the Toyota Mirai (pre-2020) is illustrated in Fig. 15.

➢ ***Hydrogen storage***

The successful commercialization of fuel cell electric vehicles (FCEVs) depends heavily on the development of efficient and practical onboard hydrogen storage systems. To compete with conventional internal combustion engine (ICE) vehicles, FCEVs must offer a comparable driving range. However, this is challenged by the inherently low volumetric energy density of hydrogen, which presents several design and performance limitations. Achieving sufficient hydrogen storage capacity requires addressing critical factors such as weight, volume, kinetics, safety, and cost. In response to these challenges, a variety of hydrogen storage technologies have been proposed and are under continuous development. These methods are outlined and analyzed in the previous sections.

In automotive fuel cell systems, hydrogen storage is a critical aspect requiring careful design, especially as oxygen from ambient air is used to generate electricity through the fuel cell reaction. To achieve energy densities suitable for practical vehicle operation, current fuel cell electric vehicles (FCEVs) primarily store hydrogen as a highly compressed gas. While this approach improves onboard energy capacity, it also introduces significant challenges related to safety and user acceptance.

According to Sheffield et al., most commercial FCEVs operate with hydrogen storage pressures around 70 MPa, which results in a hydrogen density of approximately 38 kg/m³, compared to 23 kg/m³ at 35 MPa. Compressed hydrogen storage systems typically hold about 5 kg of hydrogen, enabling a driving range comparable to conventional gasoline-powered vehicles. This storage capacity is roughly 75% greater than that of traditional fuel tanks, which usually hold around 20 gallons of petrol.

Jiang et al. investigated fuel cell operation and found that hydrogen storage systems and fuel cell stacks typically function at a stoichiometric ratio of approximately 1.2 at the anode. This necessitates the recirculation of unused hydrogen to improve fuel utilization efficiency.

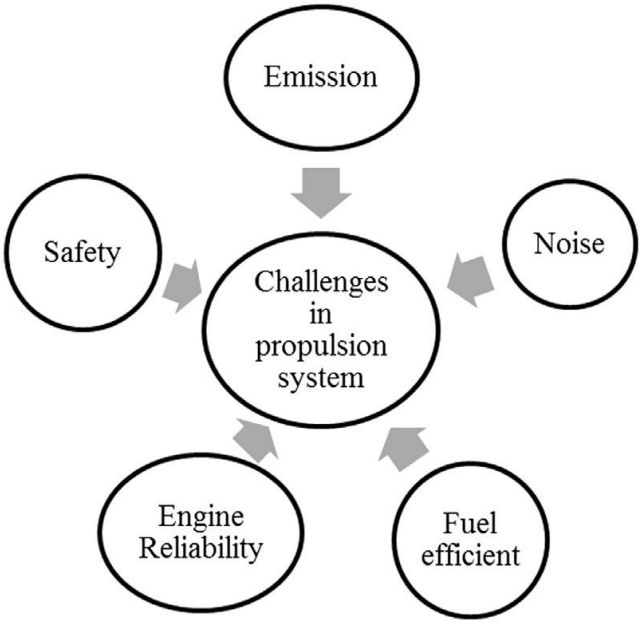
To eliminate the need for high-pressure onboard tanks, some research has focused on the use of liquid fuels as a hydrogen source. In this approach, a reformer subsystem, often integrated as a chemical reactor, converts the liquid fuel into a hydrogen-rich gas mixture suitable for use in fuel cells. However, carbon monoxide (CO) present in the reformate stream can lead to platinum (Pt) catalyst poisoning at the PEM fuel cell anode, especially under low-temperature operation, thus impairing performance.

Studies by Al-Tememy and Lei have demonstrated that CO poisoning can be mitigated through the introduction of air into the fuel stream to reduce CO concentration or by operating the fuel cell at elevated temperatures, where the impact of CO is less severe. These methods offer potential pathways to enhance the viability of onboard reforming systems for automotive applications.

3.1.2 Hydrogen powered aircraft

According to leading experts, the aviation sector is anticipated to expand steadily and at a significant rate over the coming decades. The commercial aviation segment is expected to grow by approximately 5% annually, with even higher growth projections for air cargo transportation, despite the prevailing challenges in the global economy. This growth is largely attributed to the increasing demand for passenger travel and freight services in developing nations. As such, aviation is poised to become the fastest-growing industry over the next two to three decades. Simultaneously, there is a pressing need to reduce dependence on fossil fuels. While estimates regarding the timeline for critical depletion of fossil fuel reserves differ, it is generally accepted that these resources will become severely limited within this century. Technological advancements in propulsion systems have been the cornerstone of progress in the aviation industry. Enhanced propulsion performance and efficiency have enabled aircraft to

achieve higher speeds, cover longer distances, and transport larger payloads. Currently, aviation accounts for approximately 3% of anthropogenic greenhouse gas emissions. This figure is expected to fluctuate due to the anticipated increase in air traffic and evolving strategies aimed at reducing emissions from major CO_2 sources. The challenges associated with future propulsion systems are depicted in Fig. 16.



- **Figure 16**: Vital factors for selection of tank configuration. [17]

Environmental impacts arise not only from fuel combustion but also from the entire energy supply chain, including extraction, refining, and transportation of fuel. Each of these stages contributes to pollutant emissions, which affect the global climate even before the fuel is utilized in aircraft operations.

While the precise timeline for the exhaustion of fossil fuel reserves remains uncertain, it is widely anticipated that the 21st century will necessitate a critical transition to alternative energy sources. One of the primary obstacles to employing liquid hydrogen (LH_2) in aviation is related to storage requirements. Specifically, LH_2 demands approximately four times the volume of conventional aviation fuel such as kerosene, thereby significantly increasing the weight and size of the storage tanks. Despite advancements in tank design, including the development of lightweight, durable, and thermally insulated systems, significant technical challenges persist, limiting the widespread adoption of LH_2 in airborne applications. Liquid hydrogen (LH_2) storage tanks are generally designed as thin-walled pressure vessels operating within a pressure range of approximately 0.1 to 0.35 MPa, which helps to reduce overall tank mass. Although

hydrogen possesses a high specific energy, it is also an exceptionally effective heat sink, making it suitable for component cooling. Its cooling capacity is approximately 4.9 times greater than that of Jet-A fuel and about 2.8 times greater than methane.

The design of LH_2 tanks is highly dependent on both the aircraft's airframe and its propulsion system configuration. The airframe imposes limitations on the shape and diameter of the tank, while the propulsion system defines the hydrogen demand for a given mission, influencing the required tank length. Therefore, a comprehensive tank design process is essential, accompanied by trade-off studies to balance performance, weight, and integration constraints. A significant challenge associated with LH_2 storage is boil-off mass. This phenomenon impacts tank volume, weight, and overall cost, making it critical to minimize or eliminate boil-off to ensure safety and economic viability. Furthermore, the volumetric efficiency of LH_2 tanks is reduced due to the need for insulation, which is essential for preventing boil-off losses.

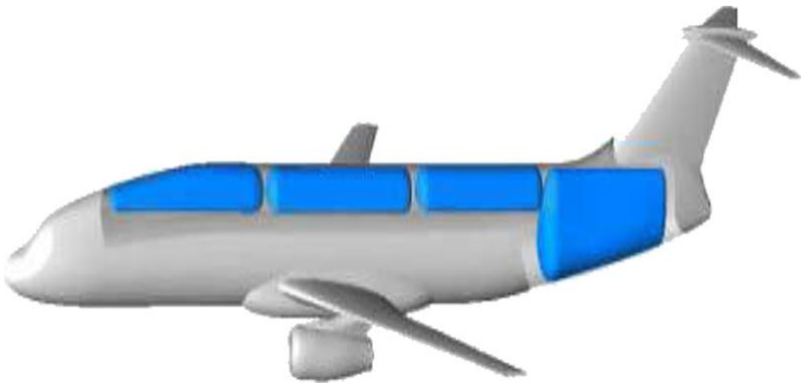
- ***Tank Shape***

Due to its inherently low density compared to other liquids, liquid hydrogen (LH_2) requires significantly larger storage volumes. However, for a given mission profile, the mass of LH_2 needed on board is typically less than that of any other cryogenic coolant. The optimal tank shape is influenced by several key factors, primarily the aircraft fuselage design and the type of tank integration.

Non-integral tanks function independently as fuel containers and must be mounted onto a conventional fuselage or structural framework. These tanks are external to the main aircraft body and are therefore required to withstand all loads associated with fuel containment. The design of non-integral tanks presents challenges related to aerodynamic efficiency and structural integration. An example of an aircraft with a non-integral tank configuration is shown on Fig. 17.

- **Figure 17**: Non-integral tank. [17]

Integral tanks, on the other hand, are incorporated into the aircraft's structural framework, serving as part of the fuselage. These tanks must withstand various mechanical loads including axial, bending, and shear stresses resulting from overall aircraft operation. A primary limitation in designing integral tanks is the geometric constraint imposed by the fuselage diameter. This configuration is generally more feasible for wide-body aircraft, as illustrated in Fig. 18.[17]



- **Figure 18**: Integral tank. [17]

During the Cryoplane project, LH_2 tanks were placed above the fuselage and extended across the wings. While this design allowed for increased fuel capacity, it resulted in thick, heavy tank walls with numerous stiffening structures due to geometric incompatibility with the required pressure. Consequently, spherical and cylindrical tank shapes, particularly those matching the fuselage diameter, are considered more practical for LH_2 storage. Spherical tanks are widely used in space applications because they offer the smallest surface area for a given volume, thereby minimizing boil-off losses through reduced passive heat flux. Despite these thermal

advantages, spherical tanks are more complex and costly to manufacture, and their higher frontal area poses additional aerodynamic penalties compared to cylindrical tanks. On the other hand, cylindrical tanks are comparatively simpler and more cost-effective to manufacture than spherical tanks. However, a notable disadvantage is their higher surface area-to-volume ratio, which results in greater passive heat transfer into the tank and subsequently higher boil-off losses. Despite this thermal inefficiency, cylindrical tanks offer superior volumetric efficiency and are easier to integrate within the fuselage structure, allowing for more effective utilization of internal space. A key structural limitation of cylindrical tanks is the non-uniform distribution of internal pressure, which can compromise mechanical integrity. To address this issue, tank designs often incorporate hemispherical end caps at both ends. This hybrid design combines the volumetric benefits of a cylindrical shape with the pressure distribution advantages of a spherical form. As a result, the cylindrical tank with hemispherical end caps has been selected as the preferred configuration for continued development and implementation.

- ***Tank insulation***

Two primary types of insulation can be applied to liquid hydrogen (LH_2) storage tanks: internal insulation and external insulation. In the case of internal insulation, the insulating material is continuously exposed to the cryogenic temperatures of LH_2. However, because of heat transfer, some of the liquid hydrogen may vaporize into gaseous hydrogen (GH_2). This GH_2 can diffuse into the tank walls, leading to a significant increase in the thermal conductivity of the insulation material, thereby diminishing its overall insulating performance. Moreover, a critical challenge associated with internal insulation is the requirement for the system to be completely impermeable to GH_2. Failure to ensure this impermeability can result in compromised thermal management and reduced storage efficiency.

When insulation is applied externally to a liquid hydrogen (LH_2) storage tank, it is referred to as external insulation. In this configuration, the tank undergoes thermal expansion and contraction as LH_2 is filled and withdrawn. This design introduces several engineering challenges, including attachment issues related to the structural support system and an increase in overall tank dimensions. Furthermore, external insulation is more susceptible to mechanical damage and must be capable of withstanding impact loads. Despite these challenges, external insulation was employed in the Cryoplane project by Air Liquide. While it does have drawbacks, they are considered less critical compared to those associated with internal

insulation systems. As a result, external insulation remains a preferred approach for ongoing developments due to its relative advantages in structural application and maintainability.

- ***Hydrogen Combustion and Safety Considerations in Engine Systems***

Hydrogen combustion presents specific challenges due to its tendency to flashback and produce high-temperature flames, which can lead to elevated NO_x emissions. A comparison between hydrogen and kerosene flame stability limits demonstrates that hydrogen, while exhibiting a higher adiabatic flame temperature at stoichiometric conditions, is also capable of stable combustion at significantly leaner equivalence ratios. Operating under lean conditions is advantageous, as it produces lower flame temperatures, thereby mitigating the risk of excessive NO_x formation. However, achieving such lean combustion requires enhanced mixing intensity to prevent the formation of local hotspots and to ensure homogeneous fuel-air mixing for a balanced flame profile. Consequently, combustor designs must be adapted to promote effective fuel-air mixing while preventing localized overheating.

Incorporating hydrogen as a fuel also necessitates system-level considerations to ensure redundancy and operational reliability, particularly due to hydrogen's high flame speed, cryogenic storage temperature, and propensity for flashback during flame propagation. Upon system startup**,** hydrogen fuel lines may contain ambient air because of hydrogen's natural tendency to escape over time. This poses a significant flashback risk during ignition if not addressed properly. To eliminate this hazard, it is critical to purge the fuel lines with an inert gas, such as nitrogen, prior to startup. This step is also recommended during shutdown to prevent residual hydrogen from mixing with air and creating an ignition hazard. However, the use of liquid hydrogen introduces additional complexity, as it may cause solidification of other gases during purging, potentially obstructing fuel flow. Before hydrogen enters the combustion chamber, it must be preheated to ensure complete vaporization at maximum flow rates from the cryogenic storage tank. To achieve this safely, a dedicated heat exchanger is required. Utilizing hot sections of the engine (e.g., combustion chamber or turbine stage) to heat the fuel is not advisable, as fuel leaks in these areas could ignite immediately, posing serious safety risks. Instead, a heat exchange system should be designed to extract heat from various engine components, such as exhaust ducts, turbine stages, or compressors and transfer it to the incoming hydrogen. This not only ensures that the fuel reaches a fully gaseous state before injection, but also improves thermal efficiency, extends component life, and enhances resilience to thermal stress by exploiting hydrogen's heat sink potential. During engine startup, an

electrical heater is needed to initiate the heating process. Once the engine reaches idle rotational speed, the heat exchanger system can take over. Additionally, a metering system must be implemented to regulate the flow of liquid and gaseous hydrogen, depending on the engine's power demands.[17]

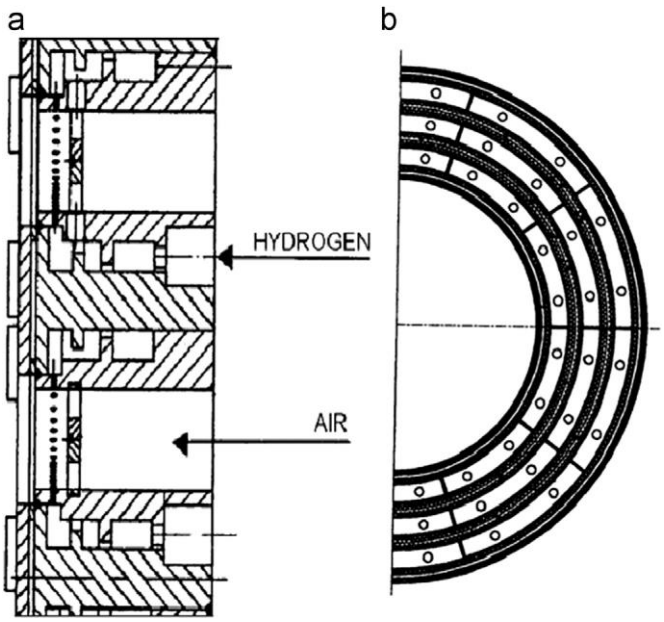
- ***Hydrogen Combustors***

The combustion process of hydrogen is more complex than merely adjusting the air-to-fuel ratio, as it heavily relies on the design of the combustor itself. While adding hydrogen to conventional fuels has shown performance improvements, using pure hydrogen in traditional combustors often yields inferior results compared to conventional fuels. This is primarily because conventional combustor geometries are not optimized to achieve effective mixing of hydrogen and air. When hydrogen burns in a standard combustion chamber, large diffusion flames develop, with stoichiometric mixtures forming near the flame front. This leads to extremely high temperatures and consequently elevated NOx emissions. To prevent inefficient combustion, various flame characteristics, such as flame stability, combustion efficiency, and acoustic behavior must be thoroughly addressed. Therefore, research efforts have focused on developing innovative combustor designs that can optimize hydrogen combustion and harness its full benefits. Two promising hydrogen combustor designs have emerged as leading candidates for further development. The first is the Lean Direct Injection (LDI) concept explored by NASA and Marek et al., and the second involves Micro-mix combustors investigated by Dahland and Suttrop. Both concepts have been validated through practical combustion testing.

Despite slight differences, these two approaches share a common goal: addressing the issue of flashback, which is critical due to the increased fuel-air mixing they aim to achieve. Both designs significantly enhance the mixing intensity of hydrogen and air to prevent the formation of large diffusion flames that contribute to higher NOx emissions. By intensifying the mixing, the flame length is shortened, allowing combustion to complete more rapidly and reducing the residence time within the flame zone. Since NOx formation depends on both temperature and residence time, this strategy effectively lowers NOx emissions. Moreover, the method of hydrogen injection plays a crucial role in ensuring efficient combustion, prompting further studies to explore alternative fuel injection techniques that can improve combustion characteristics.

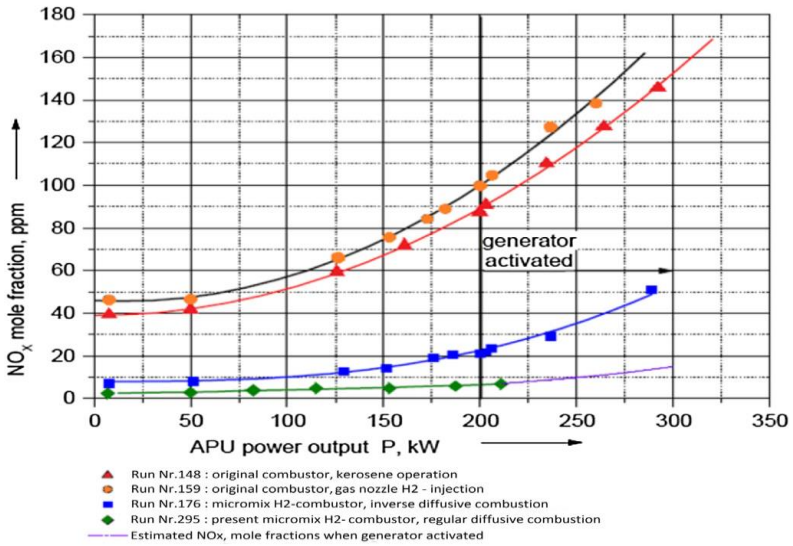
- ***Micro-mix Combustion***

Research on micro-mix combustors was initially conducted by Dahl and Suttrop, who demonstrated safe hydrogen combustion while aiming to minimize NOx emissions. Their investigation focused on converting an A320 Auxiliary Power Unit (APU) GTCP36-300 to operate safely on hydrogen. The combustor design for hydrogen operation was based on the principle of miniaturized diffusive combustion, which increases the number of localized mixing zones, thereby enhancing the overall fuel-air mixing within the combustor. This miniaturized diffusion approach was developed to address the issues associated with hydrogen combustion in conventional systems, where large diffusive flames form and create very high temperature zones. Since thermal NOx formation depends on flame residence time, as well as the amounts of oxygen, nitrogen, and temperature, especially temperatures above 1800 K where emissions increase exponentially, it is critical to avoid such conditions in combustor design.



➢ **Figure 19**: Micro-mix cross-section. [17]

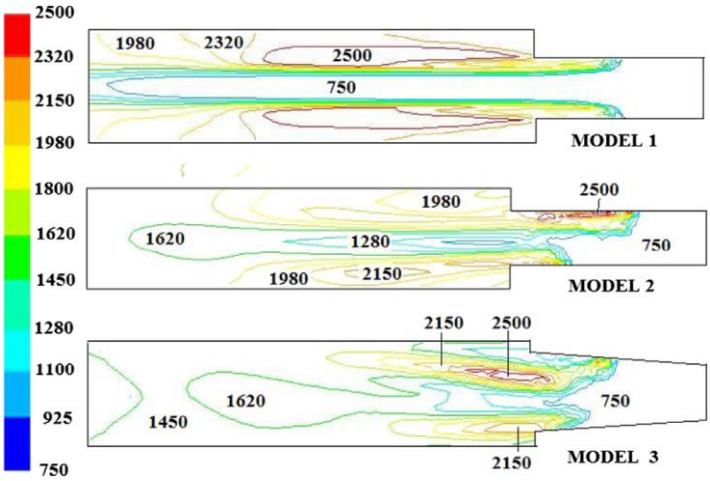
The micro-mix combustor tackles this by employing heterogeneous mixing, which creates many small diffusion flames rather than a few large ones. This is achieved by incorporating many fuel and air inlets, while adhering to a standard diffusion partial premixing (DPD) limit of 3–4% to control the amount of fuel and air introduced. The enhanced mixing benefits from turbulent flow structures and the breakdown of eddies, which reduces the local flame residence time and prevents stoichiometric pockets from forming. A schematic of the micro-mix combustor is shown on Fig. 19.



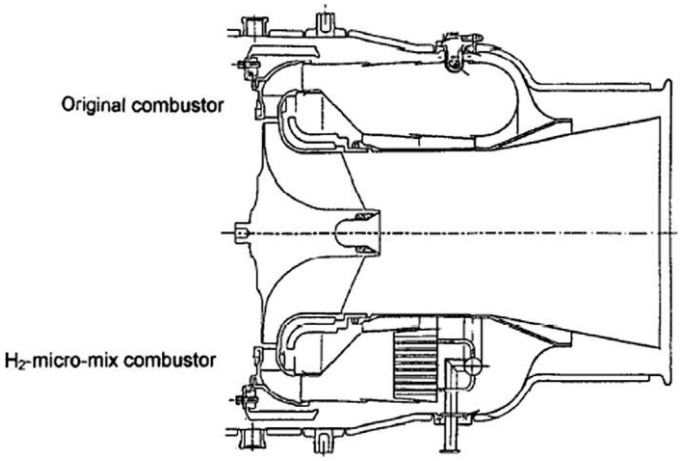
➢ **Figure 20**: Comparison of NOx emissions with a modified. [17]

Extensive testing was carried out to evaluate NOx emissions from micro-mix combustion across various equivalent ratios. The study also benchmarked the results against conventional combustors burning kerosene and hydrogen. The combustor used in the A320 APU is illustrated on Fig. 22. The data obtained by Dahl and Suttrop indicate that the highest NOx emissions occur during hydrogen combustion. However, as shown on Fig. 20, these emissions are strongly linked to the presence of stoichiometric conditions, which result in very high flame temperatures. In summary, stoichiometric conditions are characteristic of conventional hydrogen diffusion combustion, leading to elevated NOx. In contrast, the micro-mix approach primarily avoids these conditions by intensifying local mixing, thereby reducing flame temperatures and NOx emissions. The success of this testing was demonstrated by Dahl and Suttrop, who utilized rapid mixing of hydrogen while placing significant emphasis on addressing safety concerns related to flashback. They established protocols for the safe ignition of hydrogen fuel. Subsequent investigations by Dahl and Suttrop explored the performance of various micro-mix combustion configurations. Their later work showed that further reductions in NOx emissions are achievable through modifications to the micro-mix combustion approach. This led to the development and computational fluid dynamics (CFD) analysis of conceptual micro-mix injector designs at Cranfield University. Figure 21 illustrates three different micro-mix injector models examined by Murthy et al. Model 1 represents a conventional micro-mix combustor, which demonstrates significantly lower NOx emissions compared to hydrogen combustion in conventional combustors. However, as evident from Figure 21, high-temperature

hotspots still appear within the flame profile, and these zones are primarily responsible for thermal NOx formation.



- **Figure 21**: CFD analysis of micro-mix injectors. [17]



- **Figure 22**: A320 APUGTCP36-300combustors. [17]

3.1.3 Hydrogen Maritime Application

The Role of Hydrogen: Navigating the Fuel of the Future

The debate around sustainable marine fuels of the future largely centers on a trade-off between cost and the ease of onboard energy storage**,** the latter being a major technical challenge. Additionally, there are open questions regarding how ships will be powered. Hydrogen offers flexibility, as it can be used either in fuel cells or combusted in internal combustion engines**.** Among hydrogen-based fuels, pure hydrogen is the most cost-effective option. However, it is

not the easiest to store, especially compared to its derivatives such as ammonia, e-LNG, e-methanol, and e-diesel**,** which offer higher volumetric energy densities. This relatively low volumetric energy density, along with production costs, presents a significant techno-economic barrier to the large-scale use of hydrogen in maritime applications.

Hydrogen Europe has evaluated current technologies, assessing their strengths, weaknesses, and technology readiness levels (TRLs) to propose deployment scenarios for both ships and the supporting infrastructure. When examining fuel production costs alone, pure hydrogen consistently proves to be the cheapest option, since it avoids additional conversion steps, regardless of the electricity price used in production. However, the choice of future maritime fuels remains uncertain, creating a risk of delays in the energy transition. For large vessels, ammonia, produced from renewable hydrogen, emerge as the most cost-effective synthetic fuel. Still, there's a fundamental trade-off: as the energy density of hydrogen-derived fuels improves, their costs also rise.

- **Fuel Cells and Hydrogen in Maritime Use**

Fuel cells (FCs) and hydrogen have long been used in submarines, and several small hydrogen-powered vessels have already been built. Additional demonstration projects are underway to validate the feasibility of powering ships using fuel cells and dual-fuel internal combustion engines, up to a certain power level. For specific vessel types, such as inland and near-coastal vessels, a growing consensus suggests that hydrogen-powered fuel cells represent the most promising zero-emission solution. Design projects are also underway to test the scalability of fuel cells for larger vessels. However, for these larger ships, the energy and power demands remain significant, and no clear consensus has been reached on the optimal fuel strategy. Given these challenges, dual-fuel hydrogen combustion engines are seen by some as a transitional pathway, potentially accelerating hydrogen uptake in the maritime sector.

- **Pure Hydrogen as a Maritime Fuel**

Hydrogen can be used in:

- **Fuel cells** (highest efficiency: 50–60%, potentially more with heat recovery)
- **Dual-fuel combustion** with conventional fuels
- **Pure combustion** in hydrogen engines

In fuel cell systems, hydrogen conversion results in zero tank-to-wake emissions, releasing only water. The total well-to-wake emissions depend entirely on the hydrogen

production method. If hydrogen is produced using renewable energy, it can enable a 100% reduction in greenhouse gas (GHG) emissions across the entire lifecycle.

For dual-fuel combustion, hydrogen can improve efficiency and reduce emissions. A 50/50 hydrogen-heavy fuel oil (HFO) blend may reduce CO_2 emissions by up to 43% per ton-kilometer. Single-fuel hydrogen engines are also under development. However, as of 2019, over 90% of hydrogen in the EU is produced from fossil fuels, with no carbon capture and storage (CCS), a major limitation to its sustainability.

- **Energy Density Considerations**

Hydrogen has a high specific energy density (around three times that of HFO), but a low volumetric energy density due to its lightness. This can be improved through:

- **Liquefaction**: Increases volumetric energy density by 71x compared to gaseous form, but still only 16% of marine gas oil's density.
- **Compression (350 bar)**: Results in a volume 7.5 times greater than marine gas oil to store the same energy. Thus, storage remains a critical challenge.
- **Hydrogen-Based Synthetic Fuels (E-Fuels)**

E-fuels are synthetic fuels made from renewable electricity, water, and either carbon dioxide or nitrogen. The most promising hydrogen-derived e-fuels include:

  - E-ammonia
  - E-methanol
  - E-LNG

Both ammonia and methanol are already widely traded commodities, which could simplify their adoption in marine use.

- **Ammonia**

Ammonia is a hydrogen carrier that can be used in certain fuel cells or burned directly in internal combustion engines.

  - Contains no carbon (zero CO_2 and SOx emissions)
  - Produces low NOx emissions
  - Faces challenges such as:
  - Low flammability
  - Ammonia slip (incomplete combustion)
  - N_2O emissions
  - Toxicity, posing serious safety concerns for onboard use

Despite these issues, ammonia is widely traded (18+ million tons annually) and existing infrastructure (e.g., from the fertilizer industry) may support its rollout. However, ports without ammonia infrastructure will require significant upgrades. Currently, ammonia combustion is still in R&D, but several engine manufacturers are testing it for maritime use.

- **Methanol**

  Methanol is a mature, lower-emission fuel. Its benefits include:

  - 55% lower NOx and 92% lower SOx emissions than conventional fuels
  - Currently used by 11 tankers and 1 ferry in Europe
  - Carbon-based, but can be carbon-neutral if produced via direct air capture

  Additional advantages:

  - Favorable volumetric energy density (only 2–3x more space than marine fuels needed)
  - No need for compression or cryogenic storage
  - Existing infrastructure for liquid fuels can be reused or easily modified

  This also applies to LOHCs (Liquid Organic Hydrogen Carriers), which are another way to store hydrogen chemically.

- **Biofuels: Not Future-Proof**

  Although biofuels are widely used and can be blended with fossil fuels, they are not considered a long-term solution due to:

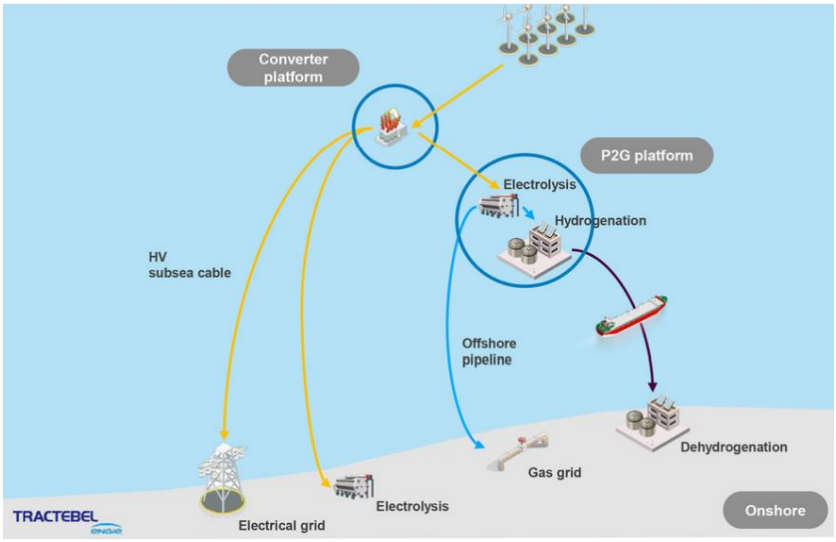
  - Sustainability concerns: Many crop-based biofuels are worse than fossil fuels in environmental impact
  - Limited feedstock availability: Advanced biofuels may help reduce emissions but are constrained in scale
  - Risk of delaying hydrogen adoption: Blending biofuels can serve as a short-term fix, delaying investment in hydrogen-based solutions

  Biofuels are attractive because:

  - They have low capital costs
  - Require minimal changes to existing infrastructure
  - Are price competitive
  - Are already in use across industries and geographies

  However, their availability and sustainability are major bottlenecks. In 2016, total biodiesel and bioethanol production accounted for only 24.5% of marine fuel demand. With aviation and other sectors competing for biofuels (and able to pay more), supply to the shipping sector is limited. Any use of biofuels must consider their impact on land use, food prices, and social conditions.

It is important to point out the central role that the maritime ports have in the transition towards the hydrogen economy. Already today a large portion of hydrogen industrial production and consumption takes place in ports or near ports. The biggest hydrogen consumers come from the oil refining, ammonia and chemical industries, which combined use around 90% of all hydrogen produced each year in the EU, and quite a lot of those facilities are in EU ports. Five industrial hubs in the Belgian and Dutch ports (Antwerp, Zeeland, Rotterdam, IJmond and Delfzijl) have a combined local hydrogen demand of 1.7 Mt per year, which is equal to around 20% of total EU consumption today. Most of that hydrogen is also produced locally, usually from natural gas through steam methane reforming, the so-called grey hydrogen. This is an important opportunity as this grey hydrogen will gradually need to be replaced with renewable or low carbon hydrogen. Having a large hydrogen demand center in port makes it possible to develop a clean hydrogen supply chain for shipping. This would be further strengthened by the fact that many port areas have industrial facilities from the hard-to-abate sectors, like the steel industry, which are also increasingly looking at hydrogen as an option for decarbonization. Furthermore, hydrogen can also be used as a fuel for most material handling vehicles used in ports' terminals to decarbonize port operations and further increase the demand for clean hydrogen. The pace at which the maritime sector can decarbonize very much depends on how fast ports will be able to store enough green hydrogen. Such a bottom-up approach would see an individual port engage key stakeholders based on the port's individual roadmap, which provides a detailed plan of pathways for the greening of the shipping and considers each port's particular circumstances. The roadmap should be accompanied by a timeline which engages all relevant stakeholders: the port, the shipping lines, the energy sector (producers and providers), and other European ports where suitable. It should also be noted that falling prices of offshore wind and solar are making renewable energy technology potentially the cheapest source of renewable hydrogen, especially in northern parts of Europe, where solar power is less competitive, making ports ideally placed to become large renewable hydrogen production hubs and demand centers. It is also increasingly likely that Europe will not be able to locally produce enough hydrogen to cover the entire future demand. A solution will be to import clean hydrogen by ships from North Africa, Australia, Chile or other countries with favorable wind/solar resources. The maritime sector will also be a major enabling partner to materialize those synergies between offshore renewables and hydrogen. Namely, hydrogen produced offshore could be transported by ships to demand hubs such as ports. Hydrogen-fueled ships will bring crew to offshore platforms and wind turbines (for maintenance). Besides, those platforms could become hydrogen hubs at sea supplying hydrogen to ships in transit.[18]



➢ **Figure 23**: Production of renewable hydrogen offshore.[18]

3.2 Industrial uses of Hydrogen

- **Hydrogen Utilization in Petroleum Refineries**

The industrial application of hydrogen in refineries began over five decades ago, initially with the use of by-product hydrogen generated from naphtha reformers to pretreat reformer feedstocks. Since then, the role of hydrogen has expanded significantly, especially in processes targeting the treatment and upgrading of heavier hydrocarbon streams, as well as in the production of cleaner fuels and lubricants.[19]

While several techniques have emerged for recovering and upgrading hydrogen from previously underutilized refinery and chemical process streams, the increasing demand for high-purity hydrogen has led refineries to rely more heavily on dedicated hydrogen production plants or external supply schemes. This trend has been driven by both regulatory pressures, including stricter product specifications and emission standards and the economic incentive to improve refining margins. Today, hydrogen consumption in modern refineries is typically around 1 weight percent of the total crude oil processed.

Hydrogen is primarily used in hydro-processing operations aimed at upgrading hydrocarbon feedstocks and products. The key functions include:

- Removal of sulfur compounds and halides
- Metal removal
- Saturation of olefins, diolefins, and cycloolefins

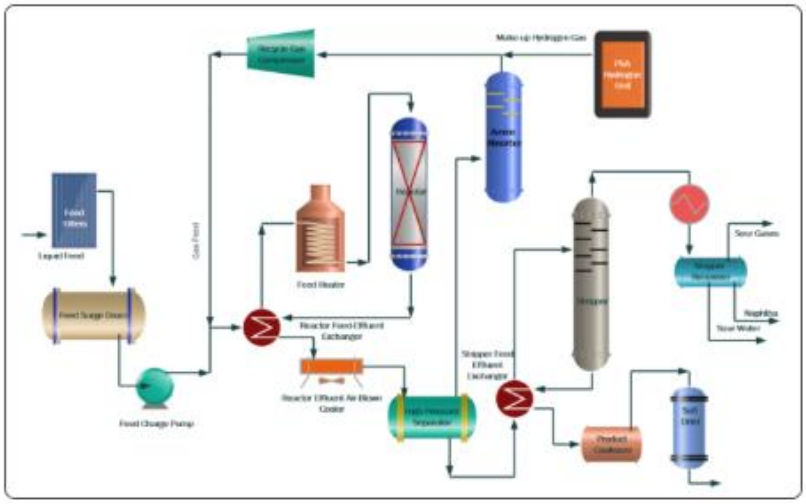
- Saturation of aromatics
- Isomerization
- Removal of nitrogen and oxygen compounds
- Decyclization (ring-opening reactions)
- Cracking of heavier molecules into lighter hydrocarbons

  Depending on the target reactions and process conditions, these operations are categorized under various names such as hydrodesulfurization, hydrodemetallation, hydrofining, hydrotreating, hydrocracking, and hydroreprocessing. Notably, multiple reaction pathways typically occur simultaneously, beyond the primary objective of the upgrading process.

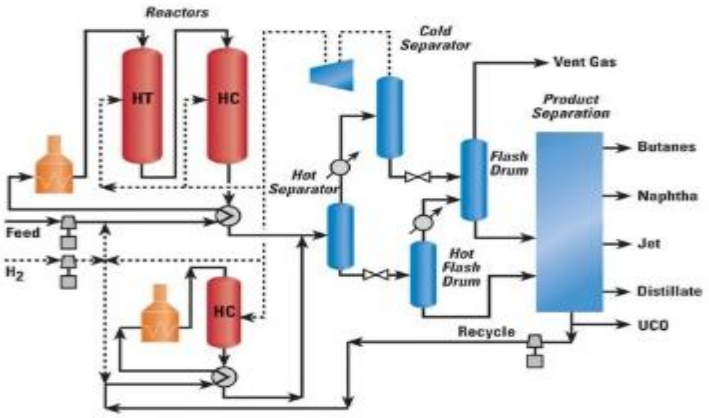
  Hydrogen may be utilized either for feedstock pretreatment or for final product finishing. Examples of feed upgrading include:

  - Pretreatment of naphtha reformer feed
  - Hydrotreating of gas oils and other components of Fluid Catalytic Cracking (FCC) feed
  - Desulfurization and hydrotreating of residual oils prior to Residual Fluid Catalytic

  Analytically, Hydrotreating serves to eliminate impurities such as sulfur from petroleum products. The removal of sulfur is particularly important, as its presence in fuels leads to the emission of sulfur oxides during combustion, contributing to environmental pollution and equipment degradation. By reducing sulfur content, hydrotreating ensures compliance with environmental regulations and improves fuel performance and engine longevity. Hydrocracking, on the other hand, involves the catalytic breakdown of heavier hydrocarbons into lighter, more valuable fractions like gasoline and jet fuel. This process, which requires hydrogen, enhances the yield of high-demand products from crude oil, thereby improving the overall efficiency and economic viability of refinery operations. Traditionally, hydrogen for these applications is sourced internally as a by-product of processes such as catalytic reforming and ethylene steam cracking. Catalytic reforming upgrades low-octane naphtha into high-octane gasoline components, while ethylene cracking is aimed at producing basic petrochemicals. Both generate hydrogen, which is subsequently recovered for downstream use. Amid growing environmental concerns and evolving regulatory frameworks, there is an increasing interest in replacing conventionally sourced hydrogen with low-carbon alternatives, particularly green hydrogen. Produced through water electrolysis using renewable energy, green hydrogen offers a significant reduction in lifecycle carbon emissions. Its integration into refinery operations is viewed as a strategic step toward reducing the environmental impact of the sector and aligning with global decarbonization targets.[20]



➢ **Figure 24**: Hydrotreating Process in Oil Refinery. [20]



➢ **Figure 25**: Hydrocracking Process in Oil Refinery. [20]

- **Challenges and Prospects of Green Hydrogen Integration in Oil Refineries**

Although green hydrogen offers notable environmental advantages, its production remains significantly more costly than conventional methods. This is primarily attributed to the high cost of electricity and the limited availability of zero-carbon energy sources. As a result, widespread adoption of green hydrogen in refinery operations will require a substantial reduction in renewable electricity costs, alongside improvements in the efficiency and accessibility of carbon-free power generation.

Several initiatives are currently underway to demonstrate the feasibility of incorporating green hydrogen into industrial-scale refining processes. A prominent example is the REFHYNE project in Germany, which involves the installation and operation of a large-scale electrolyser

at a refinery site to produce green hydrogen in substantial volumes. The REFHYNE project has served as a landmark initiative in the industrial decarbonization landscape, aiming to demonstrate the feasibility and commercial viability of utilizing green electrolytic hydrogen within a refinery environment. Despite encountering various technical and logistical challenges, the project has successfully fulfilled its primary objective—designing, constructing, and operating a 10 MW proton exchange membrane (PEM) electrolyser under actual industrial conditions. REFHYNE has already contributed to substantial advancements in both the design and operational strategies of large-scale electrolysers, setting new benchmarks for future multi-megawatt installations. Its success is largely attributed to the effective collaboration among project partners and the strategic support from the Clean Hydrogen Partnership, further solidifying its role as a catalyst for subsequent hydrogen integration projects in the refining sector.[21] This project forms part of a broader strategy to decarbonize the refining industry and aligns with global efforts to curb greenhouse gas emissions, a trend expected to accelerate throughout the 2020s. The long-term market potential for low-carbon hydrogen in the refining sector is substantial. Projections indicate that by 2050, the demand for such hydrogen could reach 50 million tons annually. The adoption of green hydrogen at this scale could contribute to a reduction of up to 35% in carbon emissions associated with global refining operations, positioning it as a key enabler of the industry's transition toward climate neutrality.

Chapter 4: Latest Developments – Concerns

- **Technological Limitations and Scalability Challenges**

Although green hydrogen is widely recognized as a promising pathway for decarbonizing sectors such as transportation and industry, its widespread adoption is hindered by several technical and scalability-related challenges. The predominant method for producing green hydrogen, as mentioned before, is electrolysis, a process that utilizes electricity generated from renewable sources to split water into hydrogen and oxygen. While electrolysis is a well-established and commercially viable technology, several technical hurdles remain. These include the need to enhance the energy efficiency of electrolysers, improve their operational durability, and develop higher energy-density hydrogen storage solutions.

Furthermore, scalability presents a significant barrier. Achieving the widespread deployment of green hydrogen will require extensive investments in renewable energy infrastructure, which may not be immediately achievable in many regions. The expansion of both production and distribution systems at the scale necessary to support a global green hydrogen economy remains a critical challenge that must be addressed through coordinated policy support, technological innovation, and infrastructure development.

Public acceptance is another critical factor influencing the widespread adoption of hydrogen as an alternative energy source. Economic incentives such as tax credits and carbon trading schemes are currently being employed to encourage investment in hydrogen technologies. It is anticipated that hydrogen production will be concentrated in regions with abundant renewable energy resources or existing oil and gas reserves, given the logistical and economic advantages such areas offer. In addition, the development of a comprehensive international framework for hydrogen demand analysis and trading regulations will be crucial in establishing a functional global hydrogen economy.

Environmental and safety considerations also present significant challenges. Hydrogen’s low molecular weight makes it susceptible to leakage, particularly in the context of natural hydrogen production. Ensuring the structural integrity of wells through proper cementing is essential to prevent subsurface leakage, which could pose serious safety risks due to hydrogen’s flammability and potential to form explosive mixtures with air. Effective control measures, including high-pressure valves and advanced leak detection systems, are vital to maintaining safe operations.

In underground hydrogen storage applications, it is imperative to assess the integrity of the caprock to avoid unintended gas migration. Detailed reservoir characterization and

simulation studies are required prior to storage operations to ensure containment security. For hydrogen transmission via pipelines, key concerns include soil corrosion and hydrogen embrittlement, both of which can lead to material failure. Selecting appropriate materials for pipeline construction under operational conditions is essential to mitigate these risks. [22]

- **Strategies and Policies for Green Hydrogen Deployment**

➢ **Figure 26**: Policies toward green hydrogen deployment.[6]

The successful deployment of green hydrogen as a sustainable and low-emission energy carrier depends heavily on the implementation of comprehensive strategies and policy measures. These strategies are designed to support the development, integration, and widespread adoption of green hydrogen technologies across various sectors. Key components include the establishment of ambitious national and regional targets, the provision of financial incentives such as subsidies and tax benefits, substantial investment in research and development initiatives, and the promotion of robust infrastructure for production, storage, and distribution.

- **Case Studies and Strategic Insights**

The experiences of the European Union, Australia, Japan, the United States, and Canada illustrate the importance of coordinated strategic planning and cross-sector collaboration in the advancement of green hydrogen technologies. Successful development and deployment efforts in these regions have been underpinned by ambitious policy targets, sustained investment in research and development, and the establishment of robust regulatory frameworks.

Additionally, fostering cooperation among governments, private industry, and academic institutions has proven essential.

Despite the progress made, several challenges persist, including technological constraints, underdeveloped infrastructure, high production costs, complex regulatory environments, and limited public awareness or acceptance. Overcoming these barriers will require ongoing innovation, coordinated policy support, and stakeholder engagement at all levels. Green hydrogen has the potential to play a transformative role in achieving global climate goals, such as those outlined in the Paris Agreement, by supporting the transition to a low-carbon and sustainable energy system. Leveraging the unique attributes of green hydrogen can significantly contribute to a decarbonized energy future for the benefit of current and future generations.

Recommendations for Overcoming Challenges and Accelerating Adoption

To fully harness the potential of green hydrogen as a cornerstone of a sustainable energy transition, a series of targeted actions must be pursued. Based on the findings of this study, the following recommendations are proposed to address key challenges and promote the widespread adoption of green hydrogen technologies:

- **Enhance Research and Development (R&D):** Continued investment in R&D is critical to advancing green hydrogen production methods, increasing efficiency, lowering costs, and expanding its application across various industrial and energy sectors.
- **Develop and Expand Infrastructure:** Building out infrastructure for the production, storage, distribution, and end-use of green hydrogen is essential for its integration into existing energy systems and to support industry growth.
- **Strengthening Regulatory and Policy Frameworks:** The establishment of supportive policies, including subsidies, tax incentives, and the inclusion of green hydrogen in broader climate and energy strategies can create favorable market conditions and encourage investment.
- **Foster Public-Private Partnerships:** Collaboration between government entities and private enterprises can facilitate risk-sharing, leverage capital, and accelerate the commercialization of green hydrogen technologies.
- **Promote International Cooperation:** Cross-border collaboration and knowledge-sharing can speed up technology transfer, harmonize regulatory standards, and scale innovation globally.
- **Invest in Education and Workforce Development:** Developing a skilled workforce is imperative to support the growing green hydrogen sector and to meet emerging demands for specialized labor.

- **Raise Public Awareness and Acceptance:** Educating the public on the environmental and economic benefits of green hydrogen can mitigate misconceptions and build broader societal support for hydrogen initiatives. [6]

By implementing these measures, stakeholders across sectors can collectively overcome existing obstacles and expedite the transition toward a clean hydrogen economy. The successful adoption of green hydrogen technologies hinges on sustained collaboration, technological innovation, and a shared commitment to climate goals. Through these concerted efforts, green hydrogen can become a cornerstone of global decarbonization strategies and a driver of sustainable energy transformation.

Chapter 5: Conclusions

This thesis has comprehensively examined the production, storage, and application of green hydrogen, positioning it as a pivotal energy carrier in the global shift toward sustainable and decarbonized energy systems. The key findings are summarized as follows:

Green hydrogen, produced primarily through water electrolysis powered by renewable energy sources, presents a viable and environmentally friendly alternative to fossil fuels. Unlike conventional hydrogen production methods such as steam methane reforming or coal gasification, green hydrogen generates no carbon emissions, offering a significant advantage in the fight against climate change.

The study analyzed in depth the technological methods for green hydrogen production, including alkaline and PEM electrolysis, thermochemical and biological processes, and hybrid systems. Among these, water electrolysis remains the most mature and scalable option, particularly when integrated with solar or wind power to capitalize on surplus energy generation.

Hydrogen storage remains a critical challenge for the practical deployment of hydrogen technologies. This thesis explored various physical and chemical storage methods, including high-pressure tanks, cryo-compressed and liquefied hydrogen, metal hydrides, and adsorbent materials. Each method presents distinct advantages and limitations in terms of energy density, safety, scalability, and cost. The development of efficient, safe, and cost-effective storage systems is essential to support hydrogen's role in future energy infrastructures.

Regarding applications, green hydrogen offers tremendous potential across multiple sectors. In transportation, it serves as a clean fuel for fuel cell electric vehicles (FCEVs), hydrogen-powered aircraft, and hydrogen-powered ships, providing a feasible route to decarbonize mobility. Industrial applications also benefit from hydrogen's high energy content, with significant opportunities in sectors such as refining, steelmaking, and ammonia production—industries traditionally reliant on fossil fuels.

Recent technological advancements, particularly in electrolyzer efficiency, hydrogen purification, and integrated renewable systems, suggest that the deployment of green hydrogen at scale is increasingly achievable. Nonetheless, several challenges persist, including high production costs, infrastructure limitations, and public acceptance. Addressing these barriers requires sustained investment, research, and supportive policy frameworks.

In conclusion, green hydrogen represents a cornerstone for a cleaner, more sustainable energy future. Its versatility, coupled with advancements in production and storage

technologies, underscores its potential to contribute substantially to global decarbonization efforts. This thesis emphasizes that continued interdisciplinary research and innovation are vital to unlocking the full potential of green hydrogen as a leading solution in the global energy transition.

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