



FACULTY OF TECHNOLOGY

Hydrogen storage technologies and implications of real-life applications – A review of case studies

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ABSTRACT

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Hydrogen is seen as the solution for a carbon-neutral future. It can be used as a fuel for traffic, transportation, industry, and energy generation. Green hydrogen is produced from renewable energy sources. It can be produced in overgeneration periods and be utilized when needed, creating energy storage.

The objective of the thesis was to find out the best hydrogen storage technologies for each purpose currently available for implementation, and options that are being developed. In addition, hydrogen strategies in the European Union and Finland were analyzed. Based on that knowledge, one case study of long-term seasonal hydrogen storage and one short-term hydrogen storage, which levels daily renewable energy generation fluctuations, are analyzed. The case studies were based on modelling. The short-term case study examines an electrical testing laboratory, located in Saudi Arabia's eastern region. The long-term case study is located in Finland. In addition, a real-life hydrogen project is analyzed to show the impacts of the integration of hydrogen storage technologies in the energy system. Calculations based on statistical data and technological parameters were used as a research method.

The results of the analysis show that compressed hydrogen, liquefied hydrogen, and metal hydrides are far-developed and most-used storage methods. Cryo-compressed hydrogen,

liquid organic hydrogen carriers, physically adsorbed hydrogen, and complex metal hydrides are still developing technologies. The advantages of integrating hydrogen storage into the energy system lie in its ability to minimize the unmet demand by storing green hydrogen produced in low-demand periods and utilizing it later. This reduces the demand for fossil-based energy, preventing carbon dioxide emissions. In addition, hydrogen storage would have a positive effect on the prices of renewable energy systems.

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LIST OF ABBREVIATIONS

CCS	Carbon Capture and Storage
CCU	Carbon Capture and Utilization
IPCEI	Important Projects of Common European Interest
LOHC	Liquid Organic Hydrogen Carriers
LNG	Liquefied Natural Gas
CFRP	Carbon Fiber Reinforced Polymers
POX	Partial Oxidation
PEM	Proton Exchange Membrane

1 INTRODUCTION

The world has witnessed a global concern over the environmental impact of traditional energy sources. Renewable energy sources are looking promising, and their demand is growing due to agreements and the goal of becoming emission neutral across the world. Their problem lies in their irregularity and unpredictability, to which hydrogen has evolved as a solution. Hydrogen can be produced from surplus energy during high renewable energy generation periods and stored for later use (Elberry et al. 2021b). Hydrogen can also be used as fuel for industrial processes, traffic, and transportation (Rosen and Koochi-Fayegh, 2016). It is abundantly available, and it has high gravimetric energy content and the ability to produce zero-emission electricity when utilized. However, it is highly volatile, and its volumetric energy density is relatively low, making it hard to store and distribute. (Abe et al. 2019) Renewable energy sources require hydrogen to create a stable and reliable energy system for a clean and sustainable future.

In this bachelor's thesis, hydrogen's road from production to end-use is presented, focussing mainly on the storage part. Hydrogen production technologies, Finland's and the EU's hydrogen strategies, and the hydrogen value chain are presented in Chapter 2. In Chapter 3, hydrogen storage technologies are researched to provide an understanding of currently available technologies and options that are being developed. In addition, two case studies with different hydrogen systems are analysed in Chapters 4 and 5 to present the scale of possible applications of hydrogen storage. One real-life project is also included to show the kind of technology that is invested in and witnessed to be the most efficient one in that purpose of use.

By examining the current best hydrogen storage methods for different purposes, this research aims to provide a comprehensive look into the most potential energy-storing technology. Calculations based on statistical data and technological parameters are used as a research method. The research questions of the thesis are as follows: What are the currently available hydrogen storage technologies and what are potential future options? What advantages, disadvantages, and implications could the integration of hydrogen storage technologies in the energy system bring for society?

2 HYDROGEN IN THE ENERGY SYSTEM

Hydrogen is a very substantial element in the universe and its number of atoms is approximately 90 % of the universe (Abe et al. 2019). Hydrogen has many benefits as a fuel. It has a very high energy content compared to its molecular weight, and it has excellent availability on Earth. When hydrogen is converted into energy, it does not have any harmful substances as a side product, only water (Abe et al. 2019). The energy need will increase in the future due to population increase. Many countries have set a goal of becoming carbon neutral and hydrogen is seen as essential to achieve that. (European Commission, 2020) Hydrogen storage enables renewable energy to be stored in low-demand and high-generation periods and hydrogen also has the potential to become a carbon-neutral fuel for traffic and transportation. (Elberry et al. 2021b) The potential of hydrogen energy is noticed, and it can be seen in the European and Finnish strategies considering energy and carbon neutrality. (European Commission, 2020)

2.1 Types of hydrogen

Producing hydrogen needs energy and the most common ways are water electrolysis and reforming from natural gas, coal, and petroleum. The most common production methods are represented in Figure 1. In the steam-methane reform method, methane is heated with hot steam. Methane-containing gases, such as natural gas, are used as feedstock.

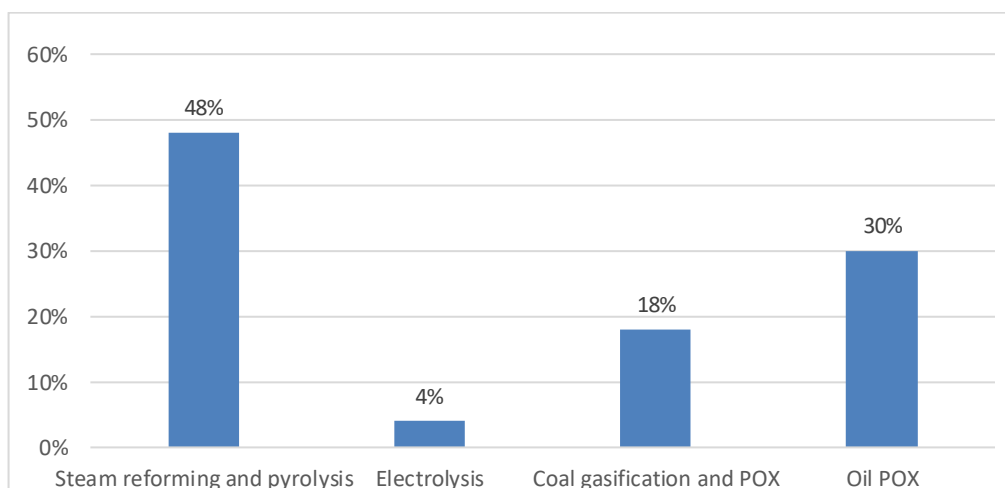


Figure 1. Hydrogen production shares worldwide (Rievaj et al. 2019).

In the reaction (1) water and methane convert into hydrogen and carbon monoxide (Tarhan and Çil 2021). In addition, carbon monoxide is converted into carbon dioxide, which also produces hydrogen (Kothari et al. 2008).



In the water electrolysis method, water is separated into hydrogen and oxygen with the aid of electrical energy, as seen in reaction (2) (Tarhan and Çil 2021).



Hydrogen production methods need energy to operate. The form of energy used in these processes determines the type of hydrogen, which is presented via a color-coding scheme.

Green hydrogen is produced with water electrolysis and the energy used in the process is from a renewable source, such as wind, solar or hydropower. There are four types of electrolysis methods, which are proton exchange membranes water electrolysis (PEM), alkaline water electrolysis (AWE), solid oxide electrolysis (SOE) and microbial electrolysis cells (MEC). For instance, in the PEM water electrolysis, water is electrochemically split into hydrogen and oxygen. In the process, water splits into oxygen, protons, and electrons at an anode. Oxygen is released and the protons are traveled through a membrane to a cathode, at which protons and electrons re-combine to produce hydrogen. (Shiva Kumar et al. 2019)

Hydrogen produced from natural gas with steam reforming is called grey hydrogen and carbon dioxide formed during the reaction is not captured but released into the atmosphere. In addition, blue hydrogen refers to the same process, but the formed carbon dioxide is captured and stored underground with carbon capture and storage technology (CCS). Green hydrogen is still expensive compared to blue and grey hydrogen due to high renewable energy prices and low efficiency in electrolyzers. In 2021, the price of green hydrogens was approximately 4.85 dollars/kg compared to greys and blues 1.2 - 2.4 dollars/kg. As the usage and development of renewable energy sources increase, the price of green hydrogen is projected to decrease in the future. (Oliveira et al. 2021).

In addition to the types of hydrogen mentioned above, hydrogen produced by gasification is another method. Gasification of biomass is considered a green hydrogen production method, as plants and other biomass sources absorb carbon dioxide in their growth process during photosynthesis. (Pal et al. 2022) Biomass contains hydrogen, carbon and oxygen, and it is available in most countries. The reactions in biomass gasification occur at high temperatures with vaporized water being the gasification agent. Carbon, carbon monoxide, methane and other hydrocarbons react with steam producing hydrogen and carbon oxides (Cao et al. 2020). Biomass pyrolysis is a process where biomass is heated to temperatures of 650 – 800 K at 0.1 - 0.5 MPa pressure. Liquid oils, solid charcoal and hydrocarbon gases are produced. These gases can be steam-reformed, and the formed carbon monoxide can be converted into carbon dioxide and hydrogen via a water-gas shift reaction. (Nikolaidis and Puollikkas, 2017)

Hydrogen produced through heavy feedstock such as coal and heavy oil is called black hydrogen. In the coal gasification process coal, plastic waste, car tires and other coal sources are converted into syngas, which contain hydrogen and carbon monoxide. Afterwards, syngas can be processed into pure hydrogen (Midilli et al. 2021). Partial oxidation (POX) is used to produce hydrogen from heavy oil and coal. It converts steam, oxygen and hydrocarbons into hydrogen and carbon oxides. The process occurs at 1150-1315 °C. Pure oxygen is used to partially oxidize the hydrocarbon source. Produced hydrogen and carbon oxides are treated similarly as in the steam-reforming method. (Nikolaidis and Puollikkas, 2017)

Turquoise hydrogen is linked to hydrogen produced via the pyrolysis of natural gas. The process is different compared to the reforming process because it does not use any steam or oxygen to occur. The reaction is done at high temperatures and due to the lack of water or oxygen, one methane molecule only produces one molecule of carbon and one dihydrogen. Therefore, the production of carbon oxides is avoided with pyrolysis. (Schneider et al. 2020)

2.2 Hydrogen strategies in the European Union

The European Union intends to invest in hydrogen and assumes it to cover a large section of energy production and usage in the future. The EU has committed to achieving carbon neutrality by 2050 and hydrogen is a key solution for that as it does not emit carbon oxides when used. Moreover, Europe is also manufacturing a high percentage of hydrogen technology and due to that will benefit from the growth of hydrogen energy. The European Commission has developed a hydrogen strategy for a climate-neutral Europe, including targets and procurement by certain years. In addition, many countries in the EU have plans to invest in hydrogen energy and already 26 countries have signed up for the so-called “Hydrogen Initiative” -project. (European Commission, 2020). This project aims to accelerate the commercial deployment of hydrogen technologies and fuels (Clean Energy Ministerial, 2023). The EU has also formulated a manifesto, which is a project to develop the European “Hydrogen Technologies and Systems” value chain. Its main objective is to guarantee Europe’s technological leadership in the hydrogen market and build a framework for the hydrogen value chain. It also supports Europe’s project for a coal-free economy and the reduction of greenhouse gas emissions. (Federal Ministry for Economic Affairs and Climate Action, 2020) The following objectives are included in the European Union’s hydrogen strategy.

The EU plans to act immediately by installing at least 6 GW of renewable hydrogen electrolyzers by 2024, and the objective is to produce 1 million tons of renewable hydrogen. The EU’s priority is to develop and use green hydrogen produced by wind and solar energy. (European Commission, 2020) It fits the EU’s goal of becoming climate neutral by 2050, as mentioned in the European Green Deal (European Commission, 2019). Expectations are that the production of electrolyzers will create jobs and strengthen the economy in the hydrogen industry. This will positively affect the EU’s exports later when green hydrogen is more common elsewhere. By 2024, the EU aims to create requirements for a well-functioning hydrogen market and increase electrolyser production. The produced hydrogen would be used in industrial processes and long-distance transport. (European Commission, 2020)

By 2030, the installed capacity of renewable hydrogen electrolyzers is planned to reach 40 GW and produced renewable hydrogen should reach 10 million tons. From 2024 to 2030 green hydrogen is expected to become cost competitive with other types of hydrogen. Wind and solar energy could be transformed into hydrogen when there is an abundant quantity of them. Due to hydrogen, energy could be stored for periods when there is no solar or wind energy available. This system would be very flexible and a feasible renewable energy system for the future. (European Commission, 2020)

By 2050 renewable energy production needs to be drastically increased, as 25 % of it is planned to be used for green hydrogen production in the EU. Hydrogen technologies should at this point reach their potential in energy efficiency and production rate. Green hydrogen technologies should also be implemented in many hard-to-decarbonise sectors, such as maritime traffic, aviation, and industry. To reach all these goals, the EU must invest a lot in renewable hydrogen technologies and energy production. (European Commission, 2020)

Planned investments from 2020 to 2030 for electrolyzers vary between 24 and 42 billion euros. To provide the required electricity for hydrogen production, investments in renewable energy sources will have to be made as well. Those investments will vary from 220 to 340 billion euros. Transporting, storing, distributing and the installation of hydrogen refueling stations will require investments worth 65 billion euros. The CCS technology is planned to be added to half of the existing black hydrogen production plants, which will require investments of 11 billion euros according to the EU's hydrogen strategy. This investment strategy will be implemented by the European Clean Hydrogen Alliance. (European Commission, 2020)

2.3 Hydrogen strategy in Finland

Finland has the facilities to be a leading hydrogen producer. It has good wind resources offshore and onshore. Wind power is growing in the country and that is crucial for renewable energy production, which is further needed for green hydrogen production. The transmission grid of electricity is also very strong in the country. Electricity generated by planned wind power plants in the north could therefore easily be transported to

southern parts of the country for green hydrogen production. (Laurikko et al. 2020) In addition, Finland has knowledge and competence in industrial processes and the energy field (Huttunen et al. 2022). Business Finland has drawn up a National Hydrogen Roadmap for Finland, which includes plans for hydrogen in Finland (Laurikko et al. 2020). In addition, the Finnish Ministry of Employment and the Economy has drawn up a national climate and energy strategy for carbon-neutral Finland by 2035, which contains a section on Finland's hydrogen strategy (Huttunen et al. 2022).

Now hydrogen production is approximately 140 000 – 150 000 t/a in Finland. Most of it is produced by fossil fuels and is used in oil and biofuel refining. The biggest consumers are the companies Neste and UPM, which use hydrogen for fuel refining and biofuel production. In 2022, there were 20 ongoing hydrogen projects in Finland, located mainly close to large industrial areas in southern and western Finland. Moreover, there are plans for a hydrogen network, located on the coast of the Bay of Bothnia and southern Finland. (Huttunen et al. 2022) The natural gas pipeline in southern Finland could be utilized and the government is discussing the project with Gasgrid Finland, the owner of the pipeline. As hydrogen production in the country increases, a complete network between the producers and users can be created. This network can be connected to other countries as well, for instance, Sweden and countries in middle Europe, with cross-border pipelines and thus produce exports. Gasgrid Finland is a government-owned company and that is why it can carry higher risks than a regular company, which is good for a project with newer technology. (Patronen and Sivill, 2022)

One possible solution for hydrogen storage in Finland would be lined rock caverns, which have reasonable costs for frequent usage (Laurikko et al. 2020). In addition, aquifers as a hydrogen storage in Finland have been researched (Elberry et al. 2021b).

Finland will prepare to take hydrogen solutions and technology into use when it reaches commercial profitability. The usage of green hydrogen will primarily be targeted at industrial processes, traffic, and Finland's energy system. The export will be a secondary subject of green hydrogen usage. Finland has set a goal of installing 200 MW of hydrogen electrolyzers by 2025 and 1000 MW by 2030. As the technology of electrolyzers improves, it is possible to create a larger capacity of electrolyzers in these periods. Finland

will also utilize the EU's funding and possibilities considering hydrogen transportation and distribution. The main target for hydrogen in the transportation sector is heavy road and maritime traffic. Finland has set a goal of hydrogen reaching a share of 3 % of all fuels used in the transportation sector by 2030. In addition, Finland will participate in hydrogen cooperations with other countries via IEA, Clean Energy Ministerial and Mission Innovation. (Huttunen et al. 2022)

In blue hydrogen production, Finland plans to implement and develop carbon capture and storage/utilization technologies (CCS and CCU). Finland has signed the EU's hydrogen manifesto and aims to participate in the 'important projects of common European interest on hydrogen' -project (IPCEI). Hydrogen projects and CCS/CCU technologies have received funding of 150 million euros from Finland's sustainable development program. Furthermore, Finland participates in the EU's hydrogen projects, cooperates with other member countries, and aims at being a leader in hydrogen technologies. (Huttunen et al. 2022)

2.4 Hydrogen value chain

The hydrogen value chain is presented in Figure 2. At first, hydrogen is produced with different methods, which also determines its color. Production methods and their color scheme are presented in Chapter 2.1. After the hydrogen is produced, it is stored either underground in a geological formation, or above ground with different technologies. Storage methods are presented in more detail in Chapter 3. When hydrogen is discharged from storage, it can be converted into electricity. The conversion is done through open- or combined-cycle turbines or fuel cells. (Quarton and Samsatli, 2020) On the other hand, hydrogen can be used as a chemical feedstock in industrial processes. It can be used for the refining of metal ores, heavy oil upgrading, and chemical and petrochemical production. Hydrogen can also be used as a fuel for urban motor vehicles, marine vessels, and aircraft. In addition, hydrogen can be transported after or before storage with pipelines, trucks, trains, and ships. (Rosen and Koohi-Fayegh, 2016) Finally, hydrogen can be used directly for heating depending on the conditions of distribution and boilers (Quarton and Samsatli, 2020).

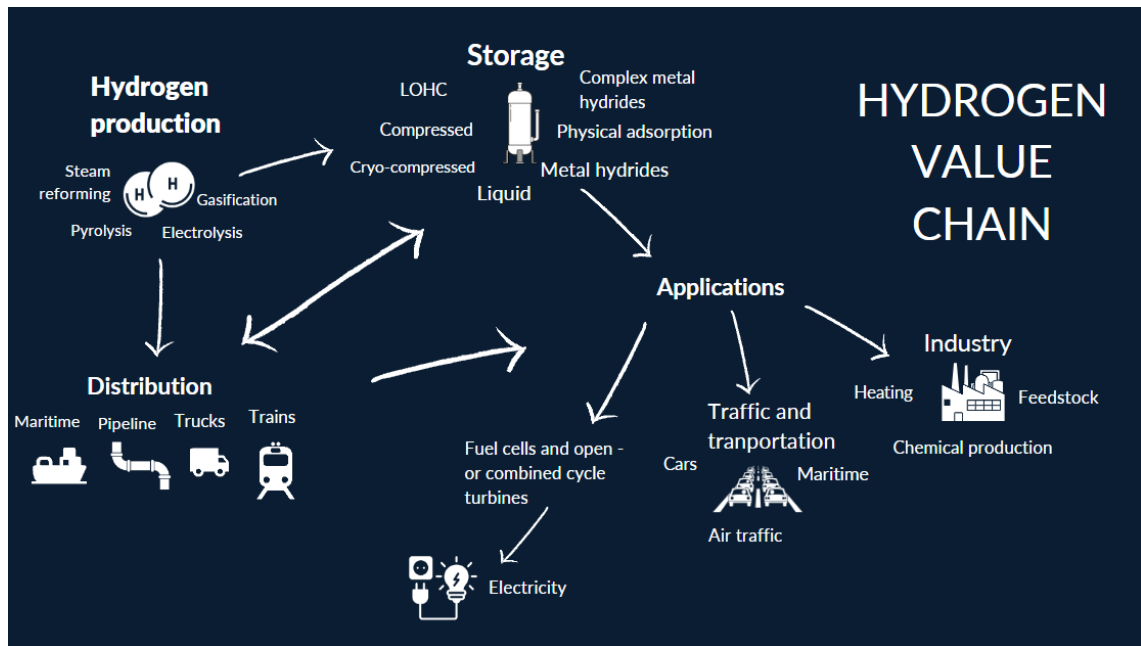


Figure 2. Hydrogen value chain (Qarton and Samsatli, 2020; Rosen and Koochi-Fayegh, 2016).

The benefits of hydrogen are in the storage. It can be stored in low-demand and high-renewable energy generation periods and discharged during high-demand periods (Elberry et al. 2021b). However, the conversion efficiency of hydrogen energy is relatively low, which leads to energy losses in different stages of the process (Qarton and Samsatli, 2020).

3 TECHNOLOGIES FOR STORING HYDROGEN

Hydrogen has its difficulties when it comes to storing it. It has a very low volumetric energy density due to its low density at normal atmospheric pressure and temperature. This requires hydrogen to be stored at high pressure, otherwise, it would not be efficient. This is a difficulty that hinders the success of the hydrogen economy. (Usman, 2022) Due to hydrogen's small molecule size, diffusion of hydrogen through substances occurs and creates yet another problem with hydrogen storage (Elberry et al. 2021a). The main matters in storing hydrogen are safe usage and efficiency (Tarhan and Çil 2021). Hydrogen technologies are developed for mobile and stationary purposes. The high-pressure storing requires heavy storage for the hydrogen, which becomes a problem in onboard applications. Both high gravimetric and volumetric energy densities are requirements in mobile applications. (Usman, 2022) Other requirements are its price, high capacity, and reasonable operating temperature (Zarezadeh Mehrizi et al. 2020). Principle methods for storing hydrogen are compressed hydrogen, cryo-compressed hydrogen, liquefied hydrogen, physically adsorbed hydrogen, metal hydrides, complex hydrides, and liquid organic hydrogen carriers (LOHC) (Usman, 2022).

3.1 Compressed hydrogen

Hydrogen can be compressed into pressure vessels. Materials mostly used for hydrogen pressure vessels are austenitic stainless- steel and alloys from aluminum, copper, and steel. (Elberry et al. 2021a) These materials must resist hydrogen diffusion, embrittlement, and high pressure. In hydrogen storage, the thickness of the vessel wall must be notably high and that causes an increase in weight. In mobile applications, that will decrease the gravimetric energy density of the whole storage system. Hydrogen is easily filled in and released from the vessel and the releasing process does not require energy. Due to that, pressure vessels are great for short-term usage. (Usman, 2022) Due to hydrogen's low density, it requires more energy to be compressed to a certain pressure than for instance methane. The compressor used in this process depends on the desired pressure. It is mostly done in multiple stages, where the compressed gas is cooled down after certain periods. That way energy used for the compression is minimized and the temperature stays at the desired temperature. (Elberry et al. 2021a)

There are four types of hydrogen pressure vessels and each one of them has its own advantages and disadvantages. Type I vessels are mostly made of carbon steel and steel alloys with aluminum. (Elberry et al. 2021a; Usman, 2022) They are mostly used in industry and are usually stationary due to their weight and low gravimetric energy density. The vessels are utilized in pressures of 200 – 300 bar and are in general widely used due to being the cheapest option for vessels. However, their high weight is a hurdle in mobile usage. (Elberry et al. 2021a)

Type II vessels are made of steel or aluminum which is wrapped with fiber resin composite (Elberry et al. 2021a; Usman, 2022). The composite is partly wrapped around the cylindrical part of the vessel. The metallic inside of the vessel functions as a liner and the fiber resin composite prevents the liner from overburdening. The composite and the liner share the structural stress. Type II has 30 – 40 % less weight than type I vessels but they cost 50 % more. Type III vessels are similar to type II vessels, but the composite wrapping is done fully with axial and hoop wrapping. (Elberry et al. 2021a) The composite in type III vessels is made of carbon fiber-reinforced plastic. Type III vessels are valid for usage at a high pressure of 450 bar. (Usman, 2022) Their cost is 50 % more than type II. (Elberry et al. 2021a)

A vessel with a polymer liner inside and fiber resin composite wrapped on top is called a type IV vessel (Elberry et al. 2021a). They are built to store hydrogen at 700 bar pressure (Usman, 2022). Their price is high, but they are perfect for onboard usage as their weight is reasonably low. Toyota Mirai (2021) for instance uses three type IV vessels with 700 bar pressure and its travel range is around 600 km on one charge. However, the high pressure of the tanks creates issues with safety at the filling stations and inside the vehicles. (Usman, 2022)

Hydrogen can also be compressed underground into salt caverns, abandoned mines, rock caverns, aquifers and depleted natural gas and oil reservoirs. Underground storage is good for long-term and large applications because charging and discharging are more laborious compared to pressure vessels. This method uses no space on top of the ground compared to large vessels or tanks. The gas injected into the formation consists of two parts: cushion and working gas. The cushion gas is the amount of gas that is permanently underground,

and its function is to keep the formation's pressure at a suitable level for the working gas to be charged and discharged in line with demand. The working gas is the actual hydrogen stored gas. Its charging and discharging occur through injection and withdrawal wells. (Elberry et al. 2021a)

3.2 Cryo-compressed hydrogen

The difference between cryo-compressed hydrogen and normal compressed hydrogen is the temperature. Hydrogen is stored at cryogenic temperature (under $-150\text{ }^{\circ}\text{C}$), and it can also be pressurized. The density of hydrogen is higher in lower temperatures, and it does not have to be pressurized as much. Therefore, a great amount of hydrogen can be stored when combining low temperature and high pressure. Cryo-compressed vessels have many similarities to type III pressure vessels. An inner liner of aluminum is wrapped with carbon fiber reinforced polymer and on top of that is a vacuum space, which is full of reflective metalized plastic covered with a metal jacket. (Zhao et al. 2022) The benefits of a cryo-compressed storage option are its density and lack of boil-off losses. Downsides, on the other hand, are high-cost vessels, and the expensive cooling and pressurizing of the hydrogen. (Usman, 2022)

3.3 Liquefied hydrogen storage

Storing hydrogen in liquid form is a widely used method of hydrogen storage. Its advantages come from hydrogen's density in low temperatures and liquid phase. Liquid hydrogen is produced via a liquefaction process which requires a high energy input. This means that one-third of the produced hydrogen is used to cover energy needs. (Wijayanta et al. 2019) Liquid hydrogen storage is already highly optimized technology. It has low adiabatic expansion energy and that helps if leaking occurs. In liquid form, hydrogen's density is approximately two times higher and that results in smaller tank sizes. Low pressure leads to thinner and cheaper tanks, although their isolation must be at a good level. Good isolation positively affects the boil-off. Hydrogen in liquid form is not corrosive, leading to the use of normal stainless steel and aluminum alloy vessels. (Usman, 2022) When liquid hydrogen is utilized after its production, transportation, and storage, it requires regasification. Like liquefied natural gas (LNG), cold energy from the

regasification process can be recovered for power generation and district cooling. (Wijayanta et al. 2019)

A boil-off phenomenon is present in liquid hydrogen storage. In boil-off, the pressure inside the vessel increases and as it reaches the maximum pressure, the blow-off valve must be opened leading to hydrogen losses. (Wijayanta et al. 2019) It is a consequence of energy input from the outside to the system (Usman, 2022). Also, ortho- to para-hydrogen conversion causes boil-off, meaning two different isomeric conditions of hydrogen form and converts from one to another. Different energy levels and the objective of achieving a state of equilibrium leads to heat formation. 0.2 % - 0.3 % boil-off occurs daily because of mentioned factors and sloshing in transportation. Several technologies have been developed to prevent boil-off, for instance, liquid nitrogen cooling, where the tank wall is covered with a liquid nitrogen “shield” and prevents outside heat from affecting the inside content. (Wijayanta et al. 2019)

3.4 Metal hydrides

Metals, metal alloys and intermetallic compounds react with hydrogen to form metal hydrides. (Tarasov et al. 2021) At first, hydrogen dissociates into atomic hydrogen and after that, it chemically adsorbs into the metal. Metal lattice acts like a sponge, receiving and releasing hydrogen. Two possible reactions are used: direct reaction with hydrogen (1) and the metal and electrochemical dissociation of water molecules (2). (Usman, 2022)



In the utilization stage, energy is required to release the hydrogen from the metal by desorption. This is done by decreasing the pressure or increasing the temperature. This results in high hydrogen release temperature. Compared to compressed and liquefied hydrogen, metal hydrides are safe to use due to their low pressure and standard temperature. (Usman, 2022)

Table 1. Metal hydrides and their properties (Usman, 2022).

	Hydrogen capacity (wt%)	Desorption temperature (°C)	Desorption enthalpy (kJ/molH₂)
MgH₂	7.6	>300	75
Mg₂NiH₄	3.59	>280	65
Mg₂FeH₆	5.5	>300	77.8
FeTiH₂	1.89	>30	28
LaNi₅H₆	1.4	>100	31

When selecting the metal hydride, several things must be considered: Its price and ease of manufacturing, kinetics in adsorption and desorption, cyclic stability, and easy activation. (Tarasov et al. 2021) Table 1 shows common metals and intermetals used as hydrides. Different hydrides have discrepancies in hydrogen capacity, desorption temperature and enthalpy. Hydrogen capacity has a direct connection with the energy density of the storage system, and too high desorption enthalpy and temperature are hurdles to some fuel cell applications. *MgH₂* is the most used and researched metal hydride and its benefits are its high volumetric and gravimetric energy density and magnesium's cheap production. On the other hand, the hydride is produced at high temperatures and pressure, its formation kinetics are slow, and it has a very high release temperature. (Usman, 2022)

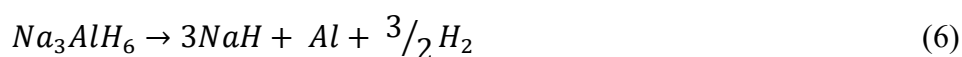
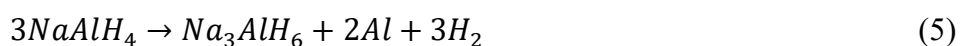
3.5 Other storing technologies

Hydrogen storage technologies include many other methods. This chapter briefly introduces liquid organic hydrogen carriers, physical adsorption, and complex metal

hydrides. In physical adsorption, molecular hydrogen is adsorbed in porous materials. (Bartolomei et al. 2015) The materials used as an adsorbent are microporous carbon structures, metal-organic frameworks, and zeolites. These materials have a large surface area, which is necessary for physical adsorption to occur. (Usman, 2022)

Complex metal hydrides are formed when hydrogen atoms covalently bond to a coordination complex. The coordination complex is an anion, such as $[AlH_4]^{-1}$, $[BH_4]^{-1}$ and $[NH_2]^{-1}$, and a cation stabilizes it. The most used cations are lithium, zinc, and magnesium. (Usman, 2022) Complex hydrides have high hydrogen density, but they have difficulties in safe handling, and they might decompose into highly stable entities. Researched complex hydrides are mostly based on alanates, borohydrides and amides/imides. (Kiruthika et al. 2023)

Alanates are aluminum containing complex hydrides. For instance, widely researched sodium aluminum hydride contains 7.4 weight percentage (wt%) of hydrogen. It is released during the following reactions (5), (6). (Usman, 2022)



Only 5.6 wt% of the hydrogen can be released, 3.7 wt% in reaction (5) and 1.9 wt% in reaction (6). It is inexpensive but requires high temperatures for hydrogen release. (Usman, 2022)

Sodium -, magnesium -and lithium borohydrides are examples of borohydrides used as hydrogen storage. They have a hydrogen content of 10 to 18 wt%. Hydrogen is released via (7) hydrolysis and (8) decomposition reactions. (Usman, 2022)



Borohydrides are more stable than alanates but it releases toxic boron hydrides in dehydrogenation reaction. Hydrogen release temperature is also high. (Usman, 2022)

Amides and imides are nitrogen-containing complex hydrides. An example of an amide is lithium amide, which is very common and widely used. It contains 10.4 wt% of hydrogen, and it has a low hydrogen release temperature. On the other hand, amides and imides have low rates of charging and discharging hydrogen. (Usman, 2022)

In liquid organic hydrogen carriers (LOHC), hydrogen is stored chemically in organic molecules. The most used LOHCs are cycloalkanes, heterocycles, and formic acids. (He et al. 2015) LOHCs can be dehydrogenated and recharged frequently, while the carbon molecule remains in the cycle. LOHCs have 6 – 8 wt% of hydrogen capacity and they maintain liquid phase at room temperature. LOHCs are suitable for both stationary and mobile usage. (Usman, 2022) Moreover, cycloalkanes are suitable for long-distance hydrogen delivery to a large extent due to their low price and high hydrogen purity. The most used cycloalkanes are cyclohexane, methylcyclohexane and decalin. The hydrogenation of cycloalkanes is endothermic, which results in a high-temperature hydrogen release. In addition, highly active catalysts are used in the dehydrogenation process. Dehydrogenation of cyclohexane is done with a sextet mechanism, in which the cyclohexane overlies on a catalyst surface and converts to benzene. (He et al. 2015)

4 CASE STUDIES OF STORING GREEN HYDROGEN

In this chapter, two case studies containing a hydrogen storage system created with simulation models and one real-life hydrogen system project in Vaasa are presented. The technologies and the planned system used in the case studies are described to create a foundation for the analysis in Chapter 5. Two different kinds of systems with hydrogen storage were chosen to present the scale of possible applications. Finally, one real-life project was also included to show the type of technology that is at present invested in and being built.

4.1 Case study 1: Seasonal hydrogen storage in Finland

Elberry et al. (2021b) have done a case study on seasonal hydrogen storage for sustainable energy integration in the electricity sector. The case study focuses on the electricity generation system in Finland and the impact of the potential installation of a large-scale hydrogen storage system. The study uses two modeling tools, which are the Low Emissions Analysis Platform and the Next Energy Modeling system for Optimization. (Elberry et al. 2021b)

The system consists of three phases, which are the electrolyzer, hydrogen storage and the fuel cell. Proton Exchange Membrane (PEM) electrolyzers are used to form hydrogen and oxygen from water. The model includes aquifers as geological hydrogen storage, which are geological underground structures in groundwater areas. The study shows that in the country thousands of aquifers are not used for water supply. These could be capitalized for hydrogen storage, and it would not affect the water supply system in the country. Aquifers consist of permeable rocks, among which the water can easily move. The formations must be layered with impermeable rocks to seal the hydrogen inside. Finally, alkaline fuel cells are used to convert the hydrogen back to energy when it is needed. (Elberry et al. 2021b)

4.2 Case study 2: PV-hydrogen storage system

Mohammed et al. (2023) have done a case study of a photovoltaics hydrogen energy system that follows the hourly energy demand of an electrical testing laboratory, located in Saudi Arabia's eastern region. The PV system provides energy directly to the laboratory during high-generation periods. The excess energy is used to produce hydrogen via electrolysis and store it in hydrogen tanks for later use. As in the first case study, PEM electrolyzers and alkaline fuel cells are used. The study formulates a Mixed-Integer Linear Programming model solved with CPLEX algorithm. (Mohammed et al. 2023)

The study uses hourly ambient temperature and solar radiation data in Dhahran city to discover hourly variations in those categories. PV energy is available from 6.00 AM to 5.00 PM and at those hours, the hydrogen storage is charged. In the evening and night, the demand is satisfied by the hydrogen storage system. (Mohammed et al. 2023)

4.3 Wind-hydrogen storage system project in Vaasa

The Power-to-X-to-Power hydrogen project in Vaasa has received project investment aid of 14 million euros from the Ministry of Economic Affairs and Employment of Finland. The project is being built by Wärtsilä, EPV Energy and Vaasan Sähkö. The project is still under construction and is planned to be fully working by the end of 2025. The objective of the project is to create a short-term green hydrogen storage system combined with wind power. The system uses compressed hydrogen vessels as short-term storage, and they are utilized when there is a shortage of wind power. Heat is a principal by-product of electrolysis and fuel cell action, and it is recovered into a rock cave heat storage in Vaasa and distributed to the city's residents as district heating. (EPV Energy Ltd, 2021; Sinclair, 2022)

5 IMPACTS OF HYDROGEN STORAGE TECHNOLOGIES AND IMPLICATIONS FOR THE ENERGY SYSTEM

In this chapter, the two case studies and the Vaasa project are discussed more deeply and compared to each other with different criteria. The goal is to discover if hydrogen storage technologies are a feasible option for the energy system when it comes to costs, carbon emissions and efficiency. The goal is also to determine the best storage technologies for each purpose and which technologies could be added to the Finnish energy system.

5.1 Advantages and disadvantages of a hydrogen storage system

As mentioned before, the benefits of a hydrogen storage system lie in the fact that it can be stored during overproduction and low demand of carbon-neutral energy production and can be used during high demand and low production. In case study 1, this can be seen when comparing the baseline scenario, which demonstrates the capacity of energy production without hydrogen storage, and the storage scenario with the hydrogen storage added to the system (Elberry et al. 2021b).

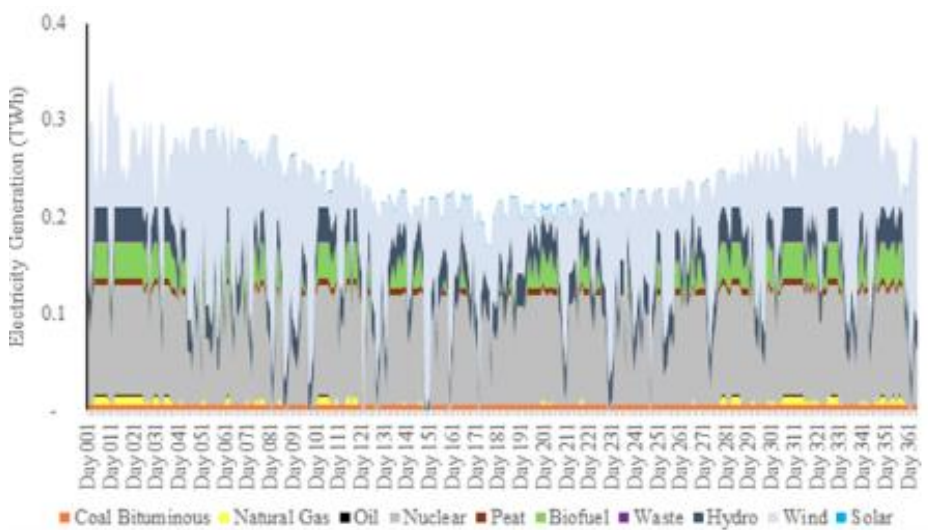


Figure 3. Daily electricity generation by each technology, baseline scenario. Reprinted from Journal of Energy Storage, Vol 44, Elberry et al., *Seasonal hydrogen storage for sustainable renewable energy integration in the electricity sector: A case study of Finland* (2021) Page 10. Open access article distributed under the terms of the Creative Commons CC-BY licence.

In Figures 3 and 4, the daily electricity generation with and without hydrogen storage can be seen. Figures 3 and 4 show that electricity generation from natural gas, oil, and waste decreases in both scenarios during the summer, and notably more in the storage scenario. The charging and discharging of the hydrogen storage can be seen as a red color in Figure 4, with charging on the negative side and discharging on the positive. It shows that hydrogen storage is mostly charged during high wind generation (light grey color) and low demand periods and discharged during low wind generation and high demand periods. This affects decreasingly the demand for fossil-based electricity, such as natural gas (yellow color) and coal (black color).

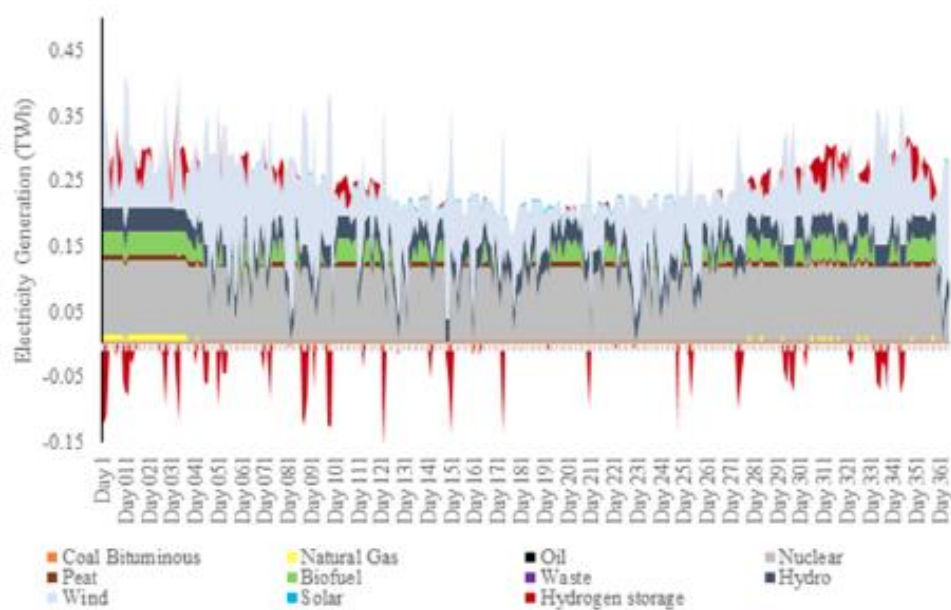


Figure 4. Daily electricity generation by each technology, storage scenario. Reprinted from Journal of Energy Storage, Vol 44, Elberry et al., *Seasonal hydrogen storage for sustainable renewable energy integration in the electricity sector: A case study of Finland* (2021) Page 10. Open access article distributed under the terms of the Creative Commons CC-BY licence.

In case study 2, a laboratory's electricity need was fulfilled by using only PV energy and hydrogen storage (Mohammed et al. 2023). This is a small project generating approximately 1000 kWh per day and its annual total cost is around 60 000 USD, including the PV system and the hydrogen production, storage, and utilization system. The price consists of the system's capital costs, maintenance costs, lifetime expectations and replacement costs. This amount of electricity purchased from the grid with a price of

0.1 USD/kWh would have an annual cost of 36 000 USD. In case study 2, the annual cost of the PV-hydrogen system is almost double compared to purchasing electricity from the grid. This leads to the conclusion that it is an environmentally friendly, but expensive system compared to non-renewable electricity production. (Mohammed et al. 2023) The study mentions that the PV panels make up the main part of the investment costs.

On the other hand, case study 1 shows that after increasing wind power and utilizing hydrogen storage seasonally in 2021, the module cost balance of the energy storage scenario becomes higher than the baseline scenario as seen in Figure 5 (Elberry et al. 2021b). The module cost balance represents the sale revenue of the electricity, minus the costs of production. In the study, both scenarios use renewable energy and only the effect of the storage can be seen positively in the price.

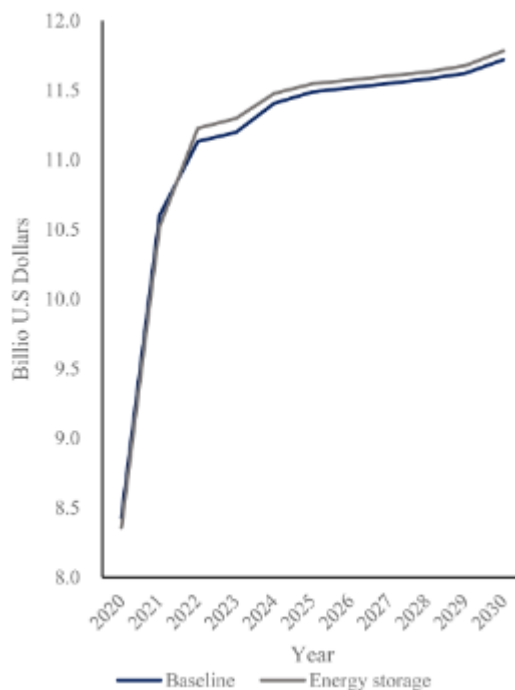


Figure 5. The module cost balance. Reprinted from Journal of Energy Storage, Vol 44, Elberry et al., *Seasonal hydrogen storage for sustainable renewable energy integration in the electricity sector: A case study of Finland* (2021) Page 11. Open access article distributed under the terms of the Creative Commons CC-BY licence.

In addition, the unmet demand is higher in the baseline scenario leading to imports of electricity and a rise in expenses. The technology of hydrogen energy systems is still

expensive, but it can be profitable in the long run, especially if renewable energy becomes the only option in energy generation. In the Vaasa project, the heat from hydrogen production and the operation of fuel cells is transported into an existing rock cavern for thermal storage and in a cold country like Finland, it can be used for district heating (EPV Energy Ltd, 2021; Joanna Sinclair, 2022). The hydrogen production plant can also be connected to a hydrogen charging station for vehicles given that the hydrogen car industry is already developed.

5.2 The purpose of long-term and short-term hydrogen storage and the most suitable storage technologies

Hydrogen can be stored for daily purposes and, if seasonal weather variation is high, for longer periods. The Vaasa project uses compressed hydrogen storage only for short-term purposes to produce electricity on calm days (EPV Energy Ltd, 2021; Sinclair, 2022). Case study 2 uses hydrogen storage to fulfill the demand during nights and cloudy days (Mohammed et al. 2023). Figure 6 demonstrates the charging and discharging amounts and hours of the PV-hydrogen tank system.

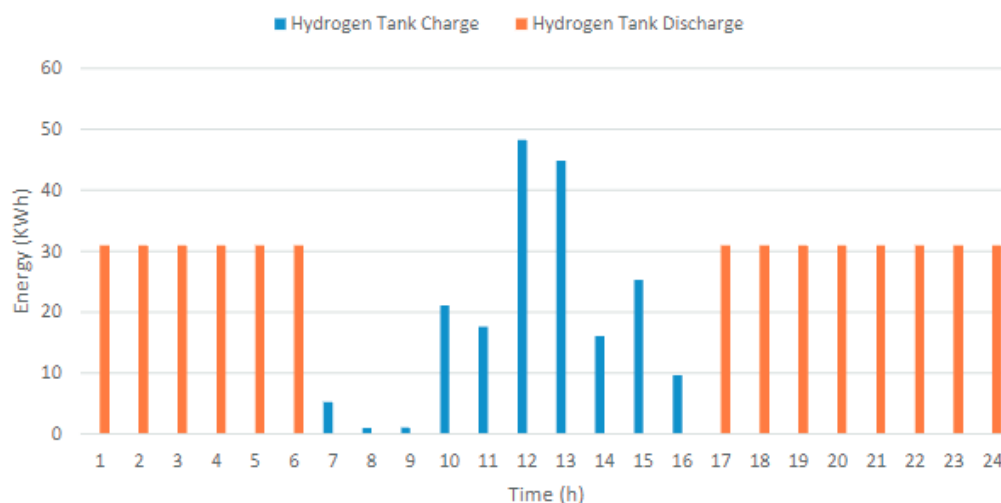


Figure 6. Hydrogen tank charge and discharge for 24 hours. Reprinted from International Journal of Hydrogen Energy, Vol 48, Mohammed et al., *A multi-objective optimization model based on mixed integer linear programming for sizing a hybrid PV-hydrogen storage system*, Page 9758, Copyright (2023), with permission from Elsevier.

It can be noted that the amount of charging is less than the discharge, meaning that the rest of the needed energy must be purchased from the grid. The study does not specify which storage technology they use, only storage tanks are mentioned. It can be assumed that in the case of short-term storage, compressed hydrogen, liquefied hydrogen, or metal hydrides are used. They are a feasible option for short-term purposes due to their ease of charging and discharging. In short-term storage, the capacity of the storage does not have to be as large as in long-term, since it is usually charged and discharged daily.

On the other hand, hydrogen can also be stored for longer periods. For instance, Finland's energy consumption is low in the summer and increases till February when it reaches its peak. From that on, the consumption decreases gradually and tumbles in June. This is due to the temperature in the country and the fact that most companies have their summer breaks in these months. The energy generation with PV and wind technologies stays even or increases and this leads to unmet demand and overproduction. The hydrogen storage technology must be able to store large amounts of hydrogen for longer periods, and that is why underground compressed storages are the best option. They do not take away space from the ground and are not susceptible to temperature changes. (Elberry et al. 2021b)

Case study 1 uses aquifers as hydrogen storage to store energy from the overproduction periods in the summer for the high demand during winter (Elberry et al. 2021b). The aquifers used in the model are based on the Stenlille aquifer storage in Denmark, which is used as a natural gas storage. It can store 4.461 GWh of natural gas, which is equivalent to 750.1 GWh of hydrogen at a pressure of 150 – 170 bar. The 750.1 GWh of hydrogen represents only the working gas capacity, and 35.37 kg of cushion gas is present on top of that. The unrecoverable cushion gas weight is equivalent to approximately 1.18 GWh of hydrogen, which is 0.16 % of the total energy. As mentioned in the case study, thousands of unused aquifers are available in Finland and other underground storage methods can be used in other countries, e.g., salt caverns. It must be noted that geological structures are location dependent, and they would require hydrogen distribution pipelines, or a stationary fuel cell system connected to the grid. Referring to case study 1, aquifer storage only costs 1.89 USD/kWh, which is around one per cent of the total system costs consisting of electrolyzers, fuel cells, and storage (Elberry et al. 2021b). As a result, great amounts of hydrogen can be stored cheaply for longer periods.

5.3 Hydrogen storage and distribution in Finland

Finland faces many challenges due to seasonal weather changes. The demand for electricity is low in the summer and due to wind power growing in the country and PV energy only being available in the summer, electricity is overproduced in the summer. The country's goal of becoming carbon neutral by 2035 forces energy storage to be used, as it can store overproduced energy from the summer and level the wind generation fluctuation on a daily basis. As in the Vaasa project, short-term compressed hydrogen storage is a feasible option, and they could also be connected to vehicle charging stations (EPV Energy Ltd, 2021; Sinclair, 2022). Combining that with geological long-term storage, charged with PV, wind and nuclear energy in the summer at low demand, a complete system would be achieved.

As discussed in Chapter 2.3, Finland is planning to create a hydrogen network located in western and southern Finland. Wind electricity generation is high in the western part of the country and the largest consumers are also located in the south and west. In addition, better conditions for solar energy production are achieved in southern parts of the country. By partly utilizing the old natural gas pipeline in southern Finland and building a new one towards the west, a complete network of hydrogen distribution could be achieved. After connecting the largest producers and consumers to the network, the pipeline could be connected to neighboring countries and used for export.

5.4 The impact of a hydrogen system on the volume of carbon dioxide emissions

In case study 2, three different scenarios were drafted (Mohammed et al. 2023). The differences between the scenarios were the loss probability of power supply and annual total cost. With the highest annual cost, the largest savings in carbon dioxide emissions were achieved. This is due to the amount of PV modules and electrolyzers being the highest, so a minimal amount of grid energy generated with non-renewable methods had to be purchased. Referring to case study 2, conventional fuel energy generation produces 0.50089 kg of carbon dioxide for 1 kWh of energy. When generating 455 MWh of energy

with a fully independent PV-hydrogen energy system, approximately 228 tons of carbon dioxide emissions can be prevented.

In case study 1, annual carbon dioxide emissions are compared with and without hydrogen storage (Elberry et al. 2021b). Figure 7 shows that the emissions are decreasing in both scenarios, but the decline is steeper with hydrogen storage. The fall is due to an increase in wind and nuclear energy generation in Finland. By adding hydrogen storage to the system, the goal of Finland becoming carbon neutral by 2035 would be achievable even faster. The total carbon dioxide savings in the 10-year period were 0.52 Mt, 52 000 tons per year on average. When green hydrogen storage is added to the system, it allows 100% renewable energy sources to be used and the energy system would no longer depend on non-renewable and carbon dioxide-emitting energy sources.

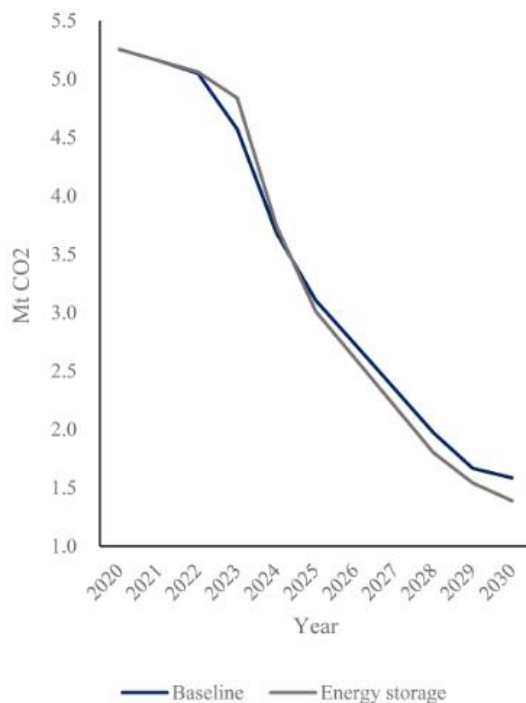


Figure 7. Carbon dioxide emissions in Finland and the effect of hydrogen storage. Reprinted from Journal of Energy Storage, Vol 44, Elberry et al., *Seasonal hydrogen storage for sustainable renewable energy integration in the electricity sector: A case study of Finland* (2021) Page 11. Open access article distributed under the terms of the Creative Commons CC-BY licence.

On the other hand, as shown in the Vaasa green hydrogen project, produced heat from fuel cells and electrolyzers can also be utilized for district heating (EPV Energy Ltd, 2021;

Sinclair, 2022). This reduces the amount of heat production with other methods, resulting also in a decrease in carbon dioxide emissions.

6 SUMMARY AND CONCLUSIONS

In this bachelor's thesis, the journey of hydrogen from production to end-use is explored, with a specific focus on hydrogen storage. The thesis presented various hydrogen production technologies, which are color-coded according to their production methods. Green hydrogen uses renewable energy to produce hydrogen with electrolysis and it is the most important method in relation to the global goal of becoming carbon neutral.

The thesis discussed Finland's and the EU's hydrogen strategies, with hydrogen being one of the main elements in achieving carbon neutrality. The EU has committed to achieving carbon neutrality by 2050, and it requires large investments in renewable energy production, electrolyzers, fuel cells, transportation, storage, and distribution. Moreover, Finland aims for carbon neutrality by 2035 and has the facilities to be a leading hydrogen producer. The country aims to target hydrogen usage in industrial processes, energy systems, and traffic. In addition, the hydrogen value chain is presented to understand the whole cycle of hydrogen.

There are several options currently available for hydrogen storage and there is an ongoing development in the field. The technologies differ in terms of price, gravimetric and volumetric density, weight, and capacity. Mobile and stationary applications, and short- and long-term applications require different characteristics, therefore favoring different technologies. Answering the first research question, compressed hydrogen into vessels and geological structures, liquefied hydrogen, and metal hydrides are the most used and far-developed technologies. Cryo-compressed hydrogen, liquid organic hydrogen carriers, physically adsorbed hydrogen, and complex metal hydrides are less used and still developing technologies.

Two case studies including a seasonal hydrogen storage system, a short-term hydrogen storage system and a real-life application in Finland are presented and analyzed by their costs, carbon emissions, and efficiency. Answering the second research question, the advantages of a hydrogen storage system lie in its flexibility and minimizing the unmet demand. It can be charged during low demand and high renewable energy generation periods for short-term or long-term purposes. Hydrogen can be utilized with fuel cells in

high-demand or low-renewable energy generation periods, decreasing the demand for fossil-based energy. One of the case studies showed that in a 10-year period, 0.52 Mt of carbon dioxide emissions would be prevented only by using hydrogen storage alongside renewable energy sources. In addition, the studies showed that hydrogen storage would have a positive effect on the price of the whole renewable energy system. On the other hand, improvements to the storage technologies, especially to the less used ones, are needed. With more research these technologies might reach higher volumetric energy density or minimize the boil-off phenomenon.

The amount of information available about real-life case studies with certain hydrogen storage technology and actual statistical data was limited. This is one thing that future studies about this topic could focus on and more statistical information is needed. Some of the storage technologies are still in development, for instance, due to boil-off phenomena and energy consumption, and they need to be researched and perfected. The findings in this thesis aim to contribute to the ongoing efforts in integrating hydrogen into the energy system and hence achieving a sustainable energy future.

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